THE 2nd CEEPN WORKSHOP ON POLYMER SCIENCE

PROCEEDINGS

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TOPIC OF THE WORKSHOP

POLYMER SCIENCE – a powerful tool for highly specialized functional materials

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PLENARY LECTURES

L1

POLYZWITTERIONS: PROPAGATION KINETICS, HYDROGELS, NON-BIOFOULING COATINGS

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This contribution will cover several principal topics of Department for biomaterials research of the Polymer Institute SAS with the mutual motif being the zwitterionic polymers. Zwitterionic polymers have been intensively studied by a number of groups worldwide owing to their suitability for the design of non-biofouling materials with a unique physical and chemical properties. Polyzwitterions are built of electrically neutral monomer units formally containing both positive and negative charges on different atoms in a monomer unit, most typically sulfobetaines, carboxybetaines and phosphorylbetaines.

The first topic will describe determination of propagation rate coefficients for radical polymerization of the amide and ester types of sulfobetaine monomers in aqueous solutions using the IUPAC recommended pulsed-laser polymerization in conjunction with size-exclusion chromatography. The second topic will be devoted to synthesis and characterization of polysulfobetaine hydrogels using newly synthesized zwitterionic crosslinkers with the role to suppress the compositional drift during the hydrogel formation. The third topic will describe the novel cationic copolymer that is light-switchable to the zwitterionic carboxybetaine used to capture and release DNA as well as to switch antibacterial surface to non-toxic one. The light-switchable principle was also used to deposit the zwitterionic non-biofouling layer to the surface of polyelectrolyte complex microcapsules designed for immuneprotection of transplanted islets in diabetes treatment.

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L2

POLYMER COMPOSITES – INTERRELATIONS BETWEEN STRUCTURE AND ELECTRICAL AND THERMAL PROPERTIES

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Last decades the growing interest to electrophysical properties of polymer composites caused by wide area of possible applications. This interest is based on the idea that the electrical and thermal characteristics of such composites can be close to the properties of metals or carbon, whereas the mechanical properties and processing methods are typical for plastics. The achievement of metallic properties in such composites depends on many factors, first of all it is structure of conductive phase controlling the electrical and thermal characteristics which determines the variety of ranges of their application. The transfer conditions of the electric charge and heat flow determine the electrical and thermal conductivity level in the heterogeneous polymer-filler system, in which the conductive phase is formed by dispersed metallic or carbon filler. The influence of the type of polymer matrix and filler on the electrical characteristics of the composite and its percolation behavior has been studied in many works however the influence of structure of the conductive phase on charge transport is not studied enough. Concerning the thermal conductivity of such composites, in spite of existing models for two-phase systems, there are only a few publications on the study of the correlation between structure and thermal properties.

In this study the experimental results of electrical and thermal conductivity in polymer/metal and polymer/carbon composites are presented. The approach is focused on the influence of spatial distribution of conductive filler and morphology of conductive phase on electrical and thermal properties. There are presented new experimental results on formation of ordered anisotropic (1D) structure of conductive phase in magnetic field and obtained electrical/thermal characteristics polymer systems including such 1D conductive structure. Appropriate models describing electrical and thermal behavior of polymer composites are used. It is analyzing the peculiarities of charge transport and heat flow through the conductive phase which restrict the achievement of high level of electrical and thermal conductivity. The possible applications are highlighted.

L3

MICROWAVE-ASSISTED DEGRADATION OF PLASTICS

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Nowadays, much attention has paid to an environmental task concerning a re-use of waste plastics and an increased usage of renewable (or biodegradable) materials for synthesis of new types of plastics. Generally, a degradation of polymers utilizing a suitable reagent for targeted cleavage of polymer chain or network is a principle of chemical recycling methods.

Recently, we have studied the degradation of common plastic wastes, such as polyurethanes (PUR) [1], polyethylene terephthalate (PET) [2] or polycarbonate (PC) waste (based on bisphenol A) by means of natural oils in microwave field. Application of the microwave (dielectric) heating significantly reduces reaction times and seems to be a new way how to overcome the problem of high energy demanding recycling processes.

Generally, the recycling process involves firstly a transesterification of the natural oils in order to introduce reactive hydroxyl groups, which are able in the second step to react with functional groups (urethanes, esters, carbonates, etc.) of polymers leading to their degradation (decomposition). The both steps can be performed in the microwave reactor, when the load (reaction mixture) absorbs microwave energy. In other words, the load has to contain dipoles and/or ions try to orient themselves in the direction of the electric field vector of the microwaves.

In this contribution, correlation between the microwave-assisted degradation of plastics and dielectric properties (i.e. dielectric constant and dielectric loss factor) of reagents is discussed. The experiments were carried out in both multi- and mono- mode microwave reactors. The dielectric properties at microwave frequencies (900 MHz and 2.45 GHz) were measured using a broadband impedance spectrometer in the temperature range of 20 – 220 °C.

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Acknowledgments

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L4

POLYPHOSPHOESTER BASED DELIVERY SYSTEMS OF ANTICANCER AGENTS

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Drug conjugation to a macromolecular carrier is a widely explored strategy especially in the field of cancer therapy. A significant number of polymer-bound antitumor agents have been developed so far including taxol, doxorubicin, etc. Among the most commonly used polymers are PEG [1] and poly(hydroxypropylmethacrylamide) [2]. Poly(oxyethylene H-phosphonate)s present a family of biodegradable, hydrophilic, and nontoxic polymers, which mimic biomacromolecules. These polymers contain PEG segments as building blocks linked by H-phosphonate groups – reactive sites for conjugation or modification. All these valuable features make poly(oxyethylene H-phosphonate)s promising candidates for immobilization templates.

Based on our experience in synthesis of polyphosphoesters we underwent a study on conjugation of anticancer drugs: bendamustine [3], melphalan [4] and platinum complexes [5]. The structure of the conjugates was elucidated by multinuclear and diffusion NMR spectroscopy, FT-IR spectroscopy, HPLC. The cytotoxic effect of the formulations was evaluated on different tumor cell lines.

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L5

STRUCTURE OF REINFORCING FILLER NETWORK DETERMINED BY ELECTRICAL CONDUCTIVITY OF THE POLYMER / CARBON BLACK COMPOSITE

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Electrical conductivity of composites of polymeric insulating matrix filled with electroconductive filler depends on a formation of conductive filler network, leading to a pronounced increase in conductivity at certain filler concentration called percolation threshold. Obviously, any change of the conductive network due to the external influence should result in a change of electrical conductivity. Thus, the changes in electrical conductivity resulting from either mechanical deformation or a change of volume due to e.g. temperature change can be used for monitoring the current state of the physical reinforcing network formed by the filler.

The principle described above was used to investigate the behavior of either vulcanized rubber or thermoplastic polycaprolactone filled with electroconductive reinforcing carbon blacks. The effect of a decrease of elongation at break in the percolation threshold region is demonstrated on composites with either thermoplastics (polycaprolactone, polyethylene, polypropylene) or rubber matices filled with conductive filler. The effects during deformation are investigated by online measurement of conductivity during mechanical deformation. Conclusions regarding the decay or reforming of the conductive network have been done and compared to the mechanical responses of the material during uniaxial tensile deformation, as indicated by stress – strain curve, or during cyclic deformation characterized by hysteresis curves. In the latter stage, regeneration of the conductive network during stress relaxation measured at constant nonzero deformation followed by recovering after release the mechanical stress was also considered.

The changes of electrical conductivity were found to be far away from simple monotonous increase / decrease during deformation. On the contrary, rather complicated dependences with several extremes on the conductivity vs deformation curves were observed. Some of these are related to Hookean part and inflex point on the stress strain curve. Yield point for composites with thermoplastic matrices is also an important parameter to consider regarding electrical conductivity. Cyclic deformation with constant or rising amplitude contributes to better understanding of more complicated mechanical responses e.g. related to Payne’s effect.

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L6

UV-VIS-NIR(*T*) SPECTROSCOPY, AS A METHOD TO INVESTIGATE THERMAL STABILITY OF POLYMER THIN FILMS

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Heat resistance of polymer thin films is important, since optoelectronic and photovoltaic devices are exposed to the effect of higher temperatures.

The analysis of thermal stability, have been performed thanks to the optical transmission measurements *in situ* during annealing and cooling films. Such investigations were conducted for the films of polyimides with azobenzene and/or tricyanovinylene groups [1] and for the films of polyazomethine PPI and its iodine (I_2) doped version [2] and also for the films of polyazomethine with the flexible side-chains BOO-PPI [3].

These investigations confirmed good thermal stability of unsubstituted, undoped polyimides and polyazomethines films. Tricyanovinylene groups in the polyimide chains worse thermal stability, while azobenzene-side groups only above the T_g temperature. The border temperature of (PPI+I) films and the iodine releasing process, have been described on the base of temperature dependence of absorption edge parameters. During heat treatment of the BOO-PPI films the structural changes were connected with the flexible side chains but conjugation in the main chain was preserved and the energy gap was constant.

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L7

PLGA-BASED NON-WOWEN FABRICS. CHALLENGES IN THE INTERPRETATION OF THE DYNAMIC MECHANICAL ANALYSIS RESULTS

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Poly(lactyde-co-glycolide)s (PLGA) are very often the copolymers of choice for absorbable medical devices due to their degradability by simple hydrolysis of the ester backbone in aqueous environments, such as body fluids. The first interest is usually oriented to studies of gradual hydrolytic degradation and release rate of acids from PLGA copolymers [1]. However, basic information like the value of the elastic modulus (E’) and the glass transition temperature (T_g) are important in the evaluation of materials. Dynamo-mechanical investigations performed on PLGA non-woven fabrics have revealed some particularities of this kind of copolymers resulted from the phenomena that overlap with in glass transition region. Also, in the flowing region an atypical trend of the viscoelastic parameters is registered because of the fiber-type material.

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L8

EFFECT OF PROCESSING CONDITIONS ON VISCOELASTIC AND THERMAL CHARACTERISTICS OF CYANATE ESTER RESIN/ORGANOCLAY NANOCOMPOSITES

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Polymer nanocomposites based on highly crosslinked Cyanate Ester Resins (CER) reinforced with low cost and commercially available thermally and chemically stable montmorillonite (MMT) seems to be promising material for numerous application areas where the combination of excellent characteristics of CER and mechanical strength and crack resistance provided by high aspect ratio MMT are required [1, 2]. Generally synthesis of nanocomposites based on thermosetting polymers consists in dispersing of nanofiller in liquid monomer (or pre-polymer) followed by thermal curing. As a result highly crosslinked polymer nanocomposite is generated [1]. At this delamination of MMT to separate layers homogeneously distributed inside the polymer matrix is very important for producing of high performance nanocomposites. Additionally, chemical nature of the components and preparation technique are crucial parameters for reaching the desirable level of clay distribution [1].

The present work aims evaluation of the effect of dispersing and curing conditions on viscoelastic and thermal properties of CER/organoclay nanocomposites.

1,1′-bis(4-cyanatophenyl) ethane under the trade name Primaset LECy, was kindly supplied by Lonza (Switzerland). Commercial surface modified montmorillonite containing 15-35 wt. % of octadecylamine and 0.5-5 wt. % of aminopropyltriethoxysilane (trade name Nanomer®I.31PS) was provided by Nanocor® Inc. The chemicals were used as received. 5 wt.% of organoclay was dispersed within CER monomer by mechanical mixing using magnetic stirrer with stirring rate ~ 1300 rpm for 30-120 min. Temperature of dispersing stage was varied from 25 to 165°C. The mixtures obtained were then degased and cured either step-by-step or dynamic curing procedure in temperature range from 150 to 280°C (Table 1).

Table 1. Sample codes of nanocomposites (NC) and conditions of synthesis

Sample code	Dispersing conditions		Curing mode applied*
	Temperature (°C)	Duration (hrs)	
NC$_1$	25	1.5	stepwise
NC$_2$	150	0.5	dynamic
NC$_3$	150	1.5	dynamic
NC$_4$	150	2.0	dynamic
NC$_5$	165	1.5	dynamic
NC$_6$	165	1.5	stepwise

* stepwise curing: 150°C (5hrs); 180°C (3hrs); 210°C (1hrs); 250°C (1hrs); 280°C (1hrs).
dynamic curing: linear heating from 150°C to 280°C with a heating rate of 0.5°C/min.

Dynamic mechanical thermal analysis (DMTA) was carried out by using a TA Instruments Q800 thermal analyzer in tension mode. Rectangular samples were cut from films within the following range of dimensions: 10 x 10 x 0.08 mm. Storage modulus (E'), loss modulus (E'') and loss factor (tan δ) were measured between 40 and 300°C at a heating rate of 4°C/min in frequency range from 0.3 to 30 Hz. Thermogravimetric analysis (TGA) was performed on a TG 209 thermo-balance under inert atmosphere. Sample pellets, with masses ranging from 10 to 20 mg, were heated from 20°C up to 900°C at 20°C/min. Differential Scanning Calorimetry (DSC) measurements were performed using Perkin Elmer calorimeter under nitrogen atmosphere. Samples were first heated from 30 to 300°C with a scan rate of 10°C/min, and subsequently cooled. A 2nd heating scan was performed under the same heating conditions. The T_g values were measured in the second run.

The DMTA results for NC$_1$ sample taken as a reference are presented in Figure 1. Temperature dependence of storage modulus (E′) shows the existence of broad relaxation transition in temperature range around 180-320 °C corresponding to glass transition process. The loss factor (tan δ) curve reveals the presence of two glass transitions with maxima at T_{g1} ~ 215°C and T_{g2} ~ 263°C. The presence of the two T_g's can be explained by the occurrence of a microphase-separated morphology with domains containing both hybrid CER/MMT (with T_{g1}~ 215°C) and highly crosskinked pure CER networks (with higher T_{g2} value). Analysis of the data presented, namely tan δ curve, allows concluding the completeness of CER network formation in the temperature range used.

The NC$_1$ reference sample was also studied by TGA and DSC (data not presented). It was found that the main degradation process occurred at Td_{onset} ~ 406°C, the maximum rate of degradation reached at Td_{max} ~ 456°C and char residue (measured at 900°C) was around 46%. DSC analysis revealed the beginning of glass transition at ~ 216°C with maxima at T_g ~230°C. Inequality of temperature values measured by DMTA and DSC for all the samples investigated can be attributed to the differences in determination of the T_g's and in heating rates

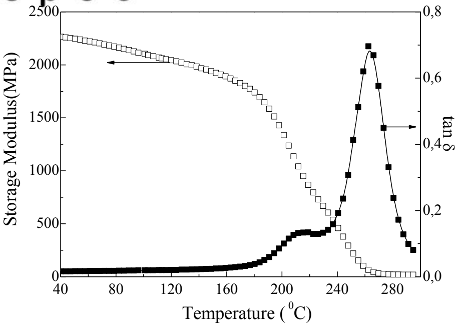

Figure 1. Storage modulus (E') and tan δ versus temperature for NC_1 sample (at frequency 10 Hz).

applied. Previously, we have detected chemical interactions between the organic modifier of the nanoclay used and CER monomer [3]. Therefore, we assumed the changes in dispersion degree at higher temperatures affecting the final viscoelastic and thermal properties of CER/MMT nanocomposites synthesized. The effect of dispersing time was studied at 150°C when gel point for individual CER monomer can be reached. The results are presented in Figure 2. One can see slight shift of single relaxation transition to lower temperatures and broadening of glass transition region as compared to the reference sample (see Fig. 2a). It was found that the longer duration of dispersing stage at 150°C the higher E' and tan δ values were observed. However, the temperature dependence of tan δ revealed only one T_g maximum in the investigated temperature range corresponding to the glass transition process of the hybrid CER/clay networks formed (see Fig. 2b). Increasing dispersing temperature from 150 °C (Fig. 2, sample NC_3) to 165 °C (Fig. 3, sample NC_5) results in slight decrease of E' values and narrowing glass transition temperature range with higher T_g value (~251°C). Thus, one can suppose generation of fully cured structure in NC_5 sample with higher T_g unlike incomplete curing for NC_3 sample evidenced by increasing tan δ value at $T > 250$ °C (post-curing of NC_3 sample, Fig. 2b).

Comparative DMTA studies for NC_5 and NC_6 samples showed that applying step-by-step curing instead of dynamic heating procedure leads to increasing E' values in the temperature range up to T~180 °C. One can suppose

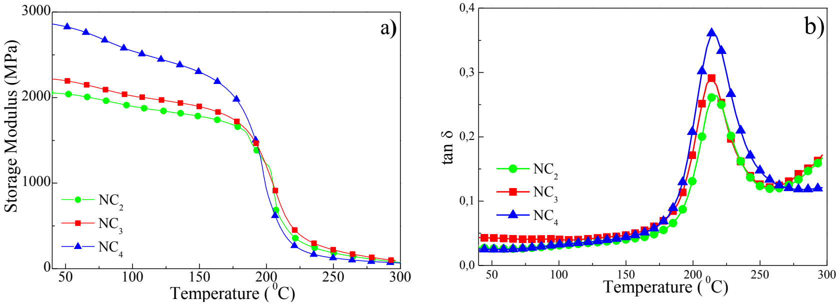

Figure 2. DMTA data for NC_2, NC_3 and NC_4 samples.

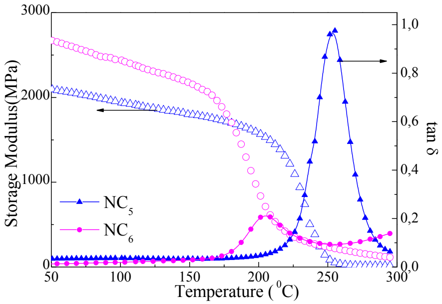

Figure 3. DMTA data for NC_5 and NC_6 samples.

that this curing schedule allows effective reinforcement of CER network by MMT nanofiller. The considerable decrease of T_g and height of tan δ values is observed as well and post-curing starts at $T > 250^{o}C$ (Fig. 3).

TGA and DSC results for all the CER-based nanocomposites investigated are summarized in Table 2. It was found that degradation of all the CER/MMT nanocomposites investigated occurs at $T > 410°C$ and the main degradation characteristics are close enough. Therefore one can assume that thermal degradation behavior of CER/nanoclay compositions synthesized mainly depends on composition and final curing temperature.

Table 2. The main thermal characteristics for CER/MMT nanocomposites synthesized

Sample code	TGA data				DSC data			
	Td_{onset} (°C)	Td_{max} (°C)	Δm at Td_{max} (%)	Char residue (%)	Tg_{onset} (°C)	Tg_{end} (°C)	ΔTg (°C)	Tg (°C)
NC_2	416	450	26	45	184	216	32	198
NC_4	426	448	21	46	170	210	40	184
NC_5	427	449	22	47	203	230	27	217

DSC data are in a good agreement with DMTA results confirming the decrease of Tg_{onset} and expansion of glass transition interval for NC_5 as compared to NC_4 sample and significant growth of Tg value for CER/MMT nanocomposite dispersed at T=165 °C and cured by dynamic mode.

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L9

FREE RADICAL REACTIONS IN BIOLOGICAL SYSTEMS – A CONCEPT APPROACHED IN THE RESEARCHES CARRIED OUT BY PROFESSOR CRISTOFOR I.SIMIONESCU

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Between 1956-1968 professor Cristofor I.Simionescu together with his coworkers carried out researches and published obtained results in the field of vegetable tumor. They studied aspects concerning induction, evolution, chemistry and inhibition following *Agrobacterium tumefaciens* (*Rhizobium radiobacter*), which is causal agent of crown gall disease (the formation of tumour). To inhibit tumor formation the polyphenols compounds were used, supposing that their action is based on inhibition of radicals involved in the cancer propagation. At present the activity of natural polyphenols is confirmed and a lot of scientific contributions were published. Continuing the preoccupations of professor Simionescu and based on biorefining principle we have separated and characterized natural polyphenols from different sources and their activity to inhibit radical formation under stress, hydrogen peroxide and UV irradiation was proved in biological systems.

L10

NANOINDENTATION AND ITS APPLICATION FOR THE STUDY OF PLASMA TREATED POLY(LACTIC ACID) SURFACE

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Nanoindentation is an important method for the evaluation of the mechanical properties of small material volumes and thin films to applied loading. In this work nanoindentation was used for evaluation of nanomechanical changes on the Poly (Lactic Acid) (PLA) films which are widely used in industry due to unique properties (biodegradable, moisture, grease and scratch resistant, heat-sealable, printable and naturally stiff). In this study PLA films (NatureWorks LLC) were subjected to air, respectively argon plasma treatment (capacitively coupled radiofrequency generator of 100 Pa pressure, for 10 minutes). Consequently various analyzes (nanoindentation, FT-IR, XPS, AFM, SEM, DSC, surface energy testing) were performed with a primary focus on nanoindentation, which provide mechanical data on nano-scale. It was shown that 10 min plasma treatment affects a surface layer of ~150 nm of the PLA foils, resulting in higher surface roughness. Air treated PLA foil presented increased hardness (H) values ~ 300 MPa, compared to ~200 MPa for untreated and 10 min Ar plasma PLA foils. The observed reduction in the E_r values indicate that the PLA foil present different elastic properties than the pristine PLA, due to PLA's degradation. Furthermore, the time-dependent and viscous behavior of the samples was tested. It was shown that both plasma treatments result in variations in the measured H and E_r values with increasing strain rate, as a result of the changes in the PLA structure. Additionally, it is observed that both plasma processes increase creep of the PLA foils, as a result of the energy dissipation in the PLA structure. More pronounced viscous behavior and higher creeping is attributed to 10 min Ar plasma treated PLA sample. Although, changes in the measured nanomechanical properties are observed for both plasma treatment processes, the etching of the air and Ar plasma result in increased surface roughness, slight chemical modification.

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L11

POLYELECTROLYTES IN CALCIUM CARBONATE MINERALIZATION

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Biomineralization refers to the “selective extraction and uptake of elements from the local environment and their incorporation into functional structures under strict biological control” [1]. Biominerals are inorganic–organic composites, in which the organic component exerts substantial control on the mineralization process, which results in the formation of structures of uniform size, specific crystallographic orientation and interesting properties [2]. Understanding the biological concepts, mechanisms, functions and design features and applying them to the development of new synthetic advanced materials and devices, makes biomineralization a very attractive subject of study.

Calcium based minerals represent more than 50% of the 60 different known biominerals [3]. Calcium carbonate is the most widely used material for skeletal purposes, representing most of the invertebrate phyla of the animal kingdom. $CaCO_3$ exists as three different anhydrous polymorphs - calcite, aragonite and vaterite, all of which occur in calcified tissues. A monohydrate (monohydrocalcite) and hexahydrate form (ikaite) of $CaCO_3$ have also been identified as metastable precursor phases during the initial stages of crystal formation. $CaCO_3$ crystals exhibit different types of morphologies: synthetic calcites normally crystallize out as rhombohedra, aragonites form clustered closely-packed needle-like structures and vaterites invariably exhibit floret-like morphology.

In living organisms, different forms of solid inorganic materials having interesting properties and hierarchical structures are synthesized in the presence of organic templates [4]. There are many studies to investigate different mechanisms for biomineralisation processes. Different substrates and proteins were used to induce the nucleation and growth of inorganic crystals. The organic additives strengthen mechanical properties and influence the mineralization process. Several studies dealt with the effects *in-vitro* of various additives (surfactants, polymers, proteins and block copolymer) on the morphology and size of $CaCO_3$ particles. However, more investigations are still needed to elucidate the mechanisms by which such additives affect the $CaCO_3$ nanocrystals structures and their aggregation to yield various morphologies of $CaCO_3$ final particles. In this context,

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our studies focused on an *in vitro* chemical approach of biomineralization using different polymeric materials, such as: soluble polymers, colloidal dispersion based on complementary polyions and some ionic insoluble matrix.

1. ***Soluble anionic polyelectrolytes***. The use of polymeric templates induce the formation of new materials with specific structure, advanced properties, and functions, the crystallization mechanism being tuned by the specific interactions with polar functional groups such as: –COOH, –PO$_3$H, –SO$_3$H.

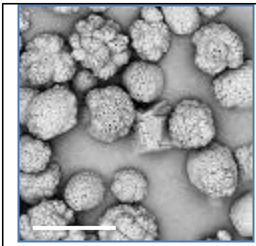
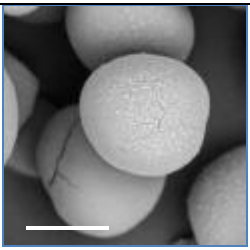
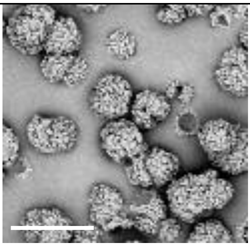
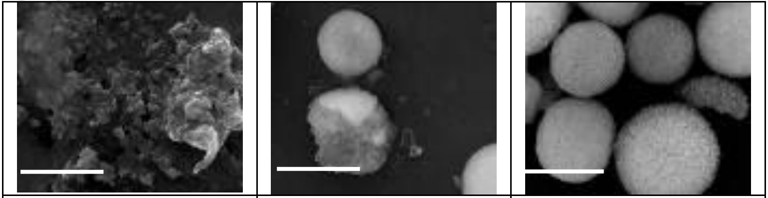
		
CaCO$_3$ [CaCl$_2$]=[Na$_2$CO$_3$]=[0.3 M] calcite 4.7% vaterite 95.3%	CaCO$_3$/0.05 % P [CaCl$_2$]=[Na$_2$CO$_3$]= [0.3 M] calcite 37.3% vaterite 62.7%	CaCO$_3$/0.04% P [CaCl$_2$ =[Na$_2$CO$_3$]=[0.1 M] calcite 100% vaterite 0%

Figure 1. SEM images for some CaCO$_3$/polymer samples; P = poly(2-acrylamido-2-methylpropanesulfonic acid – co – acrylic acid); scale bar – 10 μm.

Our studies [5-10] showed that polyanion presence during the CaCO$_3$ crystallization influence the ratio between the calcite/vaterite polymorphs in composites, the particles size and shape (Figure 1), the composites sorption capacity and their pH stability.

2. ***Mixed anionic/cationic polyelectrolytes***. In this context, we followed the effects of mixed anionic/cationic polyelectrolytes on the crystallization of calcium carbonate in supersaturated solutions [11,12]. Also, the method of introducing the polycation in the crystallogenesis of calcium carbonate has been investigated: preformed NPECs (CaCO$_3$//NPEC(PSS/PD)) or *in-situ* mixing of complementary polyelectrolytes (CaCO$_3$//PSS/PD). The molar ratio between complementary polyelectrolytes used in CaCO$_3$ composite synthesis varied between 0 (just polyanions) up to 0.95 (close to the equimolar ratio between ionic charges of complementary polyelectrolytes).

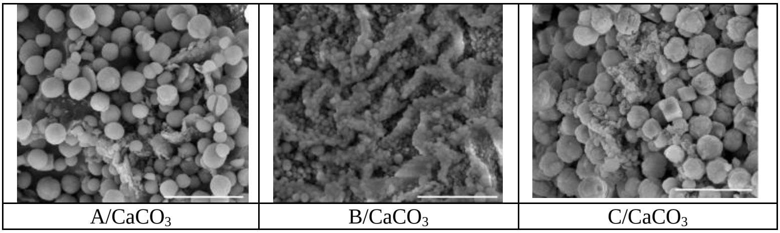


$CaCO_3$//PSS | $CaCO_3$//PSS/PD | $CaCO_3$//NPEC(PSS/PD)

Figure 2. SEM images of some samples after EDTA treatment; PSS – poly(sodium styrene sulfonate), PD –poly(dimethyldiallylammonium choloride). Scale bar – 5 µm.

The composite microparticles stability against the treatment with EDTA depends on their inner structure: removal of $CaCO_3$ nanosized crystals from $CaCO_3$//PA; increase of the $CaCO_3$//PA/PD microparticles stability against $CaCO_3$ dissolution with the polycation content; significantly increased $CaCO_3$//NPECs microparticles resistance against EDTA, the arrangement of preformed NPECs into the composites and the Ca^{2+} ions bridges formed between uncompensated anionic chains conduct to a dense network matrix.

3. ***Insoluble ionic matrix***. Gel-like crosslinked polymeric beads with weak acid (-COOH, sample A), weak basic (-NH_2, sample B), or amphoteric (both type of groups, sample C) functional groups were used.



A/$CaCO_3$ | B/$CaCO_3$ | C/$CaCO_3$

Figure 3. SEM images of beads surface after $CaCO_3$ crystalization. Scale bar – 20 µm.

The pathway for crystals growth depends on the nature of functional groups on beads surface. Thus, the formation mechanisms of $CaCO_3$ on anionic beads (sample A, Figure 3) is expected to take place first by the interaction of acidic groups on the spheres and with Ca^{2+} ions thus providing the nucleation centers upon which crystallization could occur. Primary amine functionalized polymers can exhibit strong interactions and therefore constitute an effective class of growth additives for $CaCO_3$. Thus, beads from sample B were covered by a thin layer of $CaCO_3$ crystals. The highest stability against dehydration was observed when beads from sample C were used as substrate for $CaCO_3$ growth. The functionalized side chain in sample C beads is longer. In this case the surface morphology showed a large excess of crystals, more likely that evident in sample A/$CaCO_3$.

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WELDING OF PLASTICS: FROM BASIC APPROACHES TO FUNDAMENTAL KNOWLEDGE

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Introduction

As we know polyethylene (PE) is one of the common materials in the modern world, and PE products take the major share on industrial and trade markets. For example, various types of PE like PE-63, PE-80 and PE-100 have wide industrial applications – in construction, for pipeline systems etc. But rapid development of plastics industry limits detailed investigation of welding processes and welds' formation mechanism; they stay unrevealed. There is still no final answer to the question how weld's microstructure forms. Such approach limits our way to the understanding of the problem and, respectively, prevents scientific approaches to the welding of more complicated (from chemical point of view) types of polymers than PE. In this regard the article presents results of complex investigations of various PE welds, analysis of these results, and basing on that some models of welds and welds structure formation.

Key words: polyethylene, PE-63, PE-80, PE-100, welding.

Experimental

The following samples have been used for welding experiments, for structure analysis, mechanical and thermal properties' investigations: polyethylene pipes produced of two types of high density polyethylene (HDPE) – PE-80 (MW 80000 g/mol, density 0,953 g/cm^3), and PE-100 (MW 100000 g/mol and density 0,96 g/cm^3).

The welding experiments have been carried with 63 mm diameter PE-80 and PE-100pipes, using traditional hot plate butt welding. SAT-1 hot plate welding device produced by Experimental Welding Equipment Factory of E.O.Paton Electric Welding Institute has been used for welding. Photo of PE-80 and PE-100 pipes' weld is presented on Fig. 1.

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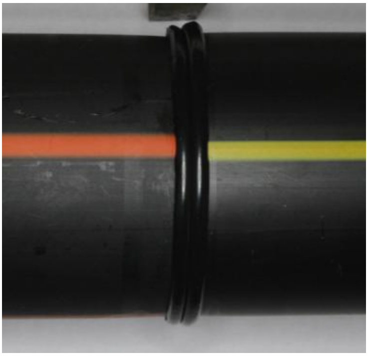

Figure. 1. Dissimilar pipes weld (PE80 and PE-100, 63 mm diameter).

Structure investigation of both PE types has been performed using wide-band X-ray spectroscopy (WAXS).

Thermal properties of the initial specimens and of the welds have been investigated by means of differential scanning calorimetry on DSC Q2000 device from TA Instruments (USA) in the inert atmosphere under temperatures from 40 to 200^{o}C with linear heating rate 20 ^{o}C/min.

Thermal stability and thermal-oxidative breakdown of the initial specimens and of the welds have been investigated on TGA Q50 device from TA Instruments (USA) in the dried air atmosphere under temperatures from 30 to 700^{o}C with linear heating rate 20^{o}C/min.

Thermomechanical behavior and deformational characteristics of the initial specimens and of the welds have been investigated on TMA Q400 EM device from TA Instruments (USA) in the dried air atmosphere, with temperature modulation 5^{o}C with linear heating rate 10^{o}/min under temperatures from 30 to 250^{o}C. Measurements have been carried in thermal expansion mode. Cylindrical fused quartz indenter (diameter 2,8 ± 0,01 mm) has been used. Applied indenter loading to the specimen was permanent and equal to 10^{-1} MPa.

Mechanical properties of initial and welded specimens have been evaluated by means of tensile axial test at room temperature.

Results and discussion

Thermogravimetric investigation results for PE-100, PE-80 and their weld are presented on Fig. 2, a. It is evidently that thermal-oxidative breakdown process curve of PE-80/PE-100 weld is located between thermal-oxidative breakdown process curves of pure PE-80 and PE-100. Such integral behavior of curves is logical and is not subject to any questions. But in the starting area of thermal-oxidative breakdown process there is a certain increased stability of PE-80/PE-100 weld comparing to the pure polyethylens. As one can see on the insert on Fig. 2, a PE-80/PE-100 weld has lower weight loss in the beginning of the breakdown and 10^{0}C increased temperature of breakdown start comparing both with PE-80 and PE-100. Such picture may indicate that some structures with higher thermal stability are formed in the weld (and such structure is absent or it’s quantity is much less in the pure materials).

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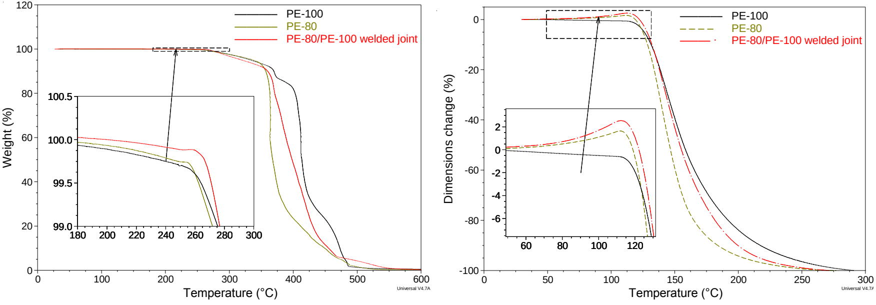
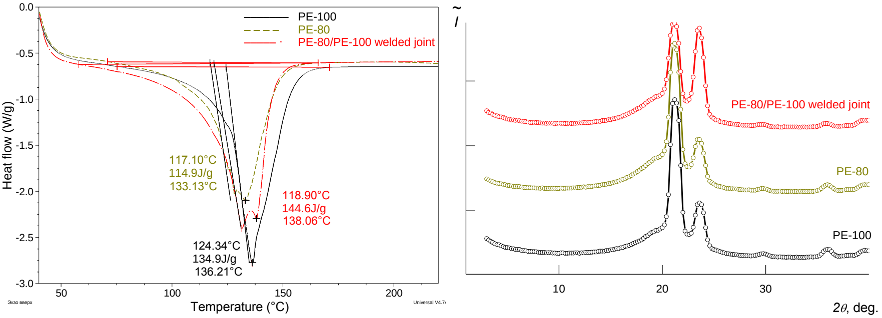


a) b)

Figure 2. Thermogravimetric (a) and thermomechanical (b) results of pure PE-80, PE-100 and their PE-80/PE-100 weld.

Similar behavior of materials is observed in the thermo-mechanical test results (Fig. 2, b). Relative strain curve of PE-80/PE-100 weld during the melting under temperatures exceeding start of melting temperature $T_m \approx 115^oC$ is located between respective curves for pure PE-80 and PE-100. Wherein under temperatures 25-115^{o}C (before start of melting) PE-80/PE-100 weld has the maximum value of thermal expansion (insert on Fig. 2, b) comparing to the pure PE-80 and PE-100, and this may indicate that areas with higher packing characteristics, and these areas are rapidly expanding under heating increasing the volume of the material.

Basing on the abovementioned data we can assume that under welding of dissimilar types of polyethylene, like PE-80 and PE-100, areas with higher thermal stability and higher packing characteristics are formed in the welding zone. This idea has been confirmed by the results received by means of differential scanning calorimetry (DSC, Fig. 3, a), and wide-band X-ray spectroscopy (WAXS, Fig. 3, b).



a) b)

Figure 3. DSC (a) and WAXS (b) spectrums of pure PE-80, PE-100, and of their weld PE-80/PE-100.

Two diffraction maximums on WAXS spectra as well as two melting minimums on DSC curves confirm the presence of two types of crystallites in both PE. The change of intensities of both maximums on WAXS spectra of the PE-80/PE-100 welded joint with the increase of the second maximum that corresponds to more dense crystalline structure, and the increased enthalpy of fusion (144,6 J/g) of the PE-80/PE-100 welded joint comparing to pure PE-80 (114,9 J/g) and PE-100 (134,9 J/g) prove the formation of more stabile nanosized crystalline phase with the increased electronic density in the PE welded joint during butt welding (Table 1). That leads to the increased strength of the welded joint and, consequently, its operational characteristics.

Table 1. Structural and operational characteristics of the PE-80, PE-100 and the PE-80/PE-100 welded joint

Sample	Crystallinity degree (DSC) (%)	Crystallinity degree (WAXS) (%)	Crystallite size ($2\Theta_{max}$= 21,2°) (nm)	Crystallite size ($2\Theta_{max}$= 23,6°) (nm)	Strength at break (MPa)	Strength at break (%)
PE-80	42	56	7,2	7,2	19,6	100
PE-100	51	57	7,2	7,2	23,1	100
PE-80/PE-100 welded joint	53	66	7,2	8,0	Destruction of PE matrix	> 100

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ORAL COMMUNICATIONS

Co1

CATIONIC COPOLYMERIZATION OF RACEMIC-β-BUTYROLACTONE WITH L,L-LACTIDE

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Cationic copolymerization of racemic β-butyrolactone (BL) with L,L-lactide (LA) initiated by alcohol and catalyzed by trifluromethanesulphonic acid proceeding by Activated Monomer (AM) mechanism will be presented. It has been found that, although both comonomers were present from the beginning in the reaction mixture, polymerization proceeded in sequential manner, with poly-BL formed at the first stage acting as a macroinitiator for the subsequent polymerization of LA. Such course of copolymerization was confirmed by following the consumption of both comonomers throughout the process as well as by observing by ^{1}H NMR the changes of growing chain end structure.^{13}C NMR analysis and thermogravimetry revealed the block structure of resulting copolymers.

Proposed mechanism of copolymerization was confirmed by studies of changes of ^{1}H NMR chemical shift of acidic proton in the course of copolymerization providing an indication that indeed protonated species and hydroxyl groups are present throughout the process, as required for AM mechanism [1].

As a consequence of a distinctly different reactivities of both comonomers in copolymerization, cationic copolymerization of BL with LA by AM mechanism provides a convenient, one-pot synthetic route to diblock or triblock copolymers of low to medium molecular weight [2].

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Co2

CONFORMATIONAL PROPERTIES OF MULTIGRAFT HOMOPOLYMERS IN GOOD SOLVENT. A COMPUTER SIMULATION INVESTIGATION

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An extensive computer investigation has been carried using Monte Carlo simulations to probe the equilibrium structure of multigraft homopolymers. They are basically branched polymers in which flexible side chains are regularly placed along a flexible backbone (main chain) at grafting nodes. The study focused on the branched architectures in which one, two or four side chains could be grafted at each node of the backbone, that is increased node functionality(Figure 1). The conformations adopted were investigated under good solvent condition using a coarse-grained bead-spring model and an efficient algorithm involving collective moves of sections of the backbone and side chains. The structural characterization of the side chains, main chain and the whole branched polymer was performed at varying the number of side chains grafted at each node, the spacing between nodes and the side chain length. The results shed light on how the properties on the branched polymers depended on increasing node functionality.

The main conclusions drawn from the results are presented in the following. (i) The scaling behaviour analysis revealed that one has to discriminate between (a) the branching density, denoting the linear density of nodes along the main chain and (b) the grafting density defined as the linear density of the grafted side chains. (ii) The scaling formalism generally employed for describing comb copolymers could be also used to describe the scaling properties of multigraft homopolymers at all branching multiplicity. The evidences were obtained by adequate descriptions in terms of power-law dependences found for the radius of gyration and the end-to-end distances of the polymers or their sub-chains. (iii) The conformations of the backbone and side chains were mainly driven by the excluded volume interactions between side chains attached to the successive nodes, whereas those acting among chains attached to the same node plays only a secondary role.

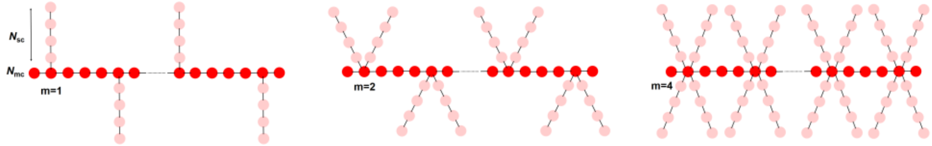

Figure 1. Schematic representation of the topology of multigraft polymer possessing main chain (red) and one, two or four side chain (light red) beads at each node, with N_{mc} is number of backbone beads, h the bead increment between subsequent nodes, N_{sc} the number of beads in one side chain, and m the branching multiplicity.

1. *Daniel G. Angelescu, Per Linse*, Monte Carlo Simulations of Multigraft Homopolymers in Good Solvent. Macromolecules 47, (2014) 415-426.

Co3

PHOTOPOLYMERIZABLE COMPOSITES BASED ON VINYL ACETATE, *P*-ACRYLOYLOXYBENZALDEHYDE AND N-METHACRYLOYLOXYETHYL-N’-FLUORESCEINYL UREA AS ORGANIC MATRICES FOR SILVER NANOPARTICLES

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Great interest has been focused on fabricating nanoparticle assemblies since they represent a popular route toward the preparation of advanced functional materials, and a modern concept in nanoscience and nanotechnology. [1] Polymer-nanoparticle (NP) composites can have various novel and improved properties originating in the synergism between organic and inorganic components. As a consequence, these nanocomposites have a large applicability in many relevant domains such as coatings [2-4], inks [5, 6], dental materials [7], optical elements [8, 9], photoresits [10, 11], and so on.

The objective of this research was to obtain hybrid polymer composites containing stable silver nanoparticles (AgNPs) prepared by the UV-assisted *in situ* reduction of silver nitrate using a matrix based on vinyl acetate (VAc), *p*-acryloyloxybenzaldehyde (AcrBzA), N-methacryloyloxyethyl-N’-fluoresceinyl urea (MA-Fl) or trietoxysilylpropyl carbamoyloxyethyl methacrylate (TCM), and phenyl-bis(2,4,6-trimethylbenzoyl) phosphine oxide (Irgacure 819) as photoinitiator. The formation of the nanoparticles (average diameter: 3-30 nm) by this method has been confirmed using UV-vis, fluorescence and energy-dispersive X-ray (EDX) spectroscopy, and transmission electron microscopy (TEM). The hybrid films emit fluorescence at 530 nm that could be quenched on the silver nanoparticles surface *via* electron and energy-transfer processes.

Since our aim was the preparation of hybrid nanocomposites, 1 wt.% and 2.5 wt.% $AgNO_3$ were embedded inside each formulation, in order to obtain a hardened structure after UV irradiation. The composition of the considered formulations is listed in Table 1.

In order to further understand the chemical composition of the photopolymerized films, the EDX spectroscopy was employed. The EDX map of element, presented in Figure 1, shows the metallic silver particles on the surface of copolymer film (F1) containing 2.5 wt.% Ag NPs. Thus, the bright spots in the map confirm the presence of silver atoms and their uniform distribution inside the polymer matrix.

Table 1. Composites formulation

Sample	AcrBzA (wt.%)	VAc (wt.%)	MA-Fl (wt.%)	TCM (wt.%)	$AgNO_3$ (wt.%)
F1	20	80	-	-	-
F1+1% Ag	20	80	-	-	1
F1+2.5% Ag	20	80	-	-	2.5
F2	15	55	30	-	-
F2+1% Ag	15	55	30	-	1
F2+2.5% Ag	15	55	30	-	2.5
F3	25	50	-	25	-
F3+1% Ag	25	50	-	25	1
F3+2.5% Ag	25	50	-	25	2.5
F4	12.5	50	25	12.5	-
F4+1% Ag	12.5	50	25	12.5	1
F4+2.5% Ag	12.5	50	25	12.5	2.5

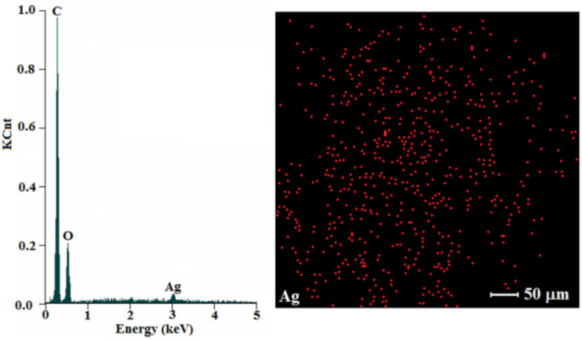

Figure 1. The EDX pattern, quantification data and corresponding EDX map collected from F1+2.5% Ag film.

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Co4

GAS AND VAPOR TRANSPORT PROPERTIES OF AROMATIC AND SEGMENTED POLYIMIDES

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The gas and vapor transport properties of a series of poly(ethylene oxide) (PEO) containing segmented polyimides (PEO-PI) and of a series of the respective aromatic polyimides (PI) with variations in dianhydrides and diamines have been reported. The polymers were synthesized by a two-step polycondensation route using 4,4'-bisphenol A dianhydride or 4,4'-oxydiphtalic anhydride, 3,3'-dihydroxybenzidine, 3,6-diaminodurene or 4,4'-(4,4'-isopropylidenediphenyl-1,1'-diyldioxy)dianiline as diamine comonomers, and a diamino terminated PEO of 2000g/mol molecular weight in 3:1 molar ratio, respectively. The obtained PIs and PEO-PIs were characterized by ^{1}H NMR and FT-IR ATR spectroscopies, DSC, TGA, WAXD, and AFM. The existence of microphase-separation in PEO-PIs was proved by the presence of two glass-transition temperatures in the DSC scans, and demonstrated in the AFM images. Pure gas permeability tests were performed at 7 bar and 30°C using O_2, N_2, and CO_2, and the effects of both incorporation of a flexible PEO segment and a rigid segment structure on gas permeation behavior were established. It was shown that introduction of PEO units in the polyimide generally led to very high gas permeability coefficients and caused significant improvement in CO_2/N_2 selectivity relative to that of the aromatic polyimides. The separation of water and methanol vapors from nitrogen streams was carried out through the selected polyimide membranes using vapor permeation apparatus. Equilibrium liquid sorption behaviors of those polymers were also studied by determining the amount of liquid water and methanol absorbed in the membranes. The results from the vapor and gas permeation investigations have been compared to those of the morphology studies.

Co5

GLASS FIBER COMPOSITES BASED ON USED POLYETHYLENE TEREPHTHALATE

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PET (polyethylene terephthalate) utilization is a very actual problem. On the Western Europe market recycling of package and films from PET are on initial level and ordinary consist next stages: 1. Crushing, 2. Washing, 3. Drying, 4. Extrusion. But, on a lot of recycling centers the main technological parameters (drying duration, drying and processing temperature) are not optimized. As a result a obtained materials are imported to China were is processed to single fibers for textile industry.

Is well-known that during to PET processing the destruction catalyst is a absorbed moisture. Was carried out a experiments on influence of moisture content in a polymer material on technological properties of PET. Basing on obtained data was determined that an optimal drying temperature begins from starting of crystallization process (120–160°C). The melt fluidity index (MFI) of used PET after extrusion depending on time and temperature of initial "flex" dry are shown in table 1.

Table 1.

T, °C	120		140		160	
Time of drying, hours	2	4	2	4	2	4
MFI, g/10min	3,426	3,348	2,554	2,392	1,915	1,696

During the conducted experiments the MFI is decreases as the moisture content changes in PET and accordingly inhibited hydrolytic destruction processes.

The main parameter of PET structure is a characteristic viscosity determined average molecular weight of the polymer. With increasing of viscosity decreases the molecular weight of the polymer. Was obtained that the characteristic viscosity of transparent "flex" is a 75 cm^3/g and for the mixture of transparent and blue transparent "flex" is a 105 cm^3/g.

Also was determined the characteristic viscosity after the screw-disc extrusion process (temperature of extrusion 255°C, disc rotation speed is a 60 rot/min).

Analyzing the data we can conclude that the characteristic viscosity after processing for transparent “flex” increases from 75 cm^3/g up to 93 cm^3/g and for the mixture of transparent and blue transparent “flex” decreases from 105 cm^3/g up to 92 cm^3/g. That can be a result of the adding to initial flex the recycled material according to “bottle to bottle” technology.

It’s widely known that molecular weight decreasing of PET is a result of –COOH group’s content during the destruction process and the molecular weight increasing can be done by using of a chain “extension” due to processing.

The melt fluidity index of used PET after extrusion depending on adding of chain “extenders” (CE) are shown in table 2.

Table 2.

CE,%	0,1	0,2	0,3	0,4	0,5	0,6	0,7	0,8	0,9	1,00
MFI, g/10 min	2,65	2,31	2,02	1,82	1,53	1,21	0,92	0,65	0,39	0,15

According to results from Table 2 we can see that the adding of the CE to used PET due to processing the MFI of composition decreases from 2.65 to 0.15 g/10 min, which can be a result of molecular weight increasing. The obtained composites got good physical mechanical properties (as example for 0,7 % CE content in used PET the tensile strength is 53 MPa, impact elasticity by Sharpie is a 109 kJ/m^2 , relative elongation at break is a 90 %)

With market saturation by expensive thermoplastic composites only high performance properties and tangible benefits in price will enter into a particular struggle with traditional polymeric materials. Consumer choice structural material is largely determined by the ratio for polymer composites and their performance properties.

As reinforcing filler was used a glass fiber “E” type as polymer matrix was used a PET with content of CE 0.7 %. In fig 1 are shown the tensile strength depending on glass fiber content.

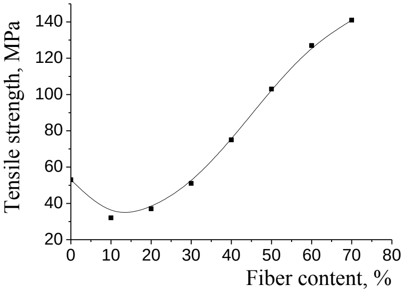

Figure 1. Tensile strength of composite based on modified used PET matrix and reinforced by glass fibers depending on glass fiber content..

Thermoplastic composites based on modified used PET matrix and reinforced by glass fibers possess the same fibre dominated properties as conventional composites but with the following benefits:

- the fibre volume fraction can be varied across the section from 0 to ~80% – this is not possible with conventional technology;
- greater component robustness due to the tougher matrix;
- improved environmental tolerance properties;
- the ability to post form and weld the material;
- raw materials are cheaper and have a much longer shelf life than conventional composites;
- potential for rapid process speeds;
- eco-friendly composites-use of recycled/reclaim, no use of solvents and are recyclable.

Co6

RAFT-MEDIATED COPOLYMERIZATION OF N-(2-HYDROXYPROPYL)METHACRYLAMIDE WITH N-ACRYLOXYSUCCINIMIDE AND SUBSEQUENT MODIFICATION OF THE COPOLYMER

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In this work we have determined the reactivity ratios of N-(2-hydroxypropyl)methacrylamide (HPMA) and N-acryloxysuccinimide (NAS) in DMSO using free radical polymerization (FRP) and reversible addition-fragmentation chain transfer (RAFT) and in DMF using RAFT.

A series of kinetic studies of RAFT mediated copolymerizations were conducted in two different feed compositions of NAS (20% and 30%). By an appropriate selecting monomer feed ratio and reaction conditions we showed that we can prepare compositionally uniform copolymers.

It was concluded that a 30% NAS feed composition in DMF led to a copolymer with minimised compositional drift and near-uniform incorporation of NAS into the HPMA backbone.

Further on, we demonstrated the post-polymerization modification of this copolymer with an aminated crown ether to yield a water-soluble HPMA polymer with pendant crown ether functionalities. This final product was investigated as modifier for quartz-crystal microbalance sensors, as an alternative for lead detection in aqueous and non-aqueous samples.

Acknowledgements.

This work was partially supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-II-ID-PCCE-2011-2-0028 and a SCIEX - Scientific Exchange Programme NMS-CH grant (The Swiss contribution to EU enlargement, for the SCIEX Fellowship 12.089).

Co7

HYBRID MEMBRANES COMPOSED OF POLYSULFONE MATRIX AND ZEOLITE OR METAL-ORGANIC FRAMEWORK PARTICLES

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Hybrid membranes (known also as mixed-matrix membranes) are expected to reveal transport properties better than pure polymer membranes being simultaneously easier processable than inorganic or metal-organic materials [1]. In this work, zeolite and metal-organic framework (MOF) particles were dispersed in glassy polysulfone to form hybrid membranes. Permeability and diffusion coefficients of N_2, O_2 and CO_2 in these membranes were determined as a function of the particles content. Presence of microporous zeolite 13X in polymer matrix was found to decrease both permeability and diffusion coefficients of all investigated gases. On the other hand, incorporation of mesoporous derivative of copper terephthalate (CuTPA) particles into polymer matrix resulted in increase of both transport parameters. For example, 1.6 times higher permeability was found for membrane containing 25wt% of CuTPA particles in polysulfone compared to pure polysulfone membrane. However, O_2/N_2 and CO_2/N_2 ideal selectivities of hybrid membranes were not affected by presence of the studied particles. To interpret the results, gas sorption measurements, positron annihilation lifetime spectroscopy and scanning electron microscopy were employed.

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Co8

THERMAL AND MECHANICAL RESPONSE IN POLYURETHANES BASED ON DBDI

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An aromatic diisocyanate (4,4'-dibenzyl diisocyanate (DBDI)) and a triol chain extender (1,1,1-trimethylol propane (TMP)) were included along with diethylene glycol (DEG) in the hard segment structure of polyurethanes urea, in order to widen the range of structures achievable and enhance the mechanical and thermal properties.

A dynamic mechanical study was performed in a systematic variation of the hard segment content in order to examine the influence of hard domain cohesiveness on the thermal and mechanical properties of polyurethanes. The ability to measure the viscoelastic parameters, which are closely coupled to mechanical properties, is important in a wide range of coating applications.

The introduction of crosslinks causes some changes into polyurethane morphology. In the glassy region the excellent mechanical and thermal properties were attributed to the presence of hydrogen bonds that held together the hard segments, combined with the effect of crosslinking. At elevated temperatures (higher than Tg) a weak cohesion force and a higher molecular mobility of hard segment chains was observed for the higher TMP content. This behaviour was explained as a result of the competitive action of at least three factors during the crosslinking: (i) weakening of the existing physical network due to hydrogen bonding; (ii) formation of a chemical network; and (iii) different reactivity of hydroxil groups of TMP.

Acknowledgements

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Co9

THERMODYNAMIC ASPECTS CONCERNING THE XANTHAN BEHAVIOR IN DILUTE SOLUTION

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The solution behavior of water soluble polymers is influenced by the characteristics of the polymer chains as well as the environmental properties.

Xanthan is one of the most studied water soluble charged polysaccharide due to unique properties generated by its structure. The primary structure of xanthan consists of a cellulose backbone bearing a side chain with three alternate glucose residues; a glucuronic acid residue flanked by a terminal mannose which is approximately 50% pyruvated and the other mannose having an acetal group. The thermodynamic characteristics of xanthan are influenced by the secondary structure and the formation of the ordered conformations is dependent on temperature and salinity conditions [1,2].

This study concerns the effect of salt nature (NaCl and KCl) and concentration (up to 3×10^{-1} mol/L) on the behavior of xanthan in dilute aqueous solution. From the viscometric data obtained at 25°C, some conformational characteristics of macromolecular chains in solution were determined. The polymer-polymer interactions, the excluded volume effects governed by polymer-solvent interactions, and chain stiffness were discussed.

The intrinsic viscosity was determined by means of Rao [3] and Wolf [4] methods. The results show that the new model proposed by Wolf provides accurate intrinsic viscosity values comparable with those obtained by using traditional method and allows the determination of some hydrodynamic parameters.

The addition of salt into xanthan aqueous solutions diminishes the repulsive electrostatic interactions between ionized groups. In these conditions, the xanthan chains undergo some conformational changes and aggregations.

The effect of extra salt addition on xanthan chains behavior in solution can be described with Boltzmann sigmoidal equation [5] (Figure 1); the upper limit of the salt concentration for which we suppose that the isolated polymer coils are as a single helix was determined [6].

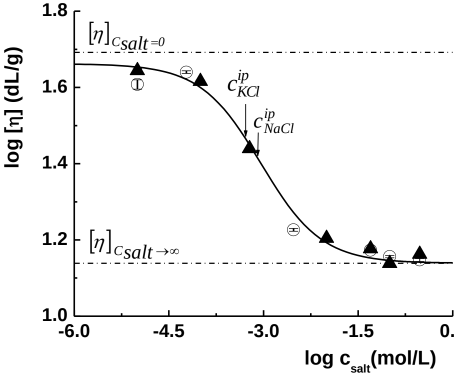

Figure 1. Dependence of the intrinsic viscosity as a function of the salt concentration for xanthan aqueous solutions at 25°C; full triangle – NaCl; open circle – KCl [6].

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS-UEFISCDI, project number PN-II-ID-PCE-2011-3-0199, contract 300/2011.

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Co10

NEW MATERIALS BASED ON POLYIMIDES CONTAINING ALICYCLIC UNITS

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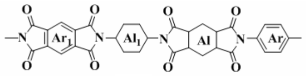
New copolyimides CPIs)containing structuralunitsderived from different combinations between the alicyclicdianhydride of bicyclo[2.2.2] oct-7-ene-2,3,5,6-tetracarboxylic acid(BOCA) and the aromaticdiamine4.4'diaminodiphenylether(ODA) with other aromatic and alicyclic monomers have been synthetized. The additionofalicyclicdiamines facilitates the control ofthe finalpolyimide properties such as flexibility, solubility,andprocessability[1, 2].

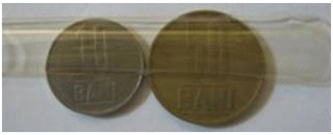
The new soluble and thermally stable CPIs are able to form both thin transparent, tough and flexible films from their solutions, and porous microspheres by suspension polymerization, in the presence of a crosslinking agent and two pairs of solvents as pore-forming diluents [3].

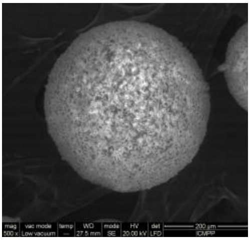
The resulting copolyimide films have a dielectric constantvalue in the range of 2.77 ÷ 3.38 and an opticaltransparencyat 430nmof90%, which was retainedafter abrief exposureat 300 °C of afilmhaving the thickness of40microns. Such materials are suitable for applications inmicro-and opto-electronic devices as excellentflexible andtransparentsubstrates.

An insight into the effect of synthesis parameters on the BOCA-based CPIs morphological modification into porous micro-particle beadsis presented.

The bead-shaped macroporous(co)polymers based on these new copolyimides could be potential candidates for applications as dielectric and/or surface-active materials.







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Co11

CRYSTALLIZATION DYNAMICS IN COPOLYAMIDE-CLAY HYBRID NANOCOMPOSITES

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Nanocomposites based on polymer matrix still offers large possibilities in many applications, results being visible at world-wide level. The most efficient way to obtain these materials is the intercalation of the inorganic-organically surface modified fillers in polymer matrix. Thus most important properties of material will be enhanced, such as tensile strength and modulus, decreased thermal expansion coefficient, enhancing ionic conductivity, increasing swelling resistance or reduced flammability. The posibility to quantify these improvements exist, so become easy to control the morphology which is responsible for structuring at macro-metric scale. Final properties will depend in fact, not only on distribution of filler, but also on the influence of interface polymer-filler which greatly affect polymer crystallization dynamic and crystallite morphology. Otherwise crystallization dynamic is one of efficient path to monitoring the efficiency of fillers added in polymer matrix, and can offer informations about level of intercalation-exfoliation of clay platelets [1].

Concerning to copolymers, the properties was greatly affected due minority of comonomer inclusion or exclusion from majority of comonomer crystals, as well as due presence of stereo-defects after the copolymerization process. Thus, hydrogen bonding formation is interrupted, so a reducing in crystallinity is expected relating to homopolymers. Measured melting temperatures are lower due to comonomer incorporation in crystal lattice [2]. Otherwise, the copolymerization of multicomponent is one of effective methods to decrease melting temperature of poyamides to enhance its prelucrability.

In this work, the the effect of three clay types added in aliphatic random copolyamide matrix [3] on the isothermal crystallization kinetic analysis and final morphology also are presented. These results was mainly done by thermal analysis (DSC) and completed by hot stage-polarizing optical microscopy technique.

From isothermal crystallization kinetic analysis results denote that MMT and o-MMT clays added in copolymer matrix induce lower crystallization temperatures, but faster crystallization rates and finaly a higher crystallinity index comparatively with bentonite and neat copolyamide. This suggest that strong interaction based on hydrogen bonds formed at interface copolymer-clay playing an important role in crystallite growth. Higher values of Avrami's kinetic parameters were obtained for the nanocomposites based on MMT and o-MMT. This indicate the ability of clays to control the crystallization process which allow the developement of bidimensional crystallites, but reduced in dimensions. The oposite situations is showed by neat copolyamide and bentonite-copolyamide nanocomposites where we observe higher crystallization temperatures and from crystallization kinetic analysis we deduced a slower crystallization rate and lower crystallinity index. This is characteristic for developement of unidimensional crystalllites in copolyamide morphology. The absence or a limited interface interactions increase ability of crystalization which start with a sporadic nucleation that allow growth of bigger crystallites.

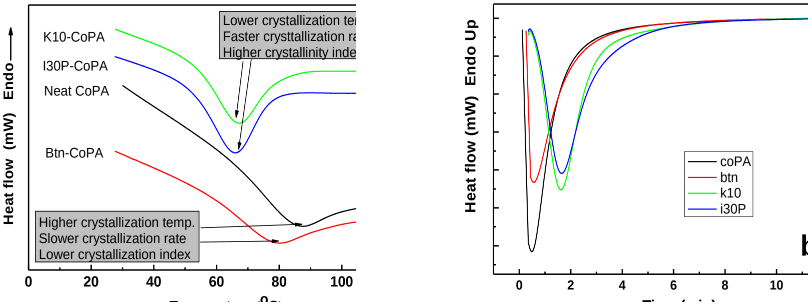

Figure. DSC analysis : a) Cooling scans and b) Isothermal crystallization.

Cross-polarized optical micrographs show that crystallite size for samples found in the neat copolyamide are much larger than those in their counterparts nanocomposite. Introduction of the nanoclays in the copolymer matrix suggests that chain mobility and crystallite dimension has reduced. On the other hand, an increasing of nucleation ability in copolyamide matrix cause an sighificant increasing of crystalline entity number. Crystallinity in the nanocomposite systems has increased as seen in cooling scans and isothermal kinetic analysis done by DSC.

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Co12

COMPARED PROPERTIES OF THIN FILMS MADE FROM AZO-POLYIMIDES

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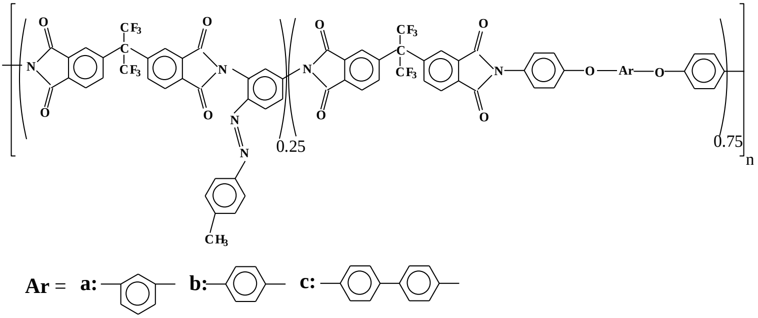
Azobenzene-containing polymers have received increasing attention due to their unique properties allowing various applications, such as in micro-fluidic or in membrane based separation systems, to optically change the materials surfaces wettability, in biology, to generate photosensitive micellar systems for drug delivery purposes, in optics or optoelectronics, to generate optical switching and data storage functions [1-5].

A series of polyimides containing azo groups (Scheme below) was synthesized and studied with regard to physical properties such as solubility, molecular weight distribution and thermal stability. The azo-polyimides have been prepared by two-step solution polycondensation reaction of hexafluoroisopropylidene-bis(phthalic) anhydride with a mixture of two aromatic diamines, one of them containing a pendent substituted azobenzene group. Thin films were prepared by casting the solutions of these azo-polyimides in dimethylacetamide followed by heating at temperatures up to 200˚C.



Co12

The dielectric, photoluminescent and structuring ability of these films were investigated by using appropriate techniques. The dielectric constant values are in the range of 3.25–3.65 being comparable and even lower than that (3.5) of polyimide Kapton film witch is usually taken as a standard for high performance dielectrics.

The films showed blue photoluminescence after irradiation with UV light. The films were also studied with regard to their structuring ability by laser irradiation. Figure 1 shows the AFM images of the patterns of an azo- polyimide.

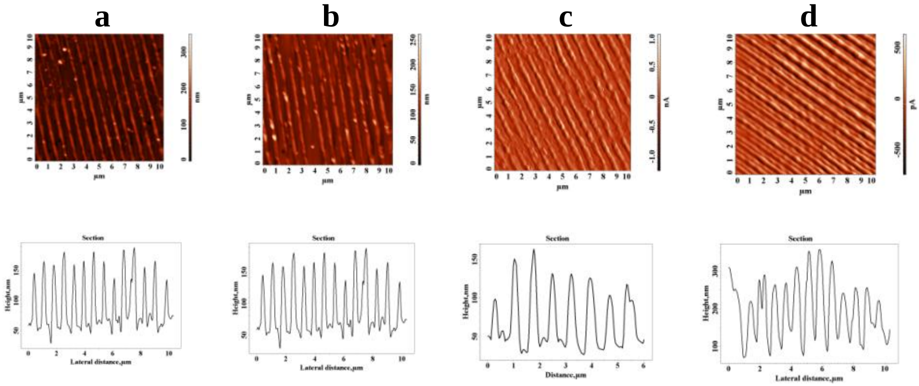


Figure 1. AFM images of the structured surfaces and diagram profiles of an azo-polyimide film after laser irradiation with 10 mJ/cm^2 and 45 mJ/cm^2 , by using 10 and 100 pulses.

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Co13

PHYSICAL HYDROGELS OF POLY(VINYL ALCOHOL)/POLY(VINYLPYRROLIDONE)

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Poly(vinyl alcohol) (PVA) and poly(N-vinylpyrrolidone) (PVP) are two polymers possessing non-carcinogenic, non-toxic, excellent transparency, film-forming capacity, biocompatible and bioadhesive characteristics.

Rheological behaviour of PVA and PVP aqueous solutions was investigated at 37 ºC as a function of PVA/PVP mixture composition. At high PVA content, the evolution of the viscoelastic parameters is influenced by solution composition. For example, Figure 1 shows the complex viscosity obtained for PVA/PVP mixtures with 15% concentration in aqueous solutions at 37 °C. It can be seen a Newtonian behaviour for all systems.

Up to 50% PVA in the polymer mixture, the viscoelastic behaviour typical to polymer solutions was observed ($G' \sim \omega^2$, $G'' \sim \omega$, $\delta >> 1$). In Figure 2 is presented the viscoelastic behaviour of 15% polymer solution which contains 50% PVP and 50% PVA. By increasing PVA content, the viscoelastic parameters evolve in time. The viscoelastic moduli reach a constant value after a period of time which is dependent on PVA content and for these systems G' becomes higher than G'' ($\tan\delta < 1$).

Physical hydrogels were prepared by freezing-thawing method and their properties were followed as a function of polymer composition, the number of freezing-thawing cycles, and aging time at 37 ºC. In Figure 3 is presented the evolution of the viscoelastic parameters in frequency sweep test for the same sample as in Figure 2 submitted to 4 freezing/thawing cycles.

Study of this kind of hydrogels is of great importance due to their ease of preparation and interesting properties which make them suited for biomedical applications, such as drug delivery, tissue engineering or wound dressing.

Acknowledgements. This work was supported by the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n°264115 – STREAM and by a grant of the Romanian National Authority for Scientific Research, CNCS-UEFISCDI, project number PN-II-ID-PCE-2011-3-0199.

Co13

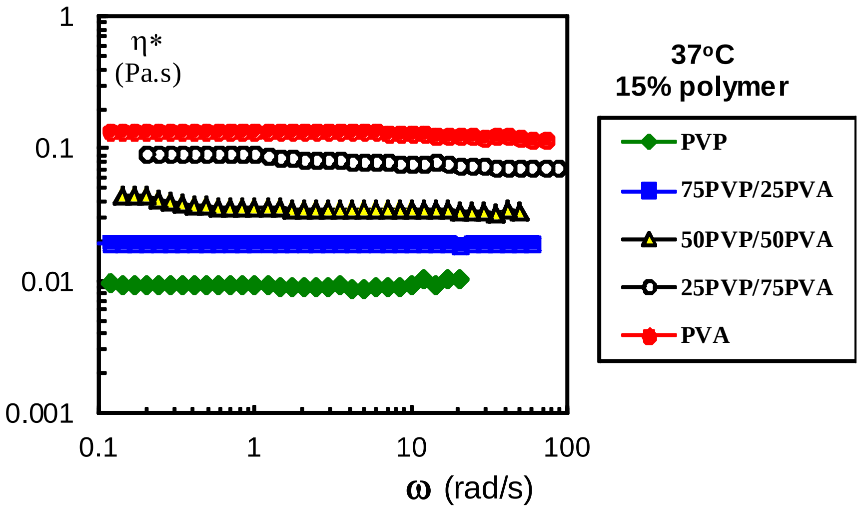

Figure 1. Complex viscosity obtained in frequency sweep experiments at 37 °C for 15% polymer solutions with different PVA/PVP compositions.

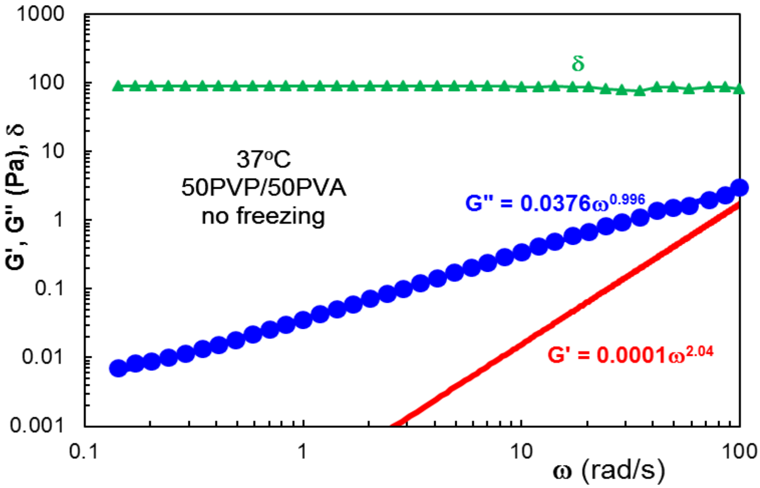

Figure 2. The viscoelastic parameters as a function of oscillation frequency for a solution with 15% polymer and composition of 50PVP/50PVA (37 °C, 1Pa).

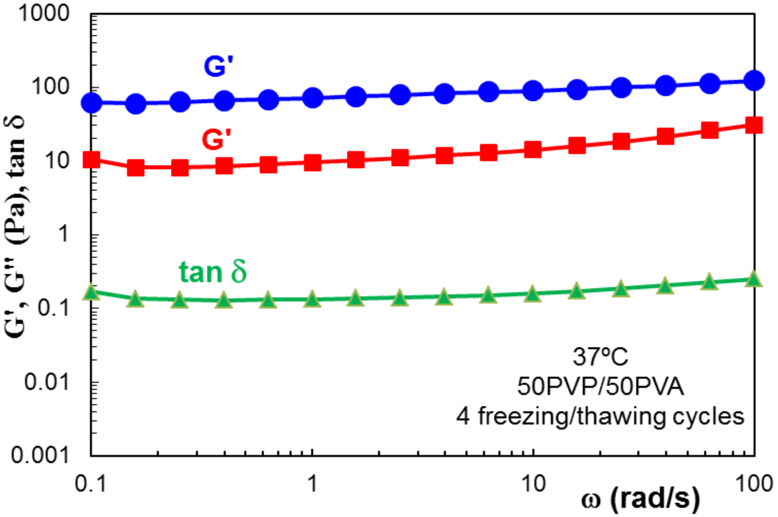

Figure 3. The viscoelastic parameters as a function of oscillation frequency for the same system as in Figure 2 after 4 freezing/thawing cycles (37 °C, 1Pa).

Co14

NEW PULLULAN DERIVATIVES.
LASER LIGHT SCATTERING AND TURBIDITY STUDIES

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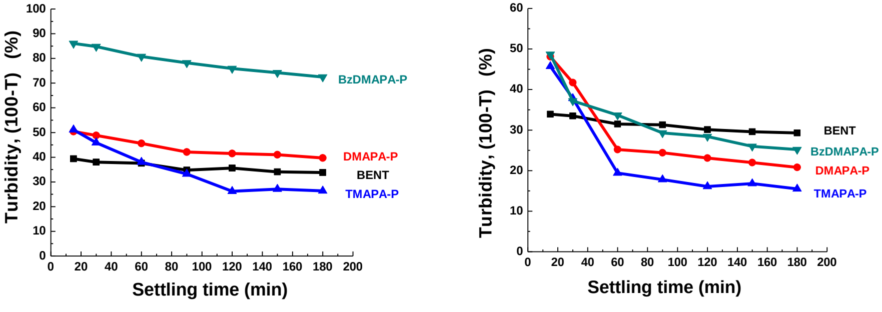
The first objective of this study was to describe the solution behavior of three new pullulan derivatives containing tertiary amine and quaternary ammonium groups (dimethylamino-propylamine pullulan DMAPA-P, trymethylammonium-propylamine pullulan TMAPA-P and benzyldimethylammonium-propylamine pullulan BzDMAPA-P) in polar and apolar solvents with salt added (0.5 M NaCl aq.sol., 0.5 M KCl aq.sol. and DMSO/0.5M LiCl) by laser light scattering. The second was to test the removal of inorganic materials from synthetic turbid water using these polysaccharides (alone or in tandem with NaCl) by turbidity measurements.



(A) **(B)**

Figure 1. Turbidity data for BENT alone, BENT with DMAPA-P, BENT with TMAPA-P and BENT with BzDMAPA-P in aqueous solutions without (A) and with 0.5M NaCl (B).

The shape of Zimm plots (Berry formalism) were related with the state of macromolecular chains in solution. The values of weight-average molecular weight $\overline{M}_w$ and radius of gyration R_g were influenced by hydrophilic-hydrophobic balance between head groups and main macromolecular chain.

The flocculation efficiency of studied compounds was related with their affinity to bentonite (BENT) particles.

Also, both study directions revealed that the nature of solvent was an important factor.

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2. *Podzimek S.*, Light scattering, size exclusion chromatography and asymmetric flow field flow fractionation. Powerful tools for characterization of polymers, proteins and nanoparticles (2011) John Wiley and Sons Inc., Hoboken, New Jersey, U.S.A.
3. *Ghimici L., Constantin M., Fundueanu G.* Novel biodegradable flocculanting agents based on pullulan // Journal of Hazardous Materials 181 (2010) 351–358.

Co15

VOLUME-STRUCTURED POLYMERIC MATERIALS WITH GIANT PERMITTIVITY

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One essential aspect related to the increasing demand for alternative energy sources represents the need to develop systems with enhanced capacity of energy storage. In this context, polymeric materials with high values of permittivity occupy an important place. One general strategy to increase the global permittivity of materials relies on the concept of inducing local variations in electrical conductivity across internal interfaces. Designing systems with enhanced permittivity implies thus to employ materials with high density of interfaces. Phase separated block-copolymers represent a natural approach to this concept. The self-structuration process driven by a disorder-order transition specific to this class of polymers leads to well–defined morphologies on the nanometric length-scale resulting in a huge density of interfaces. The incompatibility between the two polymer phases and the large difference in the miscibility toward an ionic liquid offers the possibility of an asymmetric doping leading to a nano-structuration process of the local electrical properties. This gives rise to a well-defined sequence of insulating and conductive polymer phases on the nanometric length-scale. In the present contribution we show that this approach can be used to produce materials exhibiting a giant permittivity (Fig. 1). This finding can have a great technological impact, especially in the field of energy storage.

The morphology, electrical and thermal properties of the composites based on the block copolymer PS-b-PMMA doped with an ionic liquid were investigated.

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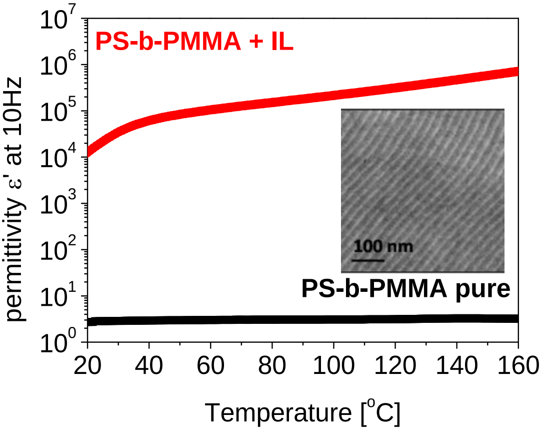

Figure 1. The permittivity value of pure PS-b-PMMA and of PS-b-PMMA doped with an ionic liquid. Insertion: sequence of insulating and conductive polymer nano-layers.

POSTERS

P1

VISCOELASTIC PROPERTIES OF INTERPENETRATING POLYMER NETWORKS BASED ON POLYURETHANE AND ORGANIC-INORGANIC COPOLYMER

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In recent decades, the problem of the development of organic-inorganic hybrid materials which have the possibility to combine properties of organic and inorganic components has gained scientific and practical attention. Such materials are distinguished by improved mechanical and thermal stability, and optimized heat transfer characteristics. The drawbacks of organic polymers such as low mechanical parameters and low thermal stability can be overcome by producing organic-inorganic interpenetrating polymer networks (IPNs) [1]. IPNs based on various modifications of poly(titanium oxide) have received particular attention due to their unique electrical, optical, and chemical properties [2]. In order to study the features of the formation of matrix nanostructures and to investigate their viscoelastic properties, IPNs based on cross-linked polyurethane (PU) and organic-inorganic copolymers (OICs) based on hydroxyethyl methacrylate (HEMA) and titanium isopropoxide **(**$Ti(OPr^i)_4$**)** were obtained by simultaneous synthesis. The PU - PHEMA ratio in the initial IPNs and the HEMA - $Ti(OPr^i)_4$ molar in organic-inorganic IPNs (OIIs) show in table.

The initial IPNs and OIIs were studied by the dynamic mechanical analysis (DMA) method. The molecular weight of the chain segments between crosslinks (M_c) was calculated via the equation of rubberelasticity.

It was shown that IPNs and OIIs are two-phase systems. Relaxation behaviour of IPN-1 and IPN-2 indicates that the phase structure of IPN composed of PU - PHEMA is significantly determined by the ratio of the components (Fig. 1).

For OII composed of PU – PHEMA - TiO_2 with a high content of the PU component (about 70 wt %) and different HEMA - $Ti(OPr^i)_4$ molar ratios, two relaxation transitions are observed (Fig. 2). The increase in the content of the (–TiO_2–) fragments leads to nonlinear changes in T_g for the OIC phase (Table).

Table. Parameters of relaxation transitions and M_c for PU, PHEMA, IPNs, and OI PNs

Sample	PU - PHEMA - TiO_2, wt. %	HEMA - $Ti(OPr^i)_4$	T_g PU, °C	T_g PHEMA / OIC, °C	M_c
PU	100 : 0 : 0		15	-	6000
PHEMA	0 :100 : 0		-	97	
IPN-1	70 : 30 : 0		15	95	5500
IPN-2	30 : 70 : 0		-	140	970
OII -1	70.8 : 28.1 : 1.1	16 : 1	20	100	2150
OII -2	69.0 : 29.6 : 1.4	12 : 1	20	65	3200
OII -3	68.5 : 29.4 : 2.1	8 : 1	15	65	4100
OII -4	67.4 : 28.7 : 3.9	4 : 1	20	90	2000
OII -5	28.6 : 69.1 : 2.3	16 : 1	10	110	1050
OII -6	29.0 : 67.8 : 3.2	12 : 1	-	140	850
OII -7	28.7 : 66.8 : 4.5	8 : 1	-	140	530
OII -8	27.7 : 64.3 : 8.0	4 : 1	-	140	180

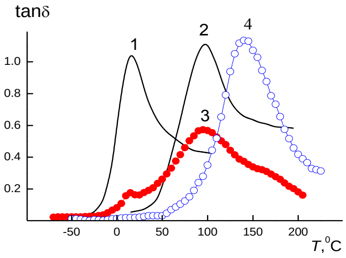

Figure 1. The temperature dependences of mechanical loss tanδ for PU (*1*), PHEMA (*2*), IPN-1 (*3*), and IPN-4 (*4*).

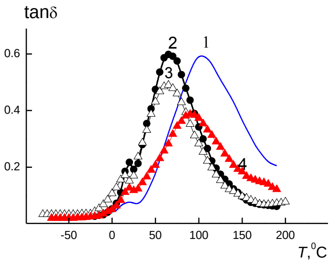

Figure 2. The temperature dependences of mechanical loss tanδ for OII-1 (*1*), OII-2 (*2*), OII_3 (*3*), and OII_4 (*4*).

The change in the M_c values as the concentration of the inorganic component increases also has a nonlinear nature. It can be assumed that some critical value of concentration of the inorganic component exists; thus, below this concentration the decrease in the content of this component leads to both an increase in the interphase interaction and an improvement in the molecular compatibility between the components, as well as a decrease in the density of the three-dimensional network. However, a further increase in the concentration of TiO_2 leads to an increase in the cross-link density in the system, as indicated by the rise in T_g values for the OIC component, as well as a drastic decrease in the M_c

values for OII-4.

In the case of OI IPNs, with a smaller content of PU component (about 30 wt %), the relaxation transition for the PU component barely occurs on the temperature dependences of tgδ (Fig. 3), but this transition is clearly visible on the temperature dependence of the loss modulus *E* '' (Fig. 4).

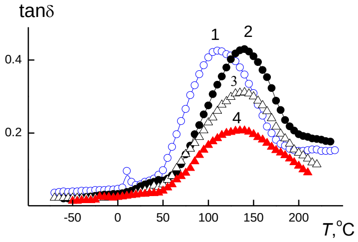

Figure 3. The temperature dependences of mechanical loss tanδ for OII-5 (*1*), OII-6 (*2*), OII-7 (*3*), and OII-8 (*4*).

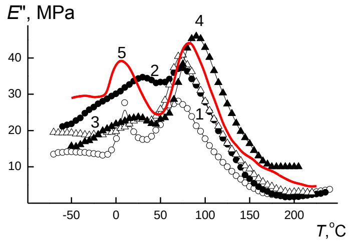

Figure 4. The temperature dependences of loss modulus *E* '' for OII-5 (*1*), OII-6 (*2*), OII-7 (*3*), OII-8 (*4*), and IPN-2 (*5*).

For OI IPNs with a low content of PU the nonlinear nature of the changes in the T_g values for the OIC component with an increase in the content of the Ti-containing component is also observed. The significant decrease in the M_c values suggests that the cross-link density enhances with an increase in the content of (–TiO_2–) fragments in OIIs with a low content of the PU component (Table). The cross-link density in OI IPNs depends not only on the content of the inorganic component but is largely determined by the composition of the polymer system.

Thus, three_dimensional cross-linked structures with the inclusion of (–TiO_2–) fragments in the polymer chain of PHEMA are formed during the simultaneous synthesis of organic-inorganic IPNs based on PU and Ti-containing copolymer. The nonlinear nature of the dependence of the changes in the physical properties of OI IPNs from the content of (–TiO_2–) fragments was found; this suggests the existence of some critical value of concentration of the inorganic component, above which the tendency of changes in the properties of organic-an-inorganic system can significantly vary.

1. *Naghash H. J.* Interpenetrating polymer networks based on poly(styrene-*co*-butyl-acrylate-*co*-hydroxyethylmethacrylate) and SiO_2 // J. Appl. Polym/ Sci. 122 (2011) 722-728.
2. *Wu Ch.*-S. In situ polymerization of titanium isopropoxide in polycaprolactone: Properties and characterization of the hybrid nanocomposities // J. Appl. Polym/ Sci. 92 (2004) 1749-1757.

P2

CORROSION RESISTANT POLYMERIC MATERIALS BASE ON OLIGODIENES WITH TERMINAL FUNCTIONAL GROUPS

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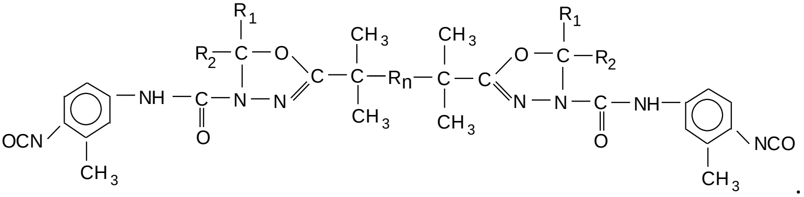
At the Institute Macromolecular Chemistry of NAN of Ukraine during many years the works on synthesis of oligodienes with terminal functional groups and based on them polymeric materials have been conducting. These are oligodienes with terminal hydroxyl, amine, hydrazide, acylhydrazone, oxyethylamide, etc. with molecular weight 500-6000, viscosity 15-90 Pa·s and functionality close to 2. On the base of oligodienes with terminal reactive groups and curing agents a range of polymeric materials which may use as sealants, adhesives, protective coatings and so on had been synthesized.

It is known that high physico-mechanical properties of polyurethanes are due to the presence in their molecules amide and carboxylic groups which are able to association. Increasing the concentration of such groups at the transition to polymers with urea groups leads to increasing physico-mechanical properties what causes interest to such polymers. So we think that at the development of materials stable to hydroabrasive wear in corrosive mediums the application of oligodienes with hydrazide and acylhydrazone groups are perspective.

An isocyanate forepolymer is obtained by interaction of oligodienedihydrazones with diisocyanate in molar ratio 1:2 in ether or ester solution at 30 °C during 20-30 min. It is found at that the cyclization of acylhydrazone groups under action of diisocyanate takes place with forming oligomers containing 1,3,4-oxadiazoline cycles:



where R: -C_4H_6-; -C_5H_8-; $R_{1,2}$: -Alk;

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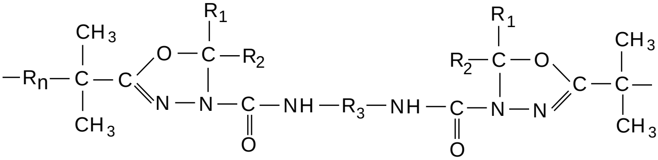
The reaction course is confirmed by the data of IR-spectroscopy: a process of oligodienedihydrazone and diisocyanate interaction is characterized by decreasing by 50 % absorbance intensity in the range of 2240–2270 cm^{-1}, typical for N=C=O groups, appearance of a 1310 cm^{-1} band of C-O-C-group valence vibrations; redistribution of intensities in the range of carbonyl absorbance, for what C=O i C=N groups of initial acylhydrazone are responsible, as well as C=O of a carbamate group, formed in the result of the reaction and an C=N group, which locates in an oxadiazoline cycle; disappearing of 3200 $см^{-1}$ band of - NH acylhydrazone group and appearing a 3300 $см^{-1}$ band of NH – hydrogen-bonded carbamate group, as well a 3410 – 3440 $см^{-1}$ band which, depending on a chosen diisocyanate, belongs to an NH hydrogen-unbonded carbamate group.

The isocyanate-containing forepolymers cured with di- and polyfunctional agents with active hydrogen atoms. The compositions were prepared directly before using. The gelatinizing time was determined by the nature of a curing agent and changed from 15-60 min. to 8-20 h. As a result polydieneoxadiazolinylcarbamates of common formula had been obtained:



where R: $-C_4H_6-$; $-C_5H_8-$; $R_{1,2}$: -Alk; R_3: -Alk, -Ar.

The study of the process of forepolymer curing showed that the best technological and mechanical characteristics of polymeric materials are achieved at using aromatic diamines as chain extenders. So, at curing an isocyanate-containing forepolymer prepared from liquid rubber and 3,3-dichloro-4,4-diaminediphenylmethane in organic solvent, which does not have in its structure active hydrogen atoms, e. g. methylethylketone, a range of polymeric materials were obtained which characterized high physico-chemical properties, depending on the ratio of elastic (forming on the base of diene chain) and hard (forming on the base of diisocyanate and a chain extender) blocks. Decreasing an elastic block length of these polymers leads to increasing their hardness and strength. The properties of linear polymers base on oligodienedihydrazones of various molecular weights and 50 % solution of 3,3-dichloro-4,4-diaminediphenylmethane in methylethylketone are given in the table 1.

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Table 1. The properties of polymers on the base of oligodienedihydrazides of various molecular weight

Molecular weight	Shore A hardness	Tensile strength, MPa	Tensile elongation, %	Residual elongation, %
1350 -2000	85-95	20-25	200-400	0-4
2350 -3000	69-85	12-20	300-400	0-8
3350 -4480	52-69	6-12	350-500	2-10

According to the amount of hydrogen bonded groups in a solution of polymer, there are associative processes that expresses in the viscosity increase of a polymer solution in nonpolar solvents. The difference in time of growth of a macromolecule and the formation of hydrogen bonds between them affects the supramolecular structure of the polymer. Study by small-angle X-ray spectrometry has shown that hydrogen bonds are the basic driving force of association, hence, segregation of blocks of the various natures of the segmented polymers.

The hydrophobicity of diene blocks in a polymer chain explains the fact that elastomers obtained have swelling as low as 10-100 times compare with urethane elastomers based on polyethers.

The resistance to hydroabrasive wear was estimated by the weight loss (the loss coefficient was determined as the ratio of wear of stainless steel to that of an elastomer). It was shown that the obtained elastomers, depending on the molecular weight, exceed in hydroabrasive wear stainless steel as much as 4-20 times (Figure 1).

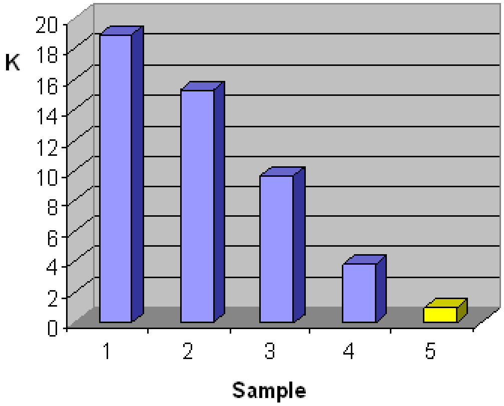

Figure 1. The relative hydroabrasive wear of stainless steel and polymers MM 2000 (1), MM 2800 (2), MM 3550 (3), MM 4400 (4), steel 12X18H10T (5), **K** - coefficient of relative hydroabrasive wear

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The resistance of elastomers to the influence of acid and alkali solutions of different concentrations was determined by the way of the comparison of physico-mechanical properties (tensile strength and tensile elongation) of the polymers obtained before and after the influence of corrosive medium. The investigation of polymer chemical resistance was carried out at the temperature 22±2 °C during 1000 h. The specimens were considered to be stable if they saved to 80 % of mentioned properties. The results of the tests on resistance of polydieneoxadiazolinylcarbamates to the influence of corrosive mediums are shown in Table 2.

Table 2. Resistance of the polymers based on oligodienedihydrazone, 2,4-TDI and 3,3-dichloro-4,4-diaminodiphenylmethane (reagent ratio 1:2:1) to the influence of corrosive mediums

Test medium	Concentration, %	Swelling degree, %
HNO_3	30	2,99
H_2SO_4	50	-0,39
HCl	10	-0,32
HF	30	2,22
NaOH	40	-1,43

.

The changes of the stability coefficient are connected with changing of the oxadiazolinylcarbamate group (formed at interaction of acylhydrazones with isocyanates) structure which are transformed to acylsemicarbazide ones under the influence of liquid corrosive mediums. It is confirmed by the IR- and UF-spectroscopy methods. It is shown from the comparison of UV-spectra of the products of the model substances interaction – butylisocyanate with benzhydrazide and benzhydrazone of methylethylketone, that they are differed. At addition of sulfuric acid during 15-20 min. their UV-spectra become identical what is of evidence of transformation of oxadiazolinylcarbamate groups in acylsemicarbazide ones. In IR-spectra of the polymers with oxadiazolinylcarbamate groups the changes are observed after treating with hot water or acid solutions what indicates on the oxadiazolinylcarbamate group to acylsemicarbazide one transformation. The 1350 cm^{-1} and 1670 cm^{-1} absorbance bands which are typical for an urea and C=O in acylhydrazide groups respectively are appeared; intensity redistribution in the region 1500-1600 cm^{-1} of NH group deformation vibrations.

The developed materials are perspective for usage as sealing materials and protective coverings stable to the influence of aqueous aggressive mediums and to hydroabrasive wear.

P3

NONISOCYANATE EPOXYPOLYURETHANES FOR POLYMERIC COMPOSITE MATERIALS

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New application of epoxy resins (ER) has required the development of the methods of modification and improvement of their properties. We have developed direction of the chemical modification of epoxide through introduction of urethane groups in ER without usage of toxic isocyanates. The using of cyclocarbonate oligomers (CCO) in the reaction with aliphatic amines leads to the formation of hydroxyurethanes. It is established regularities of the formation of polymers based on amine curing epoxy-cyclocarbonate compositions. High rate aminolysis of CCO determines the total curing process acceleration and the growth in system dynamic stiffness [1-2].

In this paper the results of modification of epoxy resin DER-331 (23.2% epoxy group (EG) by bifunctional CCO: cyclocarbonate of diglycidyl ether diethyleneglycol (CC DEG-1, 42.5% cyclocarbonate (CC) group), cyclocarbonate of diglycidyl ether 1,4-butanediol (CC DGEBD, 49.3% CC group). Diethylenetriamine (DETA) was used as hardener.

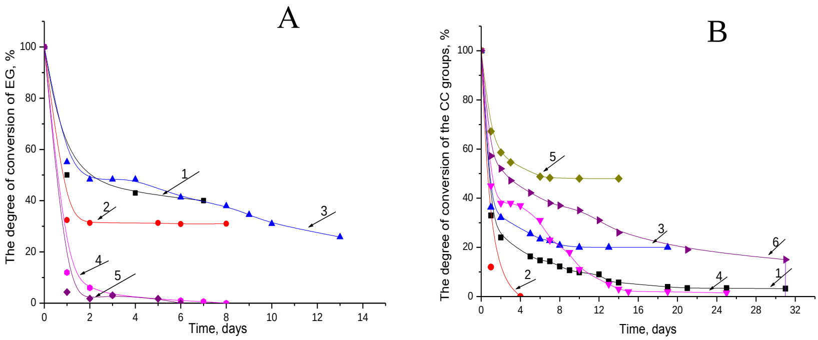
The elastic modulus, mechanical loss factor and mechanical losses of samples were measured on dynamic mechanical analyzer Q800 (TA Instruments, USA). The study was conducted in tensile mode at a frequency of 10 Hz in the temperature range from -150 to 150 ° C. Heating rate was 2 ° C / min. Glass transition temperature was determined by the position of the maximum in the temperature dependence of the loss modulus.

The rate of conversion of EG and CC group of epoxypolyurethane (EPU) have been studied by FTIR –spectroscopy. The sample properties were analyzed for two modes of polymer curing: Mode I - 25ºC / 14 days, mode II - 25ºC / 14 days + 100ºC / 5 hours.

Experimental data for conversion of EG and CC groups are presented in Figure 1. It is established the nonmonotonic dependence of rate and degree of conversion of reaction groups from ratio ER: CCO. The oligomer ratio with maximum conversion rate of EG and CC groups is determined by some processes: aminolysis slowdown because of CC groups content growth, acceleration of EG conversion on account of hydroxyurethane fragment catalysis, system depletion of primary aminogroup during the initial stage of curing because of interaction with

P3

CCO.



A - 1 Kinetic curves of EG conversion: *1* – DER-331: CC DGEBD = 90:10 +DETA, *2* – DER-331: CC DGEBD = 80:20 +DETA, *3* – DER-331: CC DGEBD = 60:40 +DETA, *4* – DER-331: CC DGEBD = 40:60 +DETA, *5* – DER-331: CC DGEBD = 30:70 +DETA

B - Kinetic curves of CC groups conversion: *1* – CC DGEBD +DETA, *2* – DER-331: CC DGEBD = 90:10 +DETA, *3* – DER-331: CC DGEBD = 80:20 +DETA, *4* – DER-331: CC DGEBD = 60:40 +DETA, *5* – DER-331: CC DGEBD = 40:60 +DETA, *6* – DER-331: CC DGEBD = 30:70 +DETA

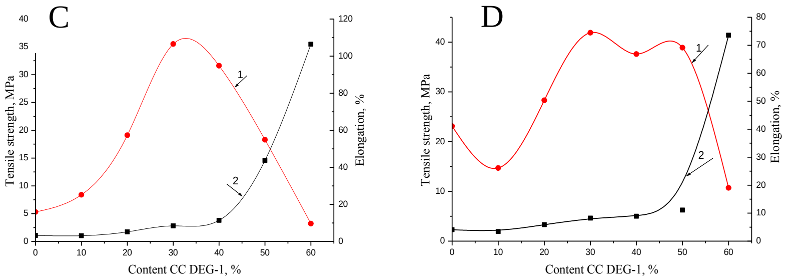
Figure 1. Kinetic curves of conversion reaction groups of EPU systems at different olygomer ratios.

Introduction of hydroxyurethane fragment to the structure of the epoxy polymer decreases the molecular mobility in the glassy state, which is due to the formation of intramolecular hydrogen bond of the urethane carbonyl and hydroxyl group. The modified polymers have high molecular mobility in the high-elasticity state.

It is established the dependence of mechanical and other operational characteristics (Figure 2) from the ratio of epoxy and cyclocarbonate oligomers in the composition. It is connected with the structure alteration when the ratio of ER and CCO in the consist was changed. It is shown the possibility to increase 1.5-3 times the cohesion, deformation and strength characteristics.

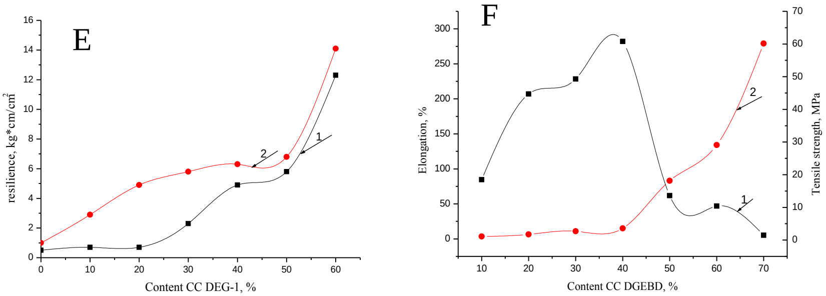
It is shown that impact viscosity and elongation have monotonous growth with a modifier quantity increase. It is explained by CC group conversion increasing. The resulting supplementary relaxators - aliphatic CCO links appear.

P3



C The dependence of mechanical properties of system (DER 331 + CC DEG-1) + DETA (schedule I):1 – tensile strength, 2 – elongation

D - The dependence of mechanical properties of system (DER 331 + CC DEG-1) + DETA (schedule II):1 – tensile strength, 2 – elongation



E - The dependence of resilience of system (DER 331 + CC DEG-1) + DETA: 1 – schedule I, 2 – schedule II

F - The dependence of mechanical properties of system (DER 331 + CC DGEBD) + DETA (schedule I):1 – tensile strength, 2 – elongation

Figure 2. The dependence of tensile strength (C,D,F), elongation (C,D,F), resilience (E) of EPU systems.

The gel-analysis data of nonisocyanate EPU has been considered. It was shown the dependence of polymer glass transition temperature, gel-fraction content from CCO quantity.

The modification composites based on nonisocyanate EPU have allowed to increase durability, elasticity, energy of deformation of polymers without reduction of polymer resistance to water and heat, adhesion characteristics.

The composites allow to obtain high solid content materials with high chemical resistance to different reagents (oil, solvent, mineral and organic acids, alcohols) at moderate and low temperatures.

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2.*Stroganov I.V., Stroganov V.F*. Peculiarities of structurization and properties of nonisocyanate epoxyurethane polymers. // Polym. Science C, Vol. 49, No. 3 (2007) 258–263.

P4

THIOPHENE-FUNCTIONALIZED BIOCOMPATIBLE/BIODEGRADABLE MACROMONOMERS: RING OPENING POLYMERIZATION (ROP) AT WORK IN THE BENEFIT OF “HAIRY-ROD” CONJUGATED POLYMERS

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As an important kind of nanoscopic macromolecule, brush polymers have been well investigated since Flory first presented the concept of hyperbranched polymers in a theoretical work in 1953 [1].

“Molecular bottlebrushes” or “molecular brushes” [2] were firstly synthesized by homopolymerization of macromonomers [3], and are a special class of graft copolymers in which the polymeric side chains are distributed densely on a flexible backbone. When the backbone is longer than the side chains, the steric repulsion between densely grafted side chains results in extended conformations and stiffening of the main chain, the whole macromolecule taking on a persistent cylindrical shape.

Because the rigid nature of the “molecular brushes” is caused by the molecular architecture rather than a specific chemical structure, they offer a unique possibility of tailoring the properties of materials through a facile selection of the polymer backbone or of the graft chains. Moreover, “molecular brushes” with controlled structures provide a precise size and shape control in each dimension, affording unique nanoscale morphologies that are unavailable by self-assembling of block-copolymers.

G. Wegner, stated that ***“shape persistence”,*** an important principle in the world of biomacromolecules, can be achieved by direct synthesis of “hairy-rods” [4], a concept based on the introduction of conformationally mobile, relatively long, flexible and densely grafted side chains to a rigid backbone and transferred this concept to the conjugated polymers field [5]. Aided by recent advances in living/ controlled polymerizations including living ring-opening polymerization (ROP), ring-opening metathesis polymerization (ROMP), atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and nitroxide-mediated polymerization (NMP), there are great opportunities in terms of flexibility, diversity, and functionality in the synthesis of various well-defined “hairy-rods” [6] and “molecular brushes” [7], recently being considered that, “hairy-rods” represent a particular case of “molecular brushes” for which the main chain is already rigid [8].

When biomedical applications are taken in consideration, the advantages of using “molecular brushes” are related to a higher stability of the micellar nanoparticles and their extended *in vivo* circulation time for diagnosis and drug delivery applications or to their capability of tuning the chemistry and surface topography of the scaffolds (switchable surfaces) suitable in tissue engineering.

On the other hand, research on semiconducting conjugated polymers for biomedical applications expanded greatly in the 1980s since it was found that these materials are compatible with many biological molecules. By the mid-1990s, conjugated polymers were also shown to tune cellular activities through electrical stimulation (conductivities from 10^{-4} to 9 S/cm) such as cell growth and cell migration [9] and this led to a considerable interest in conducting polymers and their derivatives for tissue engineering applications [10]. The scaffolds are designed to be a temporary support for cells and to promote cell differentiation and proliferation and should also totally degrade when the support is no longer needed.

Despite the many positive attributes of conjugated polymers including conductivity, biocompatibility, ability to entrap and controllably release biomolecules, capacity to undergo reversible doping, and their potential ease of modification, one inherent limitation that remains is their inability to undergo facile biodegradation *in vivo* [10].

Therefore different strategies were used to induce and enhance this property to materials based on conjugated polymers like blending of conjugated polymers with biodegradable counterparts of natural or synthetic origin, synthesis of different linear copolymers containing sequences of conjugated oligomers and other of biodegradable ones, grafting of conjugated oligo/polymers on the surface of biodegradable polymer films, hydrogels or conjugated polymers-containing biodegradable networks [9, 10].

Following our previous research interest in both, conjugated polymers “hairy rods“ [6] and the thiophene-containing polymers with designed architectures and tuned photophysical properties [11-13], in the present research we report about synthesis and structural characterization of three different macromonomers as useful building blocks for new “hairy rod” conjugated polymers, using different thiophene compounds that contain functional groups active as initiator in ROP. As monomers 2-methyl-2-oxazoline, ε-caprolactone or 3,6-dimethyl-1,4-dioxane-2,5-dione (lactide) were chosen so that thiophene-functionalized biocompatible/biodegradable macromonomers to be obtained. The synthesis and structural characterization of a random amphiphilic copolymer derived from one of the synthesized macromonomers with a PEG-containing thiophene macromonomer previously reported [14,15] is presented as well.

Photophysical properties of all the synthesized compounds were also investigated by UV-vis and fluorescence measurements.

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P5

EFFECT OF SALT AND HEAT TREATMENT ON AQUEOUS XANTHAN SOLUTIONS

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Xanthan is bacterial polysaccharide used in a broad range of products, including foods, pharmaceuticals, cosmetics, personal care, etc. Its molecular structure consists of a main chain of (1-4)-β-D-glucose substituted at every second residue with a side chain composed of one glucuronic acid flanked by a two mannose; the inner mannose may be acetylated and the terminal mannose may be pyruvated. The side chains stabilize the helical structure of backbond making the molecule a rather stiff rod with extraordinary stability to heat, acid and alkali, greater viscosity and plasticity, good solubility in hot or cold water, etc. These properties of xanthan in solutions make it to be most intensively studied both in terms of rheological properties and physical chemistry [1,2].

In this paper, the behavior of xanthan solutions on a large domain of polymer concentrations and temperatures was investigated by using dynamic measurements. The viscometric parameters of xanthan dilute solutions were evaluated as a function of salts. The viscoelastic response of xanthan concentrated solutions was studied and discussed as a function of heat treatments performed.

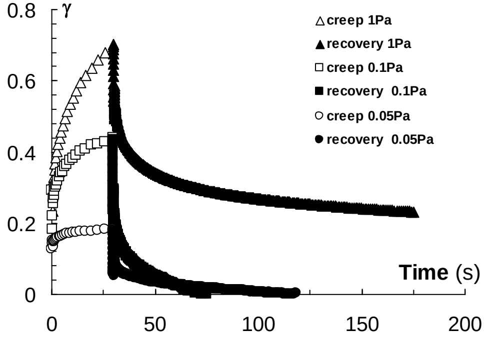

Figure 1. Creep-recovery tests for 0.4 g/dL xanthan aqueous solution at 37°C.

Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS-UEFISCDI, project number PN-II-ID-PCE-2011-3-0199, contract 300/2011.

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P6

POLYIONENS BASED ON TETRAHYDRO-1,4-OKSAZYN AND EPOXIDIZED DERIVATIVES OF 1,2-EPOXY-4,7-8-DIOKSONONEN

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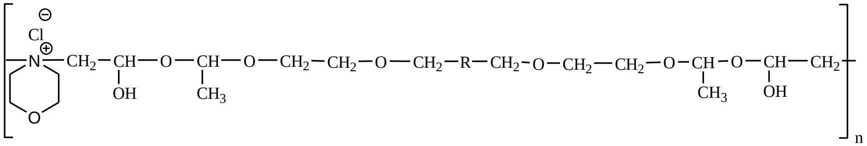
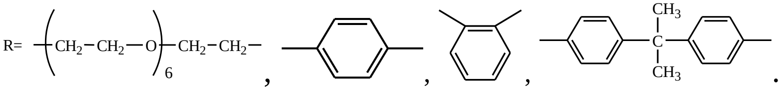
Current trends in the production and use of polymers aimed at finding ways of rational use of existing polymeric materials with improved properties. One of the promising directions of Macromolecular Chemistry also is the synthesis of new epoxidized derivatives and polyionens based on them - highly efficient polymer systems with desired properties for different classes of advanced multipurpose materials. The scientific field of chemistry that involves the synthesis of new materials and the introduction of chemical processes that reduce or completely eliminate their harmful effects on human health and the environment is important. The analysis of patent and scientific literature showed the existence of problems reducing the cost of production of polymers. This can be achieved by reducing the number of stages of the production process, or the absence of stage recycling.

Previously [1] we have conducted directed synthesis of new polyionens based on derivatives of epoxide compounds and tetrahydro-1,4-oxazyn (PIOT). The synthesized PIOT are low temperature liquid compounds amber color, soluble in water and organic solvents. It has been established physical-chemical properties of new PIOT.

The aim of this work is a systematic study of rheological and thermal properties, ionic conductivity of new PIOT general formula:



where



to establish structure-properties-application of these compounds.

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The influence of various factors on the specific viscosity PIOT in aqueous and water-alcohol solutions was been studied by rheological equipment. The thermal conversion structure PIOT has been studied by thermogravimetric analysis (the research conducted by DTA brand OD-102 of system F. Paulik, J. Paulik and L. Erde in special ceramic crucibles in air in the temperature range 0-500 °C at a constant rate rise of temperature of 10 °C per minute, for the reference substances used Al_2O_3, sample weight was 400 mg). It has been defined ionic conductivity PIOT at room temperature by conductometric method (for conductivity CYBERCAN CON 1500).

The rheological properties of PIOT in highly dilute aqueous and water-ethanol solutions have been studied (Fig. 1-2).

One of the characteristics polyionens is the concentration dependence of viscosity in aqueous solutions (Fig. 1). According to the curves of the concentration dependence of viscosity the studied polyionens are typical polyelectrolytes. It has been shown that the decrease of the concentration of the polymer leads to an increase of viscosity, this indicates a decrease in polymer-polymer interactions. In the limiting dilution increase viscosity ceases and there is a maximum, indicating the interaction of isolated macromolecules with the solvent, thus there is a deployment clutter and increase their linear dimensions. The decrease of viscosity at low concentrations indicates a decrease in the of mobile counterions inside the coil, which leads to a weakening in osmotic effect and thus to reduce swelling parameter. Among investigated polyionens the study viscosity PI 1-2 proved to be the best, while polyionen PI 4-4 was the worst.

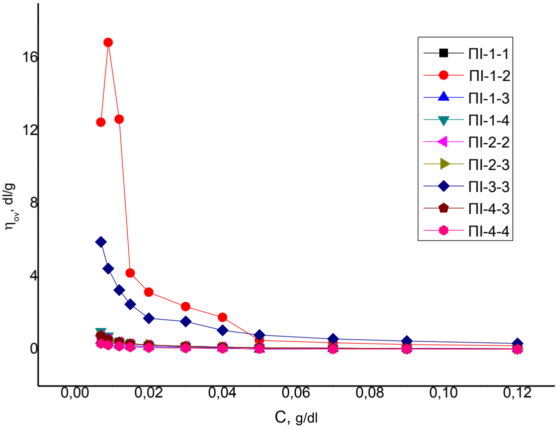

Figure 1. The concentration dependence of viscosity of polyionens based on tetrahydro-1,4-oxazyn and epoxide derivatives of 1,2-epoxy-4.7-dioksononen-8 in aqueous solutions: 1 – PI-1-1, 2 – PI-1-2, 3 – PI-1-3, 4 – PI-1-4, 5 – PI-2-2, 6 – PI-2-3, 7 – PI-3-3, 8 – PI-4-3, 9 – PI-4-4.

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In Fig. 2 it has been shown the concentration dependence of viscosity of polyionen PI 1-2 at different temperatures. The behavior of the studied polyionens explains the classical theory of polyelectrolyte swelling. The curves have been shown that with increasing temperature the viscosity decreases and the position of peak shifts at low concentrations. This can be explained by a decrease of the hydrodynamic field, which is formed macromolecules polymers with increasing temperature. It has been established that at low concentrations PIOT in water the viscosity of polyionen decreases with increasing temperature.

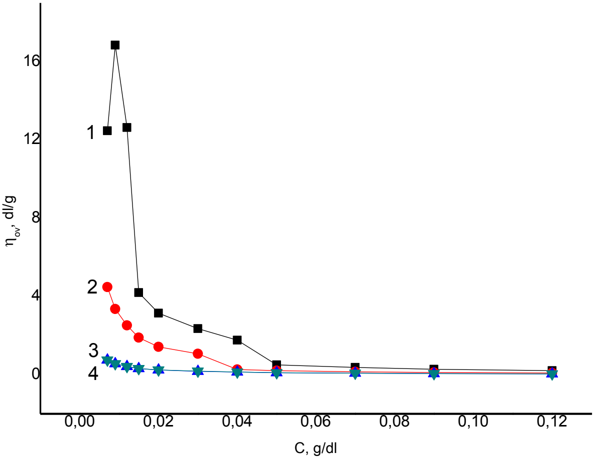

Figure 2. The concentration dependence of viscosity of PI 1-2 at different temperatures: 1 – 25 °C, 2 – 35 °C, 3 – 45 °C, 4 – 50 °C.

It has been investigated the dependence of the viscosity at different mixture of the water-ethanol to assess the behavior of macromolecules polyionens in the reaction mixture as an example compound PI 1-1. It has been discovered abnormal behavior of synthesized polyionens in water-ethanol solution. Unlike known polyionens, viscosity water-ethanol solutions lower the viscosity of the solvent. Unlike in polyionens viscosity of water-ethanol solutions is lower than the viscosity of the solvent. It has been shown the influence of the density charges macromolecules of polymers on the dependence of viscosity solution of PI in ethanol solution of solvent composition: a decrease the concentration of ethanol in water-ethanol solution viscosity of the solution PI increases for polymers with low density charges and for PI high density the same conditions the viscosity of the solution decreases.

The paper studied the ionic conductivity, resistance to thermooxidative degradation PIOT. It has been established that synthesized PIOT are thermally stable to 130-180 °C. It is shown that the ionic conductivity of new PIOT at room temperature is 10^{-2}-10^{-4} S·cm^{-1}.

Thus, new PIOT are promising low-temperature heat-ionic liquids with high ionic conductivity for various purposes.

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P7

SYNTHESIS AND PROPERTIES OF BLOCK COPOLYMERS PREPARED FROM OLIGOMERIC POLYAZOINITIATORS OF VEGETABLE OILS

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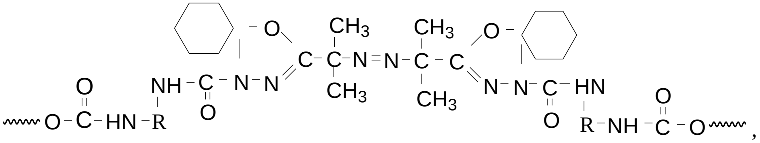
Polyazoinitiator (PAI) can be defined as a polymer or an oligomer with reactive azo- groups at chain, which are easily split to produce radicals for the initiation of polymerization of a monomer to form another block of a block copolymers (BCP) [1-3].

In this paper the results of study of synthesis and properties characterization of block-copolymers (BCP) by radical polymerization have been presented initiated by oligomeric azoinitiators on the base of vegetable oil.

The method of synthesis of oligomeric azoinitiator (OAICO) on the base of monomer azoinitiator *azo-bis*-isobutyrohydrazone of cyclohexanone (AGN-CH) and triisocyanate of castor oil (TICO) at molar ratio of AGN-CH:TICO =1:2 was developed one initiating center the OAICO 1/2 received with structure RXR, where *R* - is the castor oil block, and *X* is the initiator block:



At molar ratio of AGN-CH:TICO = 2:2 the oligomeric azoinitiators OAICO 1/1 with two initiating centers was obtained with structure $(RX)_n$ or R_2X_2. Oligomeric azoinitiators have been studied by the method of IR- and UV-spectroscopy.

Block copolymers of type $(ABA)_n$ (A – block of castor oil, B – block of oligostyrene) with various lengths of oligostyrene block were synthesized on the base of synthesized oligomeric azoinitiator of castor oil and styrene as monomer by the method of thermoinitiated radical polymerization. The BCPs were obtained at molar ratio OAI/St = 1/143, 1/200, 1/400 under the following conditions: at temperature 95^0C throughout 20 hours. In so far, as PAI formation through the

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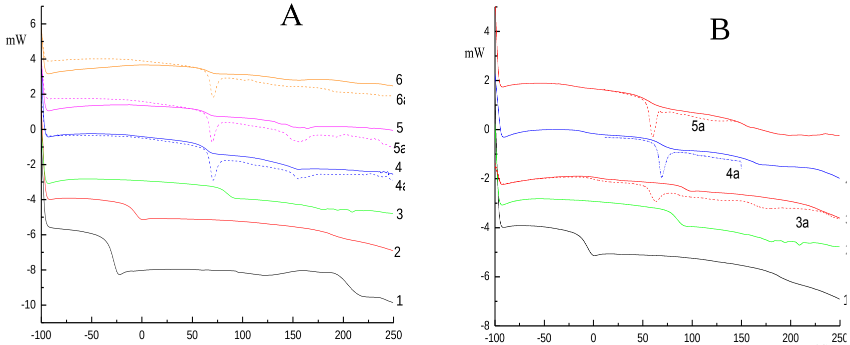
reaction between the isocyanate groups of TICO and the hydrazone groups of AGN-CH proceeds independently of the thermoinitiated polymerization of styrene, it was possible to prepare two series of polyblock BCPs of type $(ABA)_n$ (where A is the castor oil block, and B is the styrene block). The sequential one was obtained by the synthesis of PAI in the first step, and by subsequent radical polymerization of styrene thermoinitiated by PAI, while both reactions were carried out in a single step to prepare the simultaneous one. Kinetic studies of synthesis of BCP were conducted by the method of differential calorimetry on the calorimeter DAK1-1A.

Relaxation transitions in the soft (castor oil) and hard (oligostyrene) blocks of new synthesized block-copolymers were investigated by the DSC method. The specific heat capacity (C_p) of the samples in the temperature range of -100 – 240^{0}C were measured by a differential calorimeter Mettler Toledo Star SW7.00 at a heating rate of 10^0 C/min after sudden quenching of the samples in liquid nitrogen. Experimental data for heat capacity are summarized in thermograms corresponding to block copolymers are presented in Figure 1. For comparing relaxation transitions, the original castor oil with isocyanate end groups blocked by methanol to prevent side reactions (TICOUR) and oligostyrene (OSt) with hydrazide end groups (molecular weight 8000) were investigated.



A - 1 – TICOUR; 2 – polymer of castor oil; 3 – OSt; BCP of based on OAICO 1/1; 4a, 5a, 6a – first heating, 4, 5, 6 – second heating 4, 4a – BCP 1/143; 5, 5a - BCP 1/200; 6, 6a- BCP 1/400.

B - 1 – polymer of castor oil; 2– OS; BCP of based on OAICO 2/1; 3a, 4a, 5a – first heating, 3, 4, 5, – second heating 3, 3a – BCP 1/143; 4, 4a - BCP 1/200; 5, 5a- BCP 1/400.

Figure 1. Temperature dependences of heat capacity castor oil- styrene BCP. Beginning a curve 2, all the subsequent ones are displaced relative to the ordinate axe 1.1.

As a result of physical-chemical studies of synthesized BCP by method of DSC presence of two of heat capacity jump is shown at glass transition temperature of a microphase of castor oil and oligostyrene microphases that is characteristic for phase separation in polymer-polymeric systems.

Castor oil-styrene BCPs were studied by the method dynamic mechanical analysis (DMA) using a relaxometer with forced sinusoidal oscillations at a frequency of 100 Hz. Both, the dynamic elastic modulus E′ and the loss modulus E″ were measured in the temperature range from 170 to 350 K, and at heating rate of 2 K/min. The glass transition temperature (T_g) was determined as the position of the maximum of log E″ (Table 1). The block copolymers obtained are twophase polymer systems for all compositions, as it is indicated by the existence of two relaxation maxima (Figure 2). This result is due to the blocks immiscibility and their phase separation into micro-domains.

Table 1. Compositions and viscoelastic parametrs for castor oil-styrene BCPs of the type $(ABA)_n$

composition	по tgδ (T),		по E″(T)				$E'_{-40\,^{o}C}$, МПа	$E'_{20\,^{o}C}$, МПа
	$T_{\alpha1}$, ^{o}C	$T_{\alpha2}$, ^{o}C	$T_{\alpha1}$, ^{o}C	max $E''_{\alpha1}$, МПа	$T_{\alpha2}$, ^{o}C	max $E''_{\alpha2}$, МПа		
polymer of castor oil (TICO +CO)	23	-	5	58	-	-	825	18,4
BCP 1/143 (OAICO 2/1)	-	110	15	43	75	80	1460	995
BCP 1/400 (OAICO 2/1)	-	115	10	41	75	118	1690	1120
BCP 1/143 (OAICO 1/1)	-	-	15	30	78	125	1710	1260
BCP 1/200 (OAICO 1/1)	-	-	10	32	70	105	1560	915
BCP 1/400 (OAICO 1/1)	-	-	-3	41	70	98	1745	1060

The processes of synthesis and properties of block copolymers obtained on the base of oligomeric polyazoinitiators of vegetable oil by thermoinitiated radical polymerization have been investigated. Block copolymers with castor oil and styrene blocks have been synthesized. Their structures were confirmed by means of FTIR spectroscopy. Thermal behavior of these new compounds was studied by

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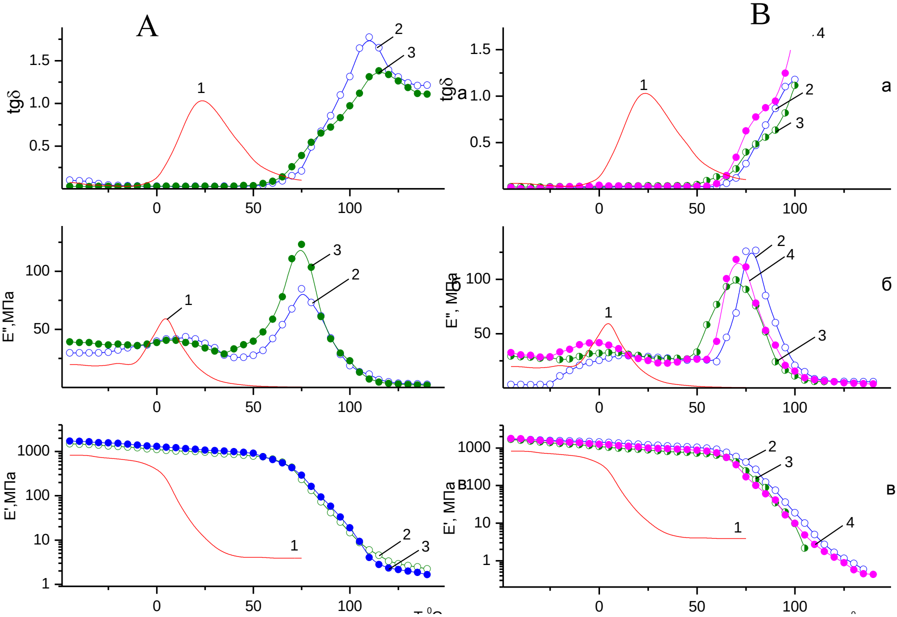
DSC and DMA. It was shown that studied BCPs are a typical two-phase polymeric systems with two glass temperatures with a formed interphase field.



A - 1 – polymer of castor oil; BCP of based on OAICO 2/1: 2 - BCP 1/143; 3 - BCP 1/400.

B - 1 – polymer of castor oil; BCP of based on OAICO 1/1: 2 - BCP 1/143; 3 – BCP 1/200; 3 - BCP 1/400.

Figure 2. Temperature dependence of the mechanical loss tangent tgδ (a), loss modulus E" (б) and dynamic elastic modulus E '(в) for castor oil-styrene BCPs of the type $(ABA)_n$

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P8

TECHNOLOGIES FOR THE FATTY ACID ESTERS SYNTHESIS USING POLYMERIC HETEROGENEOUS CATALYSTS

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Modern state and development of the polymer materials production are in the field of environmental and resource problems.

We are proposed a new method of sulfonated polymeric esterification catalyst (SEC) synthesis, which can be used along with known sulfonated polymeric catalysts Amberlyst, Nafion, Dowex, Purolite type. SEC is composite material which synthesized by condensation reaction of polyvinyl alcohol with the sulfonated phenol formaldehyde resin in 30 % aqueous solution and in presence of 50% lignin. Properties of catalyst are shown in Table 1.

Table 1. Catalyst SEC characteristics

Physical form	particles of irregular shape (0,1-1,0 mm)
Fraction mean size (95%)	0,35-0,45 mm
Total pore volume, cm^3/g	9,7
Ion exchange capacity, meq/g	3,6
Water absorption capacity, %	43

Using of an available and inexpensive raw ingredients such as polyvinyl alcohol, aromatic sulfonic acids lignin (waste alcohol production) also a water as solvent in a part of sulfonated polymeric esterification catalysts will lead to reduce production expenses due to low raw material costs

At the same time, there is a problem of processing a low quality chicken fat, with the acid value of 25 mg KOH/g and above.

The technologies of processing and utilization of fat-containing waste products was analyzed and been shown that the most promising direction is to obtain esters of fatty acids (FAEs) by alcoholysis. At the same time method of processing with the use of heterogeneous catalysis has more advantages compared with other methods (using homogeneous acidic and alkaline catalysts).

However, the use of the known heterogeneous polymer catalysts for the obtaining FAEs means or carrying out process is not less than 8 hours using a co-solvent, or a large molar ratio fat:methanol of from 1:100 to 1:300, in some cases, carrying out the reaction under the pressure, at the same time, yield of fatty acids esters up to 90% [1-3].

We have found that the waste chicken fat, can be processed in two stages. The first stage is to carry out the esterification of free fatty acids contained in chicken fat, using a 10 % wt. of heterogeneous sulfonated polymeric catalyst SKE, ratio fat:methanol 1:7. On the second stage - transesterification of the resulting product mixture from the esterification using an alkali catalyst (KOH).

Properties of methyl FAEs derived by two-step process are presented in Table 2.

Table 2. Methyl FAEs properties

Property	Value	Value according to DSTU 6061:2009
Ester content, %	97,4	96,5 min
Acid value, mg KOH/g	0,29	0,50 max
Iodine value, mgJ_2/100g	86,7	120 max
Water content, mg/kg	300	500 max
Methanol content, % wt.	0,15	0,20 max
Monoglyceride content, % wt.	0,50	0,80 max
Diglyceride content, % wt.	0,14	0,20 max
Triglyceride content, % wt.	0,20	0,20 max
Total glycerine, % wt.	0,20	0,25 max
Flash point, °C	130	120 min

The developed technology of chicken fat processing with a high content of free fatty acids provides a methyl FAEs, which meet the requirements of the standard.

Flow diagram of chicken fat processing with new heterogeneous sulfonated polymeric catalysts is shown in Fig. 1.

The heterogeneous catalyst SKE which has lost activity after alcoholysis can be treated with isopropyl alcohol and used as a filler in the synthesis of the new catalyst.

Methyl FAEs can be recommended for use as bio-diesel or as biocomponent other fuels, as well as plasticizers and polymer modifiers, paint and rubber materials.

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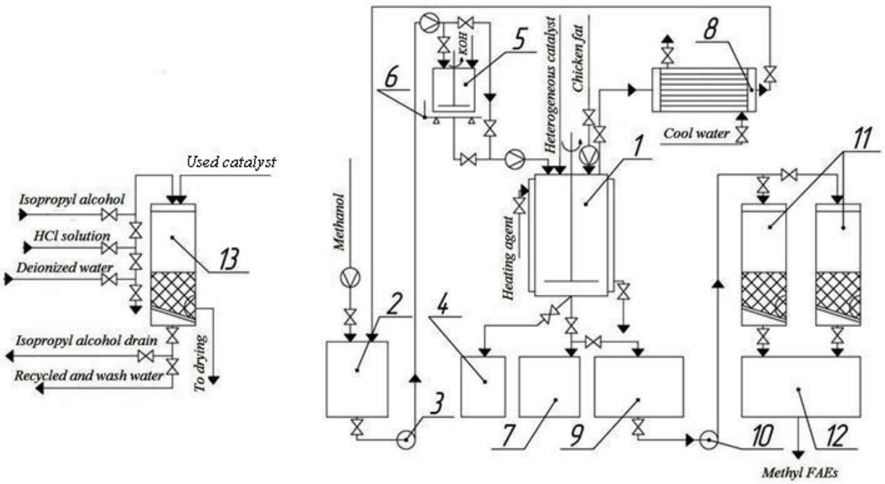

Figure 1. Process flow diagram for methyl FAEs production and catalyst regeneration unit:
1 – reactor; 2 – methanol tank; 3, 10 – pumps; 4 – tank for used catalyst; 5 – KOH solution tank; 6 – weigh module; 7 – glycerol tank; 8 – condenser; 9 – crude methyl FAEs tank; 11 – methyl FAEs purifying column; 12 – purified methyl FAEs tank; 13 – catalyst regeneration column.

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P9

THERMAL PROTECTION MATERIALS OF SPECIAL APPLICATION

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The problem of thermal protection was represented and got intensive development in aero-space technique what with the hypersound fly in athmosphere problems had to be solved. Today the production leaders in aero-space technique engadged in the developing of thin lay coatings. The main atention payed to the developing of thin lay thermal protection coatings by pneumatic spraying by the technological aspect of their application. This aproach give a chance to provide the themal protection of the any configuration of the object's size what are actual in:

- thermal protection of aero-space technique;
- pipes with hot and cold water thermal protection;
- hydroisolation of main pipes, processing equipment and reservoir.

The creation of thermal protection coatings ordinary can be solved by choosing of polymer matrix and fillers with low density also with composition optimization.

The main attention is paid to possibility of developing materials based on non-toxic and ecological compounds, and which are provide the coatings with density near of 0,4-0,6 g/cm^3 and thermally stable up to 250ºC.

The main physical mechanical and expluatation characteristics is a: density, thermalconductivity, heat resistant, and elasticity (for soft materials), pressure strenght (for hardish and half hardish materials), vibration proof, absent of shrinkage, water resistant and chemical stability.

As polymer matrixes (film-former) has been used a mixture of various polymers dispersions NeoPack E-106 (polyurethane dispersion, BASF) and Joncryl 6336 (polyurethane-acrylic water based dispersion, NeoResins). For obtaining the low density and thermal conductivity properties of the developed materials as fillers was used a glass microspheres (HGS 16 and HGS 17 type, 3M™) and polymer microspheres EXPANCEL® (Akzo Nobel). For flammability decreasing into compositions was added the chlorine containing polymer materials and metal oxides.

Thermogravimetic analysis and thermo differential analysis data are shown on Figures.1, 2, 3.

P9

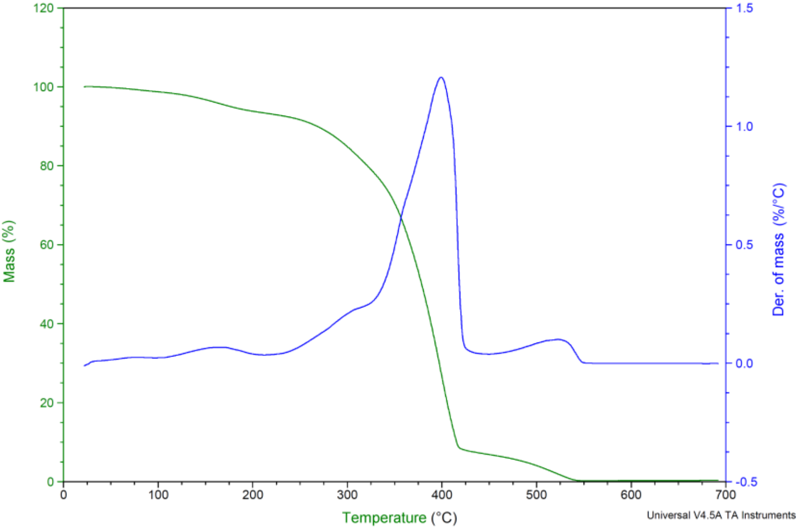

Figure 1. Thermogravimetic analysis and thermo differential analysis data of the polymer matrix based on the mixture of acryl-urethane water dispersions.

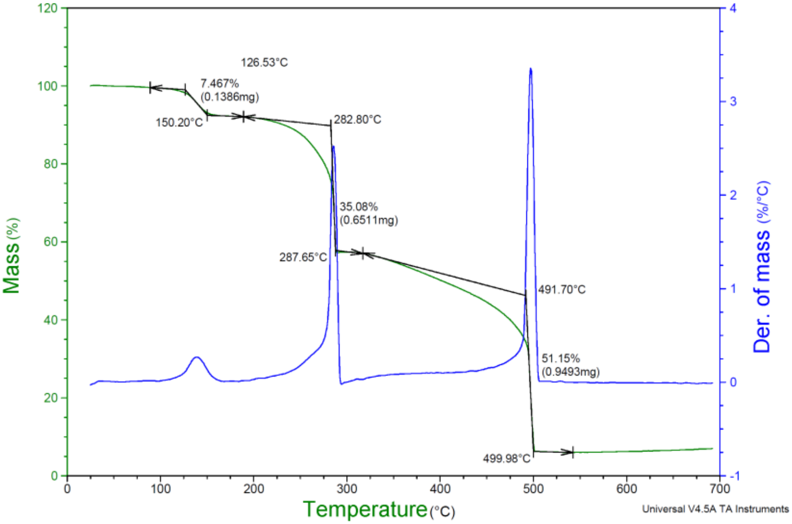

Figure 2. Thermogravimetic analysis and thermo differential analysis data of the polymer microspheres Expancel 461WE 80 d36.

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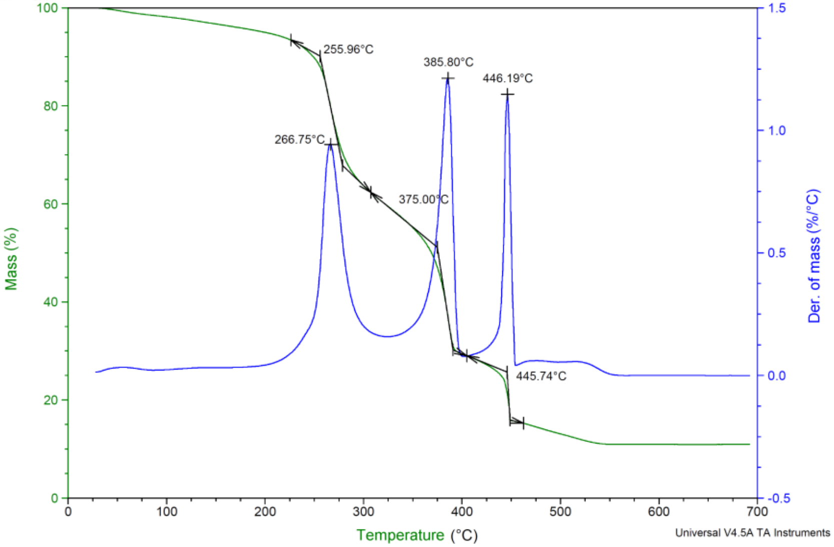

Figure 3. Thermogravimetic analysis and thermo differential analysis data of the thermal protection material with containing of microspheres 19% and density, 0.6 g/cm^3.

As a result of conducted experiments was obtained a pneumatic spraying thermal protection material with the one lay thickness ~300-400 µm, drying of every lay was conducted at room temperature. The obtained coatings are characterized by next properties:

- density 0,45-0,60 g/cm^3;
- tensile strength 1,4 MPa;
- relative elongation at break 11,1%;
- the start of destruction is observed at 250°C;
- thermal conductivity coefficient λ, 0,07806 W/m•K (at 25°C);
- specific heat Cp, 3,8436 kJ/kg•K (at 25°C).

P10

AMPHIPHILIC POLY(p-PHENYLENE VINYLENE) "HAIRY-RODS": SYNTHESIS,CHARACTERIZATION AND SELF-ASSEMBLY IN WATER

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Conjugated polymers are stimuli-responsive advanced materials with a broad application area in opto-electronics [1]. The design and self-assembly of conjugated molecules with controlled dimensions and functions remains a challenging and attractive target in nanoscience and nanotechnology. Due to their specialty properties, like electrical conduction as well as fluorescence, their use in bioapplications (others than biosensors or actuators) expands recently toward regenerative medicine (tissue engineering) [2-4] and to diagnosis and therapy [5-7].

Fluorescence imaging is an emerging modality of biomedical diagnosis and drug delivery tracking with attractive capabilities like high sensitivity, low cost, possibilities of multiplexing and molecular activation.

To date π-conjugated polymers are at the early stage of their applications as fluorescent biomarkers, used only for *in vitro* or *ex vivo* studies, but they hold great potential for *in vivo* use, particularly in a densely packed nanoparticles formulation, due to their organic nature of chemical constitution, to their water- dispersability capacity and especially to their superior light absorbing ability caused by their high chromophores density.

In the present attempt, to generate fluorescent nanoparticles with control over the size and fluorescence stability as well as supramolecular organization ability by self-assembling, an amphiphilic structure was imagined by choosing PPV as well-known highly fluorescent material and polyethylene glycol (PEG) or poly-2-methyloxazoline (PMeOx) / poly-2-ethyloxazoline (PEtOx) as non-ionic, water soluble, biocompatible polymers.

PEG was chosen being recognized as the “golden standard” in construction of the “stealthy” particles toward macrophages in reticuloendothelial systems (RES), while poly(2-alkyloxazoline)s emerged as a valuable alternative to PEG due to their comparable physicochemical properties; moreover, poly(2-oxazoline)s -that can be regarded as pseudo-peptides- could be more suitable than PEG when long term use in human body is intended because cannot undergo oxidative degradation and do not complex ions.

Amphiphilic π-conjugated rod – coil copolymers were engineered so that to be water dispersible in very high concentrations by appropriately choosing of the flexible polymers length. Micellar nanoparticles with enhanced stability can be obtained in aqueous solutions without using nanoprecipitation technique, their formation being facilitated mainly due to unique anisotropic molecular shape, the main driving force behind their self-assembling in water being the strong aggregation tendency due to the π-π stacking interactions of the conjugated moieties, the hydrophilic/hydrophobic balance and solution conditions.

For an enhanced stability of the micellar nanoparticles in physiologically media our option was driven to the “hairy rod” architecture, a particular case of “molecular brushes” [8], the backbones of which can act as “cross-links” on the hydrophobic core surface of the micelles.

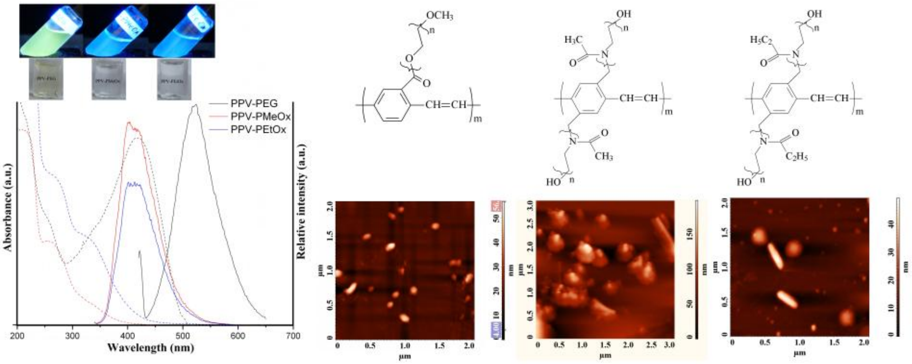

Figure 1. Properties in aqueous solutions and in thin films of the synthesized polymers.

The appropriate combination of the “macromonomer technique” with Suzuki-Heck cascade polycondensation specific for PPV synthesis can assure the obtainment of the “hairy-rod” architecture.

The synthesized materials show the properties characteristic of the two components with synergetic effect. Polymers structural characterization was performed by spectral methods (^{1}H-NMR, IR), whereas DLS and AFM microscopy (Fig.1) were complementary used to prove and to characterize as size and shape the nanoparticles formed by self-assembling in aqueous media, by diresct disolution method. The nanoparticles photophysical properties obtained by UV-VIS and fluorescence techniques were discussed in relation with their size and the influence on these properties by the proteins presence, like BSA and FBS was also investigated. The present attempt offers an alternative to conducting polymer nanoparticles encapsulation in biocompatible matrix by nanoprecipitation.

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P11

TOWARD “GREEN”, FLEXIBLE COTTON-BASED COMPOSITE MATERIALS OBTAINE BY *“IN SITU”* STEP-GROWTH POLYMERIZATION OF DIFFERENT TTTHIOPHENE MONOMERS *VIA* PHOTOINDUCED TRANSFER ELECTRON REACTIONS

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Produced for various industrial and functional requirements (medical, agriculture, automotive and packing industries, protective and sportive clothing, ecology), technical textiles have been developed based on information from different scientific disciplines.

During the past decade, the concept of “smart textiles” – as a part of technical textiles – has evolved into more than just an expression. Smart materials including photoactive materials, conductive polymers, shape memory materials, etc., are used to mimic the nature, in order to form novel textile materials with high function.

Electronic textiles are fabrics/garments that contain electronic circuits, optical fibers or sensors. Such functional textiles provide potential opportunities for boundless applications in electronic interfaces and in the field of health care. Demanding systems directly worn on soft and curved human body, fiber/textile-based platforms hold great promises for future wearable electronics.

Applications such as sensors, actuators, photovoltaics, organic field effect transistors (OFET)s, stretchable power sources, flexible electro /photoluminescent devices, electromagnetic interference (EMI) shielding or heating and cooling elements, all have in common the necessity of electrical conductivity for their function. Conductive metal wires and other rigid fibers have been used in the past to demonstrate proof-of-concept wearable electronics but, unfortunately, these materials do not provide textiles with biological compatibility, flexibility, durability and mobile comfort. Also carbon nanotubes, one of the most important conductive materials, are becoming increasingly scrutinized in terms of health aspects. Thus conjugated polymers (CP)s become relevant conductive materials for textile applications, especially through the *in situ* polymerization method.

Development of CPs allowed today commercial devices including Sony's OLED televisions or Samsung Impression cellular phone among many other examples.

However, due to the increase of plastic electronics in low-cost, large volume, disposable or throwaway applications, global environmental and social problems have created by the contemporary electronic waste (e-waste). In this context waste prevention by design is a far more auspicious strategy than end-of-life treatment and recycling.

The convergence of biodegradable materials and organic semiconductors yield abundant opportunities to produce electronic systems with unique overall material profiles. Nature offers an affluence of materials choice, so that "green" organic electronics (that are biodegradable, biocompatible, bioresorbable or even metabolizable) have already made their science debut.

Cotton, which has been used by mankind for at least 7000 years and cultivated for more than 4500 years, is a remarkable pure fiber with cellulose content greater that 95% in dray fiber and a well-defined material at both molecular and supramolecular level. Even if the topic of cotton-based CPs composites is less addressed in the literature by comparing with those based on synthetic and/or artificial counterparts (polyesters, polyamides or viscose textiles), it is remarkable the successful obtainment of various optoelectronic devices that use as active elements CPs-cotton composite materials

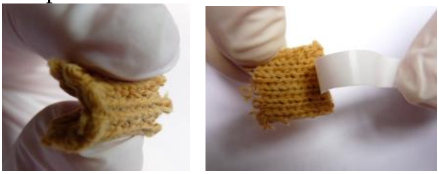

Figure 1. The obtained composite are flexible, robustly covered by polymer film (tape test).

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In this work we discuss our recent achievements aimed at obtaining new functional composites using a 3D knitted cotton fabric (a weft knitted sandwich fabric with connection through yarns) as textile support and different thiophene-containing monomers able to undergo *in situ* photopolymerization in the presence of some onium salts.

The structure of the synthesized composites was characterized by infrared spectroscopy (FT-IR) and polymer formed in the bulk by ^{1}H-NMR and FT-IR.

The polymer film morphology and the composite surface topography were examined by microscopic methods SEM and AFM and the surface wettability was evaluated by static contact angle (CA) measurements. The thermal behaviour was assessed comparatively for all the synthesized materials and their anti-adhesive and anti-microbial properties were also investigated.

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BLOCKED ISOCYANATES AS POLYSACCHARIDES MODIFIERS

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Modification of biopolymers is one of the most popular ways to obtain new biodegradable polymer systems that allows both enhancing environment protection from polymer waste and developing the renewable source of inexpensive reagents in chemical synthesis.

Isocyanates are high-reactive compounds widely used in chemical synthesis, especially in organic synthesis and polymers modification [1,2]. High reactivity and toxicity lead to special reaction conditions, reagents instability and high safety precautions during storage. Using isocyanates in latent form, e.g. blocked isocyanates, essentially simplify the reaction pathway.

A blocked isocyanate is isocyanates adduct containing a relatively weak chemical bond formed by the reaction with a hydrogen active compound (phenol, hydroxylamine, pyrokatehine, caprolactam, diphenylamine etc.). At elevated temperature, the adduct splits off to regenerate the free isocyanate group, which in turns reacts with a nucleophilic substrate. Blocked isocyanates or polyisocyanates seem to be very important in view of technical and economic aspects. They are essentially insensitive to moisture and storage conditions. In addition thermal stability of the blocked isocyanates is generally high [1].

Polyglucaneurethane networks (PGU) of various compositions were obtained via the modification of the biopolysaccharide konjac glucomannan (KGM) by blocked isocyanate (IC) – monoisocyanate, diisocyanate or polyisocyanate (PICb). The reaction passed through the interaction of PGU hydroxyl groups with isocyanate groups that are released during thermal dissociation of IC [3,4].

Blocked isocyanates were obtained through the reaction of isocyanate (orto-toluene isocyanate (o-TICb), toluene-2,4-diisocyanate (TDIb), diphenylmethane diisocyanate (DFMDIb) or polyisocyanate) with blocking agent – ε-caprolactam (ε-CL). Reaction was carried out at 80-90°C during 4-6 hours in dry argon atmosphere. Obtained product was investigated by IR-spectroscopy, mass-spectrometry and thermogravimetry.

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The deblocking temperature of blocked isocyanates was examined by thermo-gravimetric analysis (TGA) and titration method.

TGA was performed with a TGA analyzer (Derivatograph Q–1500D system F.Paulik, J.Paulik, L.Erdey). In the analysis, 50 mg of sample was heated from room temperature to 700°C with a 10°C min^{-1} heating rate. The initial deblocking temperature was defined as the temperature of the start of weight loss

The deblocking temperature can also be determined through titration. Aliquots are withdrawn from the heated flask and quenched with di-n-butylamine. The isocyanate content, release at evaluated temperature, is determined by back-titration with HCl and a color indicator – bromophenol blue.

The deblocking temperature range of o-TICb, TDIb, DFMDIb and PICb were 100-110, 115-120, 125-130, and 125-130°C, respectively.

A representative FTIR spectrum of the blocked adducts are presented in Figure 1. Spectra of blocked isocyanates are similar and does not show intensive NCO absorption peak at 2270-2275 cm^{-1}. Strong absorptions at 1695-1715 cm^{-1} (C=O stretching), 3200-3450 cm-1 (N-H stretching), 1530-1560 cm^{-1} (N-H bending) and 1210-1240 cm-1 (the stretching vibration of the C=O group of urea combined with the N-H group) confirm the formation of blocked o-TIC, TDI, DFMDI and PIC adducts.

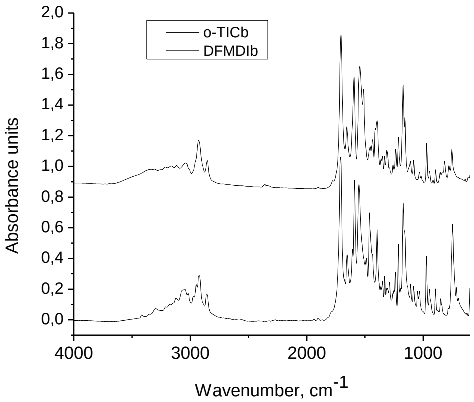

Figure 1. FTIR spectra of ε-caprolactam blocked o-tolyl isocyanate and ε-caprolactam blocked diphenylmethyl diisocyanate..

According to TGA data shown in figure 2 the o-TIC degraded in a single step with an onset degradation temperature of around 115°C while for the TDIb, DFMDIb and PICb, the degradation process exhibited two stages.

It is obvious that the process of weight loss of PICb and DFMDIb differs from TDIb. Above 130 °C the weight loss of approximately 40% for DFMDIb and PICb and 55% for TDIb is likely to be associated with the thermal deblocking of blocked groups, involving formation of ε-CL and isocyanate. It was shown in [5] that the weight loss in this temperature region is due to the removing of ε-CL. That is why the changes in weight loss relate to the different content of the ε-CL in isocyanates with different structure.

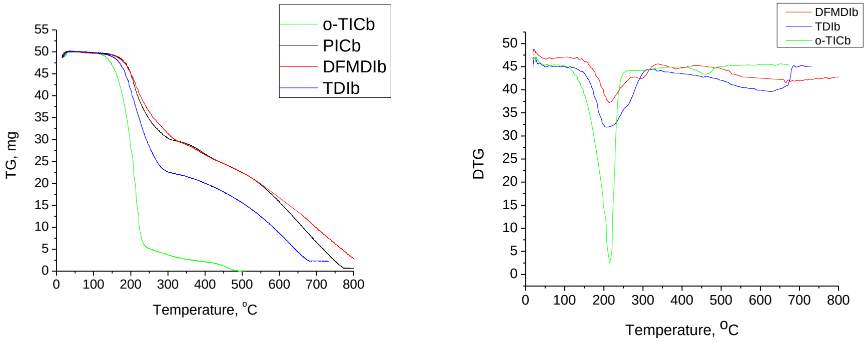

Figure 2. Thermogravimetric analysis of ε-CL blocked adducts.

It should be noted that during the degradation of ε-CL blocked isocyanate adducts, the chemical transformation can pass without weight loss and/or oxidative destruction. In particular, carbamide bond thermal dissociation results in releasing of ε-CL and free NCO-group. NCO-groups releasing is often accompanied by the structuring of the system. In the temperature region of 100-200°C the formation of isocyanurate cycles are prevailed, while the formation of linear and cyclic carbodiimide structures predominates in the region of 180-300°C. [6-9].

Ion current temperature dependence and ionic fragments of pyrolytic decomposition were investigated by pyrolytic mass-spectrometry method. Ion current intensity as well as number and types of ionic fragments were recorded on mass-spectrometer MX-1321. According to obtained results the pyrolytic decomposition for all ε-CL blocked adducts pass through the formation of the similar ion fragments. The ion fragments with mass numbers that correspond to isocyanate and ε-CL have the main contribution to ion current intensity at the temperature of ion current maximum.

Obtained ε-CL blocked adducts were used for the modification of the biopolysaccharide – KGM. In such way, PGU based on KGM and different ε-CL blocked IC with various substitution degree of hydroxyl groups of KGM were obtained. The reaction passed through the interaction of hydroxyl groups with isocyanate groups that release at thermal dissociation temperature. PGU synthesis was carried out in solid phase during 30 min at 150°C. Reaction pathway was controlled by FTIR-spectroscopy and mass spectrometry.

In [4] was shown that the decrease of ion current intensity as well as the reduction of number and types of ionic fragments of PGU pyrolytic decomposition in temperature region common to decomposition of PIC refer to binding of PIC with polysaccharide. During reaction the formation of thermostable structure is observed, which amount correlates with calculated substitution degree of polysaccharide hydroxyl groups. Obtained results agree with FTIR spectroscopy data and confirm the formation of PGU.

Thermooxydative destruction of PGU occurs in several stages. First stage in range of temperature 30 – 150°C corresponds to absorbed water removal. The amount of absorbed water depends on hydroxyl groups substitution degree. Second stage (150 – 220°C) can be referring to dehydratation of glucopyranoze cycle. Third stage (200 – 350°C) related to decomposition of urethane group. High temperature stages commonly correspond to decomposition of carbohydrate chain.

Thus, the ε-CL blocked ICs were successfully synthesized and characterized. The temperature of thermal dissociation of blocked isocyanates, which was determined by the TGA and titration methods, were 100-110, 115-120, 125-130, and 125-130°C for of o-TICb, TDIb, DFMDIb, and PICb, respectively. These blocked isocyanates can be used as potential crosslinkers for biopolysaccharides.

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P13

PYROLYTIC MASS-SPECTROMETRY OF SOME LIQUID RUBBERS OBTAINED BY RADICAL POLYMERIZATION

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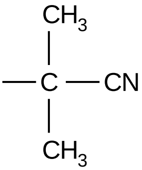
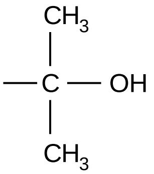
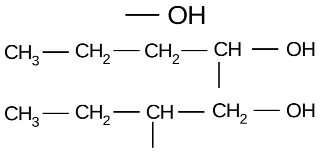
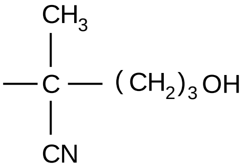
Oligodienes (liquid rubbers) obtained by radical polymerization using hydrogen peroxide (HP) as initiator (ORD - oligomers radical dienic) [1] are the most accessible on economical point of view because of their low cost and ecological harmless of HP. The cost of other initiators amounts to considerable value and often forms a main part [2] of the cost of radical polymerization oligodienes. Taking into account the high chemical activity of HP, first of all in oxidation reactions [3], the task was set to determine thermal stability of the ORD oligomers and compare it with that of radical polymerization oligomers obtained with another initiators. For comparison, oligoisoprene obtained with an azo-bis-isobutyronitrile (AIBN, porofor) and oligobutadiene obtained with azo-bis-isocyanpentanol (ACP) were studied (tabl. 1).

Table 1. The radical polymerization oligodienes obtained with various initiators

No.	Brand	Monomer	Initiator	End fragment	Funct. group content, wt.%
1	GOD-P	Isoprene	AIBN	 $-C(CH_3)_2-CN$	–
2	ORD-IPS	Isoprene	HP in isopropan	— OH	1,81

			ol	 $-\overset{CH_3}{\underset{CH_3}{C}}-OH$	
3	ORD-n-Butanol	Isoprene	HP in n-Butanol	 $-OH$ $CH_3-CH_2-CH_2-\underset{\vert}{CH}-OH$ $CH_3-CH_2-\underset{\vert}{CH}-CH_2-OH$	2,45
4	SKD-GTR	Butadiene	ACP	 $-\overset{CH_3}{\underset{CN}{C}}-(CH_2)_3OH$	1,10

The investigation of thermal stability of liquid rubbers was performed by the pyrolysis mass-spectroscopy method [4], which permits to evaluate the peculiarities of their thermal degradation from the composition of degradation products. The mass-spectra of volatile products of thermal destruction of liquid rubbers obtained with HP as an initiator are presented in Fig. 1.

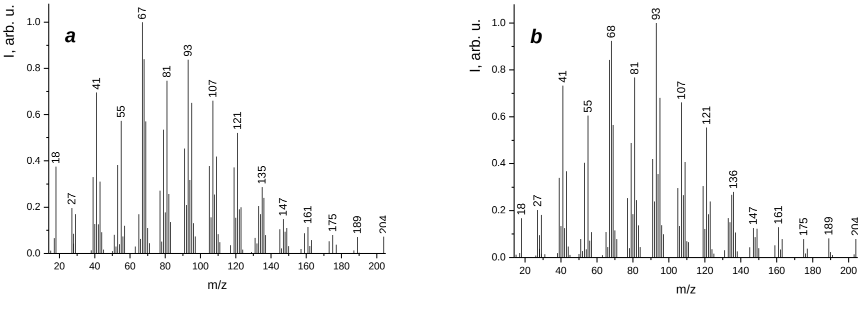


Figure 1. Mass-spectra of volatile products of thermal destruction of liquid rubbers obtained with HP as an initiator: *a* – in isopropanol; *b* – in n-butanol..

The results of measuring thermal stability of samples 1-4 in general ionic current - temperature coordinates are presented on Fig. 2. The fragment compositions and individual intensities are collected in a Tab. 2.

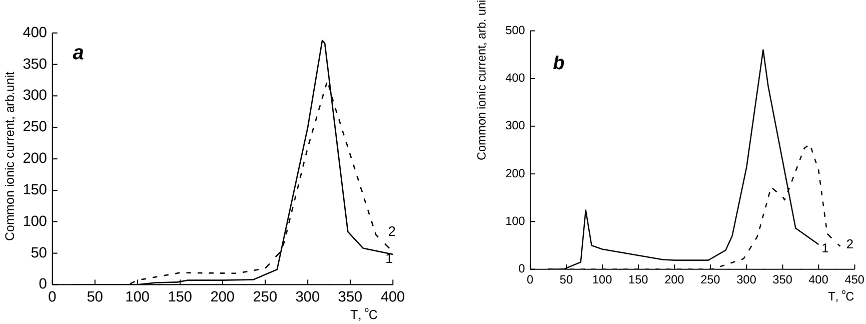


Figure 2. The temperature dependence of common ionic current of volatile product emission at thermal destruction of liquid rubbers, obtained with various initiators: a) 1 – AIBN; 2 – HP in isopropanol; b) 1 – HP in n-butanol; 2 – ACP.

Table 2. Indices of thermal destruction at pyrolysis of liquid rubbers

Sample	Monomer	T, ºC	*J*, arb. units	*K*, units	Max. *m/z*
1	Isoprene	321	388	77	205
2	Isoprene	321	324	85	204
3	Isoprene	78, 322	124, 460	35, 88	214, 204
4	Butadiene	342, 387	172, 262	58, 93	147, 175

Let us consider data presented on Fig. 1 and Tab. 2. It is seen that the temperature, which corresponds to maximum emission of volatile products, is equal for isoprene oligomers (samples 1-3) – 321-322 °C and does not depend on an end group (hydroxyl, nitrile). For butadiene rubber (sample 4), it is higher and has two intensity peaks – 342 and 387 °C. So, butadiene rubber is more stable by 20-65 °C. It is caused, more probably, the presence of methyl group in the units of isoprene oligomers, which electron donor affinity stabilizes free radicals formed at pyrolysis.

We are interesting in oxygen-containing fragments, which are included in the composition of hydroxyl groups. The molecular ions with m/z = 18, 28, 29, 31, 43, 44, 55, 71 are found among such fragments. The first one is water; the second one is fragment HCO. Presumably, they appear as a result of sequential processes and correspond to the most stable fragments at these temperatures [5]. Note, that in sample 2 the volatile product of C_3H_7O (m/z = 59 or near to it), corresponding to the end fragment of isopropyl alcohol was not found. The most probably, this fragment transforms with formation of the molecular ion CH_3CHOH with m/z =

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45. In sample 3, the fragments C_3H_5O (m/z = 57) and $HOCCH_2O$ are present (m/z = 57). Apparently, these ionic fragments appear in the process of transformation of unstable end groups of n-butyl alcohol. Obviously, week bonds are present in some parts of the molecules of samples 3 and 4, which cause a chain rupture at comparatively low temperatures. These bonds do not often succeed to be identified chemically, but their presence is revealed by thermal methods. The presence of double bonds and ramifications in oligodienes is favored decreasing their thermal stability [6].

In summary, on the base of the data of the pyrolytic mass-spectrometry, it have been determined that temperatures of the gas emission onset and the maximum as well as the content of ionizable particles, thermal stability of oligodienes obtained with hydrogen peroxide as an initiator of radical polymerization (samples 2 and 3) corresponds to the indices of an oligomer obtained with initiator AIBN. Despite of high oxidative ability of HP as an initiator and the presence of oxygen-containing groups in the ORD oligomers themselves, their thermal stabilities don’t decrease. In the sample obtained in n-butyl alcohol, a low temperature peak appears that is caused the presence some quantity of week bonds.

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P14

Ceramic fibers of NiO, ZnO and NiO-ZnO based on a electrospun PSU/nickel and zinc acetate precursor

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Nanostructured metal oxide materials attracted a lot of attention due to their potential optical, magnetic, electrical and catalytic properties which can stimulate many promising applications [1]. Electrospinning is a low expensive procedure of preparation of micro- or nanoscale polymer fibers [2]. The electrospun fibers have long lenghts, high surface to volume ratio, excellent mechanical flexibility and especially diversified in composition.

NiO, ZnO and NiO-ZnO/polysulfone composite nanofibers have been fabricated by electrospinning technique using a solution containing the metal acetate and polysulfone. Metal oxide/polysulfone composite fibers were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis, UV-VIS absorption and emission spectra.

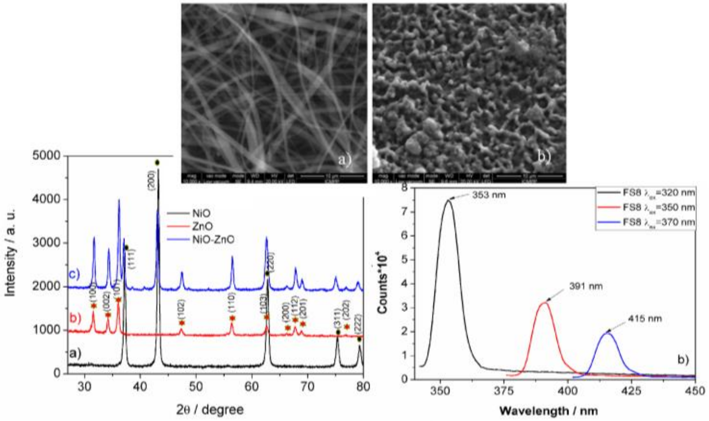

Figure 1. Properties of NiO, ZnO and NiO-ZnO/polysulfone composite nanofibers.

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XRD results confirm that the obtained products present the pure wurtzite structure for ZnO nanofibers and crystalline structure with cubic phase for NiO ceramic nanofibers. Emission spectra show that the emission bands of both ZnO and NiO-ZnO exhibited red-shifts from 353 to 404 nm and 353 to 414 nm. Emmision spectra of ceramic nanofibers are dependent on the excitation wavelength. According as the excitation wavelength was progressively increased the fluorescence band exhibited a red-shifts.

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Acknowledgements

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P15

COMPLEX MACROMOLECULAR TEMPLATES FOR CALCIUM CARBONATE MICROPARTICLES GROWTH

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An important method of biomimetic synthesis is the use a soft organic template and to control the morphogenesis of inorganic materials with complex forms. Among biocompatible inorganic materials, calcium carbonate has received considerable interest for industrial applications including coatings, fillers, and components of drug and personal care formulations, for its abundance in nature [1], and in environmental applications, where it has potential uses in carbon-capture [2]. In addition to a high natural abundance, it exhibits a unique combination of properties which include pH sensitive decomposition, nontoxicity, biocompatibility, low cost, and thus it is considered as a potential delivery vehicle for compounds such as drugs and proteins [3].

Even if there are numerous studies on polyanions control of $CaCO_3$ growth, and also with the polyanion used in this study [4], to our knowledge no studies concerning the use of *in-situ* mixing of complementary polyelectrolytes as templates for controlling $CaCO_3$ crystals growth have been reported, except our previous study, our group followed the composite calcium carbonate microparticles formation from supersaturated inorganic aqueous solutions in the presence of some strong/weak anionic polymers or nonstoichiometric polyelectrolyte complexes (NPEC) dispersions with anionic charges in excess, and with low molar ratio between charges (0.2 and 0.4) [5].

In this context, the aim of this study was to follow the effects of mixed anionic/cationic polyelectrolytes on the crystallization of calcium carbonate in supersaturated solutions in comparison with polyanions based-$CaCO_3$ composite structures [6]. Also, the method of introducing the polycation in the crystallogenesis of calcium carbonate has been investigated: preformed NPECs or *in-situ* mixing of complementary polyelectrolytes. For this purpose a polyanion which contain strong anionic groups – poly(sodium vinylsulfonate), PVS – and poly(diallyl-dimethylammonium chloride), PD, as polycation were used. Different molar ratio between complementary polyelectrolytes (n^+/n^-) were used in $CaCO_3$ composite synthesis, between 0 (just polyanions) up to 0.8. The composite particles characteristics as a function of polyanion structure and the preparation mode were evidenced by scanning electron microscopy (SEM), FTIR-ATR spectroscopy, and energy dispersive X-ray diffraction (EDAX). The particles morphology after dialysis against 20 mM ethylenediamine tetraacetic acid (EDTA) has been also followed, as a function of molar ratio between complementary polyelectrolytes and preparation mode.

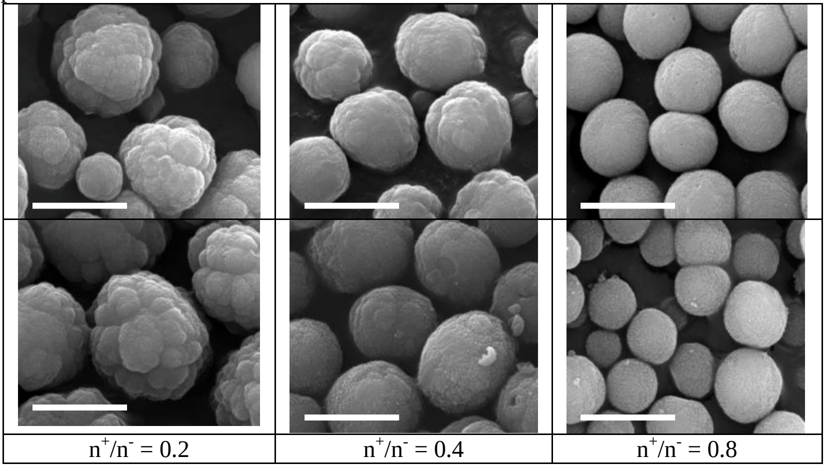
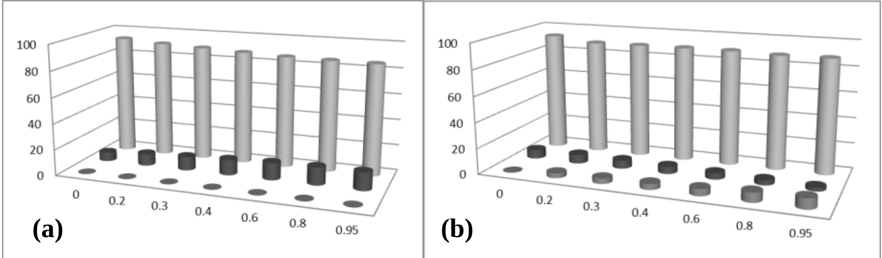

$n^+/n^- = 0.2$ | $n^+/n^- = 0.4$ | $n^+/n^- = 0.8$

Figure 1. SEM images of $CaCO_3$ based microparticles template by complementary polyelectrolytes as a function of molar ratio between ionic charges: top line - $CaCO_3$//PVS/PD, bottom line - $CaCO_3$//NPEC(PVS/PD); scale bare 5 μm.

At molar ratio between the charges of polycation and polyanion lower than 0.4 (i.e. at low polycation amounts) PVS based particles shown cauliflower shape, each aggregate being composed by nanocrystallites (Figure 1, top line). By further increasing of the molar ratio between the charges of polycation and polyanion up to 0.8 spherulitic structures were obtained, with smoother surface morphology. At the same time, the particles diameter slightly decreases with the increase of PD content in the initial mixture. The other tested method of introducing the polycation in the crystallogenesis of calcium carbonate is as preformed NPECs with the same molar ratio between charges as in the previously studied systems (Figure 1, bottom line). Comparable average size particles were obtained with NPECs, for all investigated polyelectrolyte pairs, with surface morphology very similar with that of particles prepared using *in-situ* mixed polyions.

FTIR-ATR spectra were also used to quantify the polymorph content, as described in the experimental part, taking into account the absorption peaks at 745, 713 and 700 cm^{-1}, the results being summarized in Figure 2. When both polyions were added *in-situ* during the microparticles formation, vaterite is the main polymorph, whereas calcite content increases slightly (up to 14 %). On the other side, when NPECs were used as templates in $CaCO_3$ crystallization small amount of aragonite were formed, the percentile amount increasing with the increase of PD content into the NPECs nanoparticles.



(a)

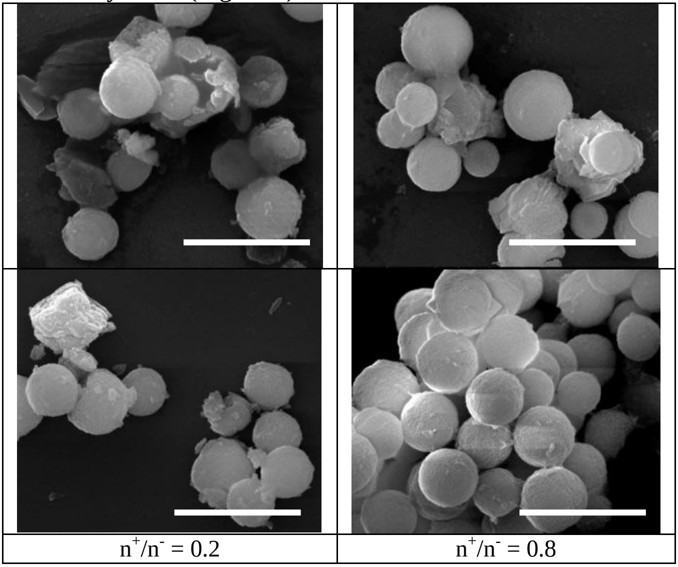
	0	0.2	0.3	0.4	0.6	0.8	0.95
■ Aragonite	0	0	0	0	0	0	0
■ Calcite	6.92	9.25	10.59	12.05	13.39	13.88	14.06
■ Vaterite	93.08	90.75	89.41	87.95	86.61	86.12	85.94

(b)

	0	0.2	0.3	0.4	0.6	0.8	0.95
■ Aragonite	0	3.71	4.03	4.51	5.34	7.44	8.07
■ Calcite	6.92	6.97	6.41	5.72	4.87	3.91	2.91
■ Vaterite	93.08	89.31	89.57	89.78	89.79	88.64	89.02

Figure 2. Polymorph content of $CaCO_3$ based microparticles template by (a) *in-situ* mixing of complementary polyelectrolytes or (b) preformed NPECs as a function of n^+/n^-.

The EDTA treatment of polymer/$CaCO_3$ composites would allow the $CaCO_3$ nanocrystals formed in the composites to be etched away and to expose the polyion/Ca^{2+} matrix. The microparticles morphology after treatment with EDTA has been followed by SEM (Figure 3).



$n^+/n^- = 0.2$	$n^+/n^- = 0.8$

Figure 3. SEM images of some $CaCO_3$/polymers microparticles after EDTA treatment: top line - $CaCO_3$//PVS/PD, bottom line - $CaCO_3$//NPEC(PVS/PD); scale bare 10 µm.

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Adding polycation besides polyanion in the crystallogenesis medium seems to increase the microparticles stability against $CaCO_3$ dissolution, the composites stability increasing with the polycation content (Figure 3, top line). The *in-situ* formation of some NPECs along with the polyanion in excess probably conducted to the formation of a denser crosslinked network comparative with PA-based microparticles and therefore to a lower capacity of chelating agent to remove $CaCO_3$ nanosized crystals. The use of NPECs in composite microparticles formation significantly increased microparticles resistance against EDTA as chelating agent for all investigated molar ratios and irrespective of polyanion structure (Figure 3, bottom line). The arrangement of preformed NPECs into de composites and the Ca^{2+} ions bridges formed between shorter anionic chains remained uncompensated by the cationic polymer probably conduct to a dense network matrix which could better protect the $CaCO_3$ against dissolution in EDTA.

The synergetic action of the $CaCO_3$ intrinsic characteristics and the multi-functionality of as prepared composite particles, given by the polyanion in excess and the method of introducing the polycation in the crystallogenesis systems make the new composites act as versatile materials for different possible applications, such as drugs or proteins encapsulation, bio-sensing platform beside drug delivery, imaging and other applications.

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P16

EFFECT OF MULTIWALLED CARBON NANOTUBES ON CRYSTALLINITY OF *IN SITU* POLYMERIZED OLIGOMERIC CYCLIC BUTYLENE TEREPHTHALATE

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Since cyclic butylene terephthalates (CBT) oligomers became commercially available, a number of scientific papers on investigation of process of their polymerization and structure-property relationships have been published [1,2]. Recently the nanocomposites based on poly(butylene terephthalate) (PBT) and multiwalled carbon nanotubes (MWCNTs) were investigated [3] and it was found that the presence of MWCNTs significantly promoted the crystallization rate of PBT because of heterogeneous nucleation.

The aim of this work was to study an effect of MWCNTs content and a method of samples preparation on crystalline characteristics of PBT matrix in PBT/MWCNTs nanocomposites produced by different *in situ* reactive extrusion methods using the low viscosity mixture of oligomeric CBT.

Macrocyclic oligo(1,4-butylene terephthalate) was a mixture of cyclic oligomers of butylene terephthalate with polymerization degree of $n \approx 2 \div 5$, (trademark “CBT 160”, “Cyclics Corp.”, USA). The temperature of melting (T_m) of CBT was T_m ~140 °C, the viscosity (η) was $\eta \sim 20$ мPa•s (at T_m). CBT before using was dried in vacuum for 12 h at $T \approx 80$ °C. The MWCNTs used (trademark “C100”, “Arkema”, France) has such main characteristics: density was ~50 ÷ 150 кg/m^3; outer diameter of the nanotubes was 10 ÷ 15 nm; length of the nanotubes was 0,1 ÷ 10,0 µm.

The nanocomposites were obtained using *in situ* reactive extrusion methods by synthesis of PBT from the CBT in the presence of 0.01 ÷ 2.00 wt. % of MWCNTs. CBT and MWCNTs were first dry mixed in a flask and then blended in a "DSM 15" twin-screw compounder (DSM Research Netherlands) at T ~ 220 ^{o}C and at screw speed of 100 rpm for 15 min. The extruded material was then used as a strand for measurements as obtained (series 1), or as films prepared by hot pressing of strands (series 2) or obtained by injection molding (series 3). Note, that such method of samples forming as hot pressing of extrusion strands exposes the composite material to an additional heating and cooling that can change the properties of the crystalline phase of PBT-matrix in the nanocomposites studied. All these stages contribute to the final properties of the PBT/MWCNTs nanocomposites, and therefore the impact of nanofiller on their phase structure and properties is essential.

Differential scanning calorimetry (DSC) investigations were carried out using "TA Instruments 2920 MDSC V2.6A" in helium atmosphere in the range of temperature of $T \approx 15 \div 250^{o}$C. Data of DSC measurements were analyzed utilizing TA Instruments Universal Analysis 2000 (ver. 3.9A). Degree of crystallinity (X_c) of the samples was determined using the value of melting enthalpy (ΔH_m) for 100% crystalline PBT: $\Delta H_m^0 = 142$ J/g [4].

During synthesis of PBT from CBT using the method of reactive extrusion (at $T \approx 220$ ^{o}C) the several processes occur: 1) melting of CBT; 2) dispersing of MWCNTs in the molten CBT; 3) polymerization of CBT with formation of PBT; 4) dispersing (due to significant shear stress) of MWCNTs in the PBT being synthesized; 5) crystallization of the PBT at further cooling of the PBT/MWCNTs samples.

The DSC investigations have shown that depending on the nanofiller content the thermal-physical properties of amorphous and crystalline phases of PBT-matrix in the PBT/MWCNTs nanocomposites change non-monotonically (Table 1), namely, melting temperature T_m (by 0.1 ÷ 4.5 ^{o}C), crystallization temperature T_c (by 3,1 ÷ 18,2 ^{o}C, cf. Fig.1), melting enthalpy ΔH_m (by 1÷ 10 J•g^{-1}), degree of crystallinity X_c (by 1.0 ÷ 8 %) etc.

Table 1. Typical thermal-physical properties for different series of PBT/MWCNTs nanocomposites studied

MWCNTs content, wt.%	T_m, ^{o}C			ΔH_m,J•g^{-1}			X_c, %		
	Series1	Series2	Series3	Series1	Series2	Series3	Series1	Series2	Series3
0	225.1	227.7	222.8	52	55	58	37	39	41
0.10	225.5	229.2	222.5	42	57	51	30	40	36
0.30	226.2	229.1	226.7	50	51	56	35	36	39
0.50	226.1	227.9	225.7	46	57	61	32	40	43
1.00	226.3	228.4	226.2	47	57	60	33	4	42
2.00	225.6	228.7	225.6	50	58	68	35	41	48

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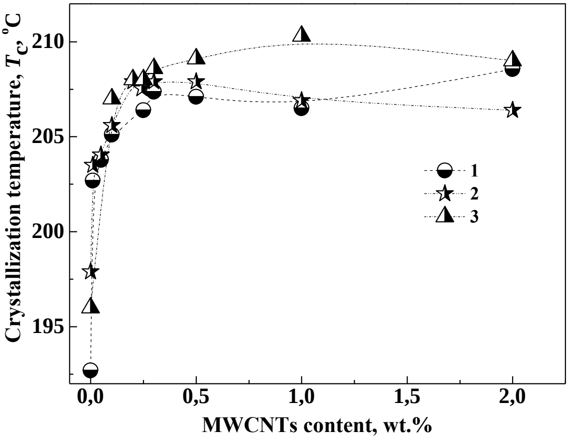

Figure 1. Effect of MWCNTs content and molding technique used on crystallization temperature T_c of the PBT crystallites in the PBT/MWCNTs nanocomposites studied: 1 – extrusion strand (series 1); 2 – hot pressing (series 2); 3 – injection molding (series 3).

It was found (Fig.2) that increase of MWCNTs content in the nanocomposites leads to changes in a shape of melting thermograms of the PBT crystallites, especially at a 2nd heating scan (Fig. 2b). One can see that for most of

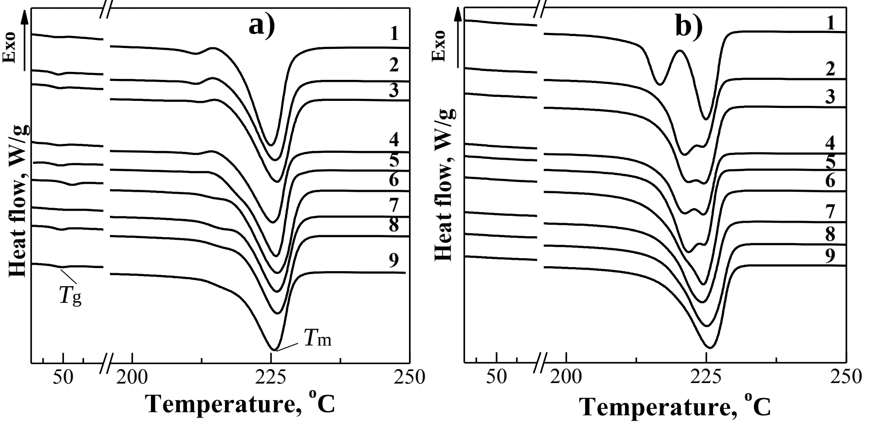

Figure 2. DSC thermograms for PBT/MWCNTs nanocomposites (extruded strands) with different content of MWCNTs, wt. %: 1 – 0; 2 – 0.01; 3 – 0.05; 4 – 0.1; 5 – 0.25; 6 – 0.3; 7 – 0.5; 8 – 1.0; 9 – 2.0; a) 1st heating scan; b) 2nd heating scan.

the nanocomposites two melting peaks are presence in the thermograms (at a 2nd heating scan) that evidence of melting of defective or less perfect PBT crystallites. During the further heating of the sample the recrystallization of the crystallites is occurred followed by formation of larger crystallites of PBT which are characterized by higher T_m value.

It can be seen (Fig. 2) that in the DSC thermograms of the nanocomposites with MWCNTs content equal ≥ 1 wt. % the melting peak corresponding to smaller PBT crystallites (in a temperature range of $T \sim 212 \div 223$ °C) is absent. It can be concluded that increasing to 1.0 ÷ 2.0 wt. % of MWCNTs content provides formation of larger PBT crystallites in the PBT/MWCNTs nanocomposites (compared to other samples).

For the two other series of PBT/MWCNTs nanocomposites (formed by hot pressing method or by injection molding) some increase of T_m (by 1.0 ÷ 3.4 °C) and X_c values (by 1.6 ÷ 6.9 %) compared to the unfilled PBT has been fixed at increasing up to 1.0 ÷ 2.0 wt. % of MWCNTs content in the nanocomposites. It was found also that during cooling of the nanocomposites (after first heating scan) the crystallization process started much earlier and at higher temperatures (by 3 ÷ 18 °C, depending on the composition and the method of sample molding, Fig. 1) compared to unfilled PBT sample. It was concluded that the MWCNTs play the role of heterogeneous nuclei at process of PBT crystallization during cooling of the PBT/MWCNTs nanocomposites produced.

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P17

PLASTICIZERS BASED ON RENEWABLE RAW MATERIALS FOR MIXED POLYMER COMPOSITES

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Polymer composite materials (PCM) are of primary importance in various branches of technology. Among PCM, an important place belongs to highly filled high power materials (HPM). To the main components of such composites belong plasticizers (PL) used for intensifying pulverous components dispersion, viscosity decrease and increase in mass plasticity under conditions of processing [1]. The last-mentioned fact is especially significant for processing PC, for instance, through the method of open vacuum casting. That is why elicitation of the rheological properties regulation mechanisms represents a relevant objective of research and practice.

The plasticizers for HPM include primarily the ethers of synthetic dicarboxylic acids: dioctyl phthalate (DOP), dioctyl sebacate (DOS) etc. They are the products of processing non-renewable raw carbohydrates, the shortage of which is currently felt.

The aim of the present research is to examine the possibility of complete or partial replacement of traditional (DOP) plasticizers for highly filled polymer composites (HFPC) with the products of processing renewable raw materials of vegetable origin. The research also seeks to elicit the mechanisms of influence of a plasticizer on the rheological properties of a compound.

The following compounds (PL) have been used as those expected to have plasticizing properties: hydrated soybean oil (HSO), products of interaction between furfuryl glycydil ether (ET) and fatty acids: neodecanoic (NDA-ET), 2-ethylhexanoic (EHA-ET), palmitic (PA-ET), oleic (OA-ET) and stearic (SA-ET). DOP was used as a standard plasticizer.

With due regard to physicochemical similarity between separate stages of polymer dissolution and plasticization, we considered a possibility of using a solubility criterion suggested by Askadsky [2] in order to assess compatibility of the studied PL and liquid nitrile rubber (LNR) as well as to predict their influence on the rheological properties of HFPC.

The calculations showed that the condition of compatibility is met for all the studied PL. An experimental test proved total compatibility of PL and LNR in a wide interval of their correlation, which points out to the possibility of using the aforementioned criterion for a priori assessment of components compatibility.

Rheological research demonstrated that PC are typical pseudo-plastic fluids characterized by effective viscosity decrease with shear stress growth (Fig. 1):

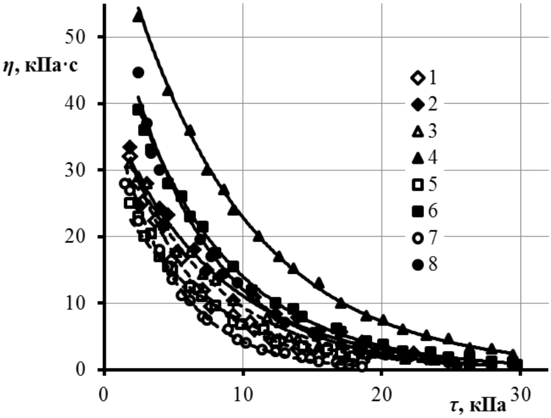

Figure 1. Relation of dynamic viscosity η to shear stress τ of composites containing 4,3 % of the following plasticizers: DOP (1, 2), NDA-ET (3, 4), PA-ET (5, 6), HSO-ET (7, 8) at temperatures of 40 °C (1, 3, 5, 7) and 50 °C (2, 4, 6, 8)

The obtained $\eta(\tau)$-relationships for all PLs, DOPs and PL:DOP correlations are approximated by exponential trend lines, the coefficient of determination being $R^2>0{,}985$:

$$\eta = Ae^{-\alpha\tau} . \qquad (1)$$

where η stands for viscosity, Pa·s;
A is a pre-exponential factor;
α is a coefficient;
τ is a shear stress, Pa.

As we can see, the coefficient A in equation (1) meets the condition $A = \lim_{\tau\to 0}\eta$. That is why it is reasonable to interpret it as a value corresponding to the so-called highest Newtonian viscosity η_o of pseudo-plastic fluids and use it as a characteristic parameter. The coefficient α may be interpreted as an index of system responsiveness to shear load or as a characteristic of energy density of all non-chemical bonds that form a fluctuation network.

The η_o values obtained at 40°C point out to the fact that in terms of effectiveness of their influence on the rheological properties of HFPC, the studied

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PL, except for OA-ET, match and in some cases even surpass DOP.

It has been proved that instead of the traditional plasticizer – DOP – it is possible to use compounds obtained from products of processing renewable vegetable raw materials: furfural, fatty acids and soybean oil. In order to assess thermodynamic compatibility of a plasticizer and a binder, it is possible to use an approach applicable to the assessment of polymer solubility.

It has been demonstrated that for all the model HFPC under the study, the relation of dynamic viscosity to shear stress is adequately described by exponential relation. The coefficients of the approximating function may be interpreted as characteristic indicators for a comparative analysis of the plasticizers influence on the rheological properties of highly filled fluid viscous polymer composites.

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P18

HYBRID MATERIALS BASED ON (ALLYL-BENZOXAZINE)S

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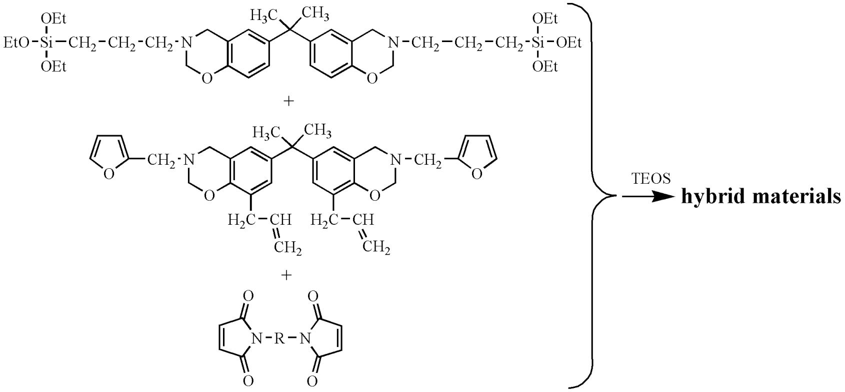
Novel hybrid materials based on allyl-benzoxazine-maleimide multicomponent systems were prepared (as illustrated in Scheme 1) and characterized. The reactions of the hybrid materials formation (reaction of hydrolysis-condensation of silanol groups) take place simultaneously with the crosslinking reaction of allyl-benzoxazine-maleimide multicomponent systems.

The characterization of resulting materials was performed by thermal and spectroscopic methods.



Scheme 1

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SPECIFIC LAYER-BY-LAYER BUTT WELDING OF MULTI-LAYER POLYMERIC COMPOSITE PIPES BASED ON POLYPROPYLENE AND GLASS FIBERS

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Abstract

Possibilities of three-layer polypropylene pipes (with glass fiber middle layer) butt welding are investigated. It is proved that traditional hot tool butt welding cannot provide sufficient strength. Specific butt welding technology of multi-layer pipes within the limited volume is developed.

Introduction

Multi-layer composite pipes based on polypropylene are widely used for cold and hot water supply systems' construction [1]. Such pipes due to the glass fiber layer have higher strength [2], lower thermal expansion coefficient [3] and higher thermal-insulation properties [4] comparing to the usual pipes. As a rule such pipes are joined by means of hot tool socket welding [5]. Shortcomings of this method are connected to the necessity of using of special joining fittings, and to the high temperature of the process that can deteriorate molecular structure of material and can cause high stresses concentration [6]. Hence, developing of non-traditional methods of the butt welding technology for multi-layer composite pipes is of high relevance.

Experimental basis

Three-layer pipes FIRAT KOMPOZIT (diameter 63 mm) with external and internal layers of polypropylene type 3 (PP-R) and with middle layer of the same polypropylene filled with short glass fibers (PPR-GF) have been welded. Multi-purpose welding device (Fig. 1) designed on the basis of SAT-1 butt welding machine produced by Experimental Welding Equipment Factory of Paton Welding Institute has been used for the experimental welding.

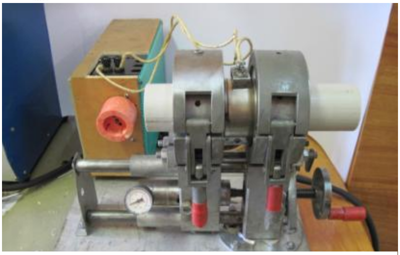
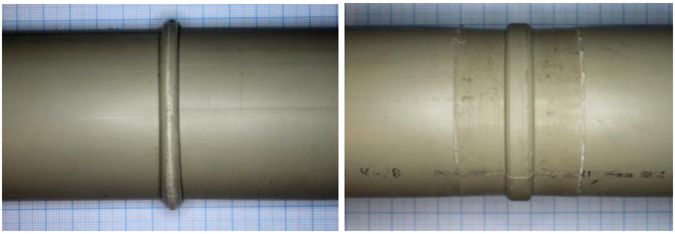


Figure 1. Multi-purpose device for traditional polymeric pipes hot tool butt welding equipped with the specific unit for welding within the limited volume.

This device makes possible to receive butt welds using traditional flat tool. Special unit for welding within the limited volume (Fig.2) have been developed in the Plastics Welding Department of Paton Electric Welding Institute. This developed unit is currently under patent obtaining, so it is not presented in detail here.

Welding quality has been evaluated basing on flash parameters and on the grinded specimens macroscopic investigations, as well as by means of mechanical testing (tensile tests) according to the GOST 11262 standard.



a) b)

Figure 2. Welded joints of three-layer polypropylene pipes diameter 63 mm: butt welded (a) and welded within the limited volume (b).

Discussions

Under traditional hot tool butt welding of multi-layer composite pipes the weld has, as a rule, three-zone structure (Fig. 3, a), caused by the inter-layer flow of melted middle-layer material (in our case – polypropylene filled with glass fibers) normally to the axis of the pipe, and actual welding happens only in this glass-filled zone. This material, which has worse weldability comparing to the pure polypropylene due to the glass filling (fibers prevent formation of flawless seam), is located along the joining line and reduces the strength of the weld.

Destruction of the specimen during tensile test happens (as it is presented on Fig. 3, b) exactly through the middle layer of glass filled polypropylene, with less than 60% of strength of the basic material (Table 1).

Under the multi-layer pipes restricted volume welding using unique instrument modulus there is practically no axial displacement of the pipes and no molten material flow towards outer surface of the pipe. Hence, there is no molten

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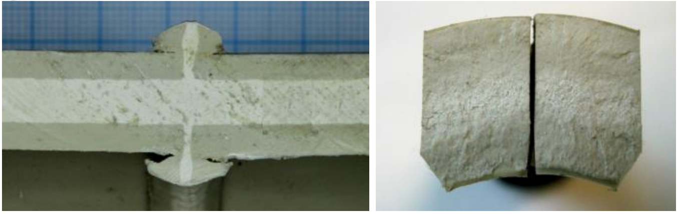
a) b)

Figure 3. Cross sections of the hot tool butt weld (a), and general view of the destroyed specimen after tensile test (b).

material flow from the middle part of the pipe which is usual for upsetting phase of traditional hot tool welding. As a result we obtain a weld with unchanged layer-by-layer structure similar to the one of the basic material (Fig. 4 and Fig. 5).

In order to obtain a high quality weld within the restricted volume it is necessary to provide heating of the pipe material up to the melting temperature over the whole wall thickness. In the case of multi-layer pipe this tusk is complicated due to the higher heat-insulation features of the glass-filled layer. In the case when developed welding parameters are violated the heating of the wall is insufficient and lack of fusion is observed; weld's strength drops to 25-30% of basic material strength (Fig. 4).

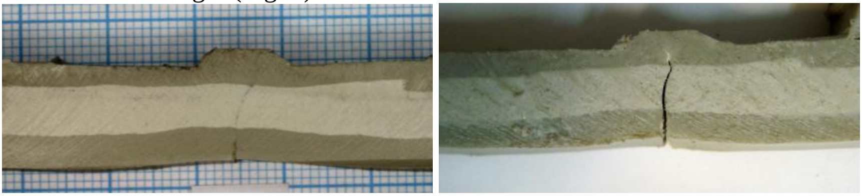
a) б)

Figure 4. Cross-section of the specimen welded within the limited volume, with lack of fusion along the welding interface before (a) and after (b) tensile test.

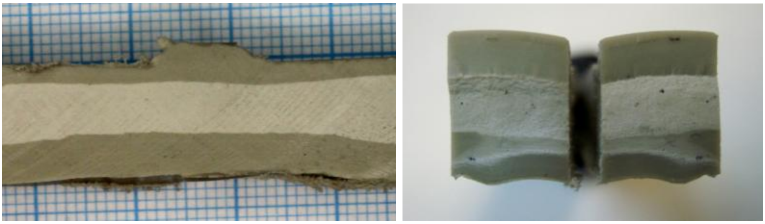
a) b)

Figure 5. Cross-section of the specimen welded within restricted volume under optimal parameters before (a) and after (b) tensile test.

In order to obtain even heating of the multi-layer pipe's wall step heating schedule and longer heating time have been applied; weld's cooling time has also been increased. In this case a three-layer welded joint has been obtained, with structure similar to the one of the basic material (Fig. 5), and with tensile strength equal to 80% of the basic pipe strength (Table 1). The main obstacles of 100% strength achieving are small notches and lack of fusion on the inaccessible internal side of the pipe's wall.

Welds' strength data are presented in Table 1 (tensile strength of the three-layer basic pipe is 33 MPa).

Table 1. Comparison of welds' tensile tests results

Welding process	Tensile strength of the welds, MPa	Tensile strength comparing to the basic material, %
Traditional hot tool butt welding	**18,9**	**57**
Limited volume welding, unbalanced heating mode	**8,2**	**25**
Limited volume welding, optimal heating mode	**26,5**	**80**

Conclusions

It is presented that maximal strength of the multi-layer composite pipes butt welds can be received under welding within the limited volume when unchanged layer-by-layer structure similar to the structure of the basic material is obtained. Solution of the notches and lack of fusion on the internal side of the pipe's wall is the last step to develop competitive technology of multi-layer composite pipes' welding within the limited volume.

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P20

NEW NANOCOMPOSITES BASED ON POLYURETHANEACRYLATES WITH MODIFIED MONTMORILLONITE, PREPARED BY *in situ* POLYMERIZATION

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In order to create polymer nanocomposites on the basis of polyurethane acrylates with high performance properties the method of modification of montmorillonite (MMT) with a new modifier oligourethane methacrylate ammonium chloride (OUMAAC) has been developed. Exchange capacity of the MMT surface was determined by adsorption of indicator "methylene blue". Intercalation of modifier into the interlayer space of MMT was confirmed by X-ray analysis; the content of organic component in the MMT modified with OUMAAC (MMT/M) was determined by thermogravimetric analysis. The resulting organoclay is purposed for the formation of nanostructured composites based on cross-linked polyurethane acrylates with improved physical and mechanical properties. The new modifier oligourethane methacrylate ammonium chloride provides high affinity of MMT/M with polymer matrix due to the possibility of physical and chemical bonds formation. The intercalation of modifier into the interlayer space of MMT (increased on 0.7 nm distance between the layers after modification), as well as exfoliation of MMT/M in polyurethane acrylate matrix (disappearance of the absorption peak, which is responsible for the layered structure of MMT), was proved by X-ray analysis. The physic-mechanical tests of the polymer nanocomposite with MMT/M concentration of about 3% have shown the strength increase in almost 3 times as compared to polyurethane acrylate (PUA) matrix.

Patent Ukraine № 80405 (2013). Savelyev Yu. V., Gonchar A.N., Sokolov M.Yu. Publ. 27.05.2013. Bul. №10 (in Ukrainian)
Patent Ukraine № 80913 (2013). Savelyev Yu. V., Gonchar A.N. Publ. 10.06.2013. Bul. №11 (in Ukrainian)

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P21

PREPARATION AND OPTICAL PROPERTIES OF HIGHLY HYDROPHILIC POLYMER STABILIZED ZnO NANOHYBRIDS

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To the date zinc oxide (ZnO) attracts a great attention of the scientists because of their exhaustive characteristics, namely optical (including luminescent and UV-absorbing), semiconducting, bactericidal properties, strengthening effect on polymers etc [1]. Introducing ZnO into the polymers allows to produce the composites combining characteristics of inorganic constituent and technological advantages of polymer components. Additionally, hybridization of the components of polymer/ZnO composites via *in situ* synthesis of nano-sized ZnO in a polymer matrix is a perspective way to manufacture modern high-performance composite materials [2].

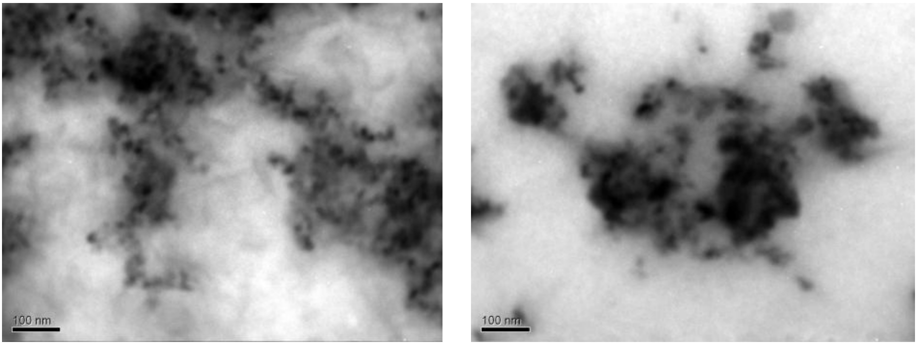
There are different approaches to prepare hybrid polymer/ZnO composites, like sol-gel synthesis, polymerization techniques, reactive processing [3]. A one of the most usable methods is sol-gel synthesis in hydro- or solvothermal conditions or base-induced process at ambient conditions [3]. Sol-gel polyol process is very attractive synthetic pathway for preparation nano-scaled ZnO particles. Using organic (alcohol) media for preparation ZnO allows to simplify a stabilization of ZnO nanoparticles and to combine the nano-dispersed phase with functional polymer to achieve hybrid structure of final composites [4].

In this work we propose an effective synthetic method of preparation of stable dispersion of ZnO nanoparticles hybridized with highly hydrophilic functional polymers to the hybrid composites. Morphology and optical characteristics of the materials obtained have been studied.

For preparation of dispersions of hybrid ZnO nanoparticles a zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and ethylene glycol (both of chemical grade) were used as received. As the polymer stabilizers a poly(N-vinylpyrrolidone) (PVP) of M_w = 70000, poly(ethylene glycol) with M_w of 1450 and 6000 (PEG^{1450} and PEG^{6000}, respectively), poly(vinyl alcohol) (PVA) of M_w=27000 and poly(2-ethyloxazoline) (PEOZ) of M_w = 50000 were used.

Solvothermal synthesis of ZnO-based nanohybrids includes dissolving zinc precursor in fixed volume of ethylene glycol followed by increasing a temperature up to 80-90 °C and a mixing the reactive blend for 30 min. In the next step as prepared solution of a polymer in ethylene glycol was dropped into reactive media and the mixture reacted for different period of time. Finally a temperature of the mixture was reduced to 20 °C and transparent dispersion of polymer/ZnO nanohybrids are obtained. Morphology of hybrid ZnO nanoparticles was studied by transmission electron microscopy (TEM) by JEOL JEM 1230 instrument at an accelerating voltage up to 120 kV. Optical characteristics of the nanodispersions were tested via UV-vis spectroscopy using Shimadzu RF-5301 spectrometer in a spectral region of 200-800 nm.

Formation of ZnO nanoparticles is carried out by the similar way as described earlier [4]. The main difference of the method developed from aforementioned technique is using a water of hydrated Zn^{2+} precursor as an initiator of hydrolysis of zinc salt in organic medium. During the synthesis hydroxyl-containing zinc complexes formed followed by their condensation and water elimination that provides a formation of ZnO nanoparticles [4].

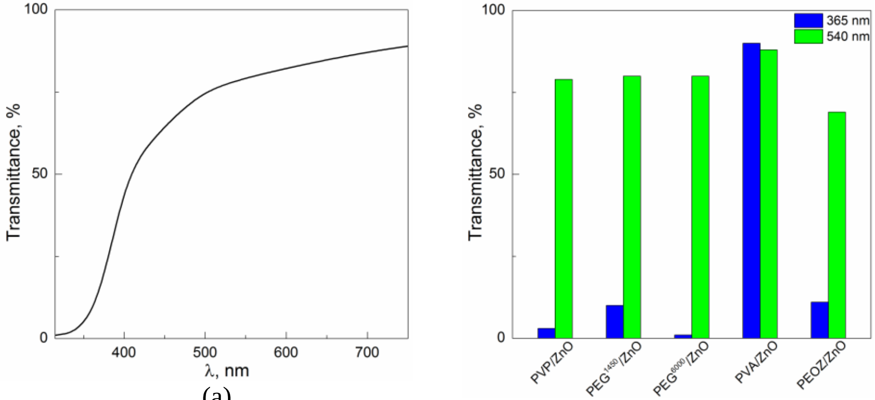


(a) (b)

Figure 1. TEM microphotograph of PVP/ZnO nanohybrids prepared at different treatment time: (a) 2 hrs and (b) 8 hrs.

Studying morphological features of prepared PVP/ZnO nanohybrids (*see* Fig. 1) shown a formation of stable ZnO nanoparticles coated by polymer layer that provides an improved stability of dispersed inorganic constituent in polar organic medium and a formation hybrid structure. An appearing of substantial quantities of stabilized hybrid ZnO nanoparticles in reactive solution was identified even after minimum solvothermal treatment time (2 hrs). Increasing treatment time up to 8 hrs induces some growing of particles size with minimal level of aggregation of hybrid nanoparticles.

Optical properties of nanohybrid samples are presented in Fig. 2. As it shown transmission spectrum of PVP/ZnO nanoparticles dispersion is characterized by high absorption level at λ < 400 and enhanced transmission in visible region (*see* Fig. 2a) [5]. From the previous experience it was stated out that successful *in situ* preparation of nano-sized ZnO phase and the polymer/ZnO hybrid composites with enhanced optical properties are highly depend on stabilizing and structurizing effect of polymer constituent. Comparative studies of an influence of polymers on formation of polymer/ZnO nanohybrids (Fig. 2b) evidence that presence of PVA is not allowed to prepare hybrid materials with enhanced optical characteristics result in poor optical properties of the composite. Oppositely, other polymers have significant stabilizing and structurizing effects on formation polymer/ZnO nanohybrids and enhance an absorbance in near UV region. Hybrid samples based on PVP and PEG^{6000} show highest level of UV absorption that reaches 97-99 % at 365 nm and low absorption in visible spectral region (10 % at 540 nm).



(a)

(b)

Figure 2. Optical properties of nanohybrid obtained: (a) UV-vis spectrum of PVP/ZnO and (b) transmittance values of polymer/ZnO nanohybrid at fixed wavelength.

Aforementioned results allowed to conclude the follow. Proposed synthetic approach provides simple and highly efficient formation of nanodispersed polymer/ZnO hybrids with improved aggregative stability in organic media and enhanced optical characteristics. Hydrophylic polymers used in this work play a stabilizing and structurizing role in a formation of nanohybrid materials. Obtained composite materials are characterized by enhanced absorption in near UV and high transparency in visible spectral region. ZnO based hybrid composites could be used in manufacturing photocatalysts, sensors, UV-absorbing materials and glasses for special application.

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STRUCTYRE AND OPTICAL PROPERTIES OF THE COMPOSITES POLYVINILBUTYRAL/ZnO OBTAINED VIA SOL-GEL APPROACH

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There are different approaches to prepare hybrid polymer/ZnO composites, like sol-gel synthesis, polymerization techniques, reactive processing [1]. A one of the most usable methods is sol-gel synthesis in hydro- or solvothermal conditions or base-induced process at ambient conditions [2]. ZnO-containing polymer nanocomposites with enhanced optical properties have been obtained via sol-gel approach [3]. Proposed method allows to produce optically transparent polymer systems with ZnO of 3 nm in a size, which are well-dispersed in polyvinylbutyral matrix. The composite film with a thickness of <100 μm and ZnO content of 1 wt% is characterized by transparency of 95% in visible region and UV absorbance as high as 48% [4,5]. Follow increasing ZnO content do not increase UV-absorbing characteristics of the composite systems probably because of aggregation of particles of the active nanofiller.

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P23

PHISICO-CHEMICAL AND MICROBIOLOGICAL EVALUATION OF TWO POLY(CARBOXYBETAINES) DERIVED FROM POLY(4-VINYLPYRIDINE)

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The salted solutions of two poly(carboxybetaines) derived from poly(4-vinylpyridine) P4VP, and having methylene (P4VPB-1) or ethylene (P4VPB-2) spacer between N^+ and COO^- groups, were investigated from physico-chemical and antibacterial points of view. The viscometric measurements revealed "antipolyelectrolyte" behavior for P4VPB-1 and P4VPB-2, both in NaCl and $CaCl_2$ aqueous solutions (0.1 M or 0.5 M). Generally, due to a better screening of polymeric charges, the values of refractive index increment dn/dc and weight-average molecular weight $\overline{M}_w$ decreased, while hydrodynamic radius R_h increased with increasing of low molecular weight salt concentration in solutions, as the refractometric and laser light scattering measurements showed. Particle size distribution in these solutions was monomodal or bimodal depending on the solvent type and balance between molecular forces.

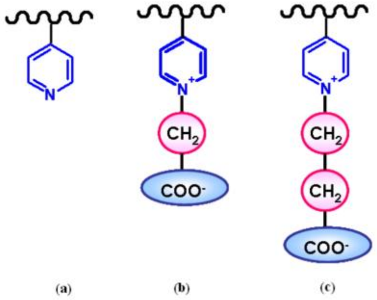

Figure 1. Structural units of poly(4-vinylpyridine) (a), P4VPB-1 (b) and P4VPB-2 (c).

P4VPB-1 did not interfere with the metabolism of *Escherichia coli* ATCC 25922 or *Staphylococcus aureus* ATCC 25923. P4VPB-2 inhibited the growth and multiplication of *S. aureus* and recorded a minimum inhibitory concentration (MIC) of 6.4 mg mL^{-1} by resazurin test. The effective antimicrobial activity against S.aureus of P4VPB-2 was due to introduction of ethylene as spacer of the zwitterion.

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P24

INNOVATING FOOTWEAR DESIGN BASED ON BIOMECHANICAL AND PHYSIOLOGICAL PARAMETERS

(international project)

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Biomechanical and physiological parameters are key points in innovative shoe design and in the prevention of foot problems. In the FOOTyWEAR project, both aspects will be investigated with the aim to support shoe manufacturers in designing innovative footwear. This includes the adaptation of shoe structure and shape to the individual foot posture and the unroll of the foot, and the optimization of the micro-climate at the foot skin by selecting proper shoe materials.

This research project will be executed by two complementary partners, MOBILAB (orthopedics & rehabilitation technology) from Belgium and IPS-PIPS (shoe manufacturing and material selection) from Poland.

The assessments of the dynamic foot type and suited shoe materials allow a founded and appropriate selection of shoes, contributing to the prevention of (overuse) injuries, foot deformities, skin wounds and foot diseases. This is beneficial to the entire shoe sector. It reinforces the competitive position of our shoe industry with respect to the shoe industry of the far east.

Additionally, this research is of great value for orthopedic shoe technologists, physicians and rehabilitation scientists : the method for foot type classification will serve as an important innovative aid for adequate diagnosis and treatment of foot related problems and pathological feet, and the design of orthopedic devices, insoles and shoes.

P25

ELECTRICAL AND ELECTROMECHANICAL PROPERTIES OF SOME NANOCOMPOSITE POLYIMIDE FILMS

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New polyimide composite films were prepared by physical incorporation of different amounts of TiO_2 nanotubes (TNTs) and carbon nanotubes into a poly(amic acid) solution, followed by film casting and thermal imidization. The poly(amic acid) was synthesized by polycondensation reaction of 4,4′-(1,3-phenylenedioxy)dianiline with 4,4′-oxydiphthalic anhydride, in N-methyl-2-pyrrolidone as solvent. TNTs having outer diameters of approximately 10-12 nm and length of several hundred of nanometers were obtained by hydrothermal method. 3-Aminopropyltriethoxysilane was used to modify the surface of TNTs with the aim to enhance organic-inorganic interfacial cohesiveness and to minimize the tendency for agglomeration of the inorganic filler. The films were flexible, tough and exhibited high thermal stability. The influence of TNTs content on the electrical and electromechanical properties of polyimide films was investigated. The dielectric constant and the dielectric loss increased with the increase of TNTs content. The films exhibited nanoactuation, when an electric voltage was applied on their surface.

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P26

OPTICAL CHARACATERISTICS OF SOME FLUORINATED POLY(OXADIAXOLE ETHER)S IN NEAT AND MIXED SOLVENTS

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Fluorinated poly(1,3,4-oxadiazole-ether)s possess a unique combination of properties that makes them good candidates for various applications as high temperature fibers, reinforced materials and membranes for gas separation. On the other hand, they are characterized by high electron affinity [1]. The electronic properties combined with other properties made them attractive for applications in microelectronics, optoelectronics, advanced telecommunications or other related fields [2-4]. From this point of view, the investigation of photophysical behavior and preferential solvation of some polyethers bearing oxadiazole units and trifluoromethyl groups, in neat and mixed solvents seem to be quite interest.

Solvatochromic behavior and information about local compositions of a solute in different binary solvent mixtures has been rarely found in the literature. In this paper, environment effects on the photophysical behavior, repartitioning of cosolvent between local and bulk phase and the fluorescence quenching process by nitrobenzene for some fluorinated poly(oxadiazole ether) in two binary solvent mixtures were investigated.

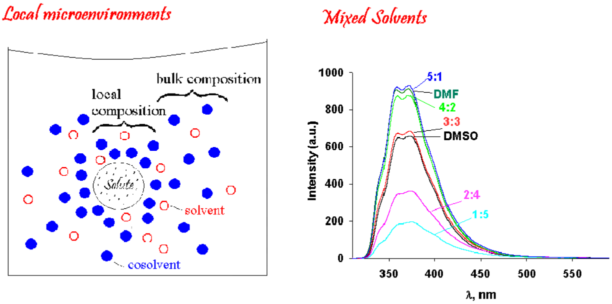

Figure 1. Schematic representation of preferential solvation process of a solute in mixed solvents and their effect on the spectroscopic data.

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Absorption and emission properties of these polymers and copolymers were investigated in various medium conditions by UV-Vis absorption spectroscopy and fluorescence measurements. They are affected strongly by the nature of solvent and composition of the system.

Preferential solvation process in mixed solvents and their effect on the spectroscopic investigations were suggestive depicted in Fig. 1.

Correlation between solvatochromism and the parameters of the neat and mixed solvents (acidity, basicity and polarity/polarizability) was evaluated. Optical properties are influenced by the composition of each solvent mixture, being dependent on the type of interaction between the solvents. These aspects were discussed in terms of preferential solvation.

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P27

ELECTROPHYSICAL PROPERTIES AND RELAXATION BEHAVIOUR VERSUS STRUCTURAL ORGANIZATION OF THE ELECTROACTIVE HYBRID POLYMERS CONTAINING IONIC LIQUIDS

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Introduction

The development, investigation and implementation of electrolyte systems of different nature, notably organic liquid electrolytes, ionic liquids, polymer electrolytes and inorganic solid electrolytes, are of interest. In brief polymer electrolyte systems can be conditionally divided as follows: polymer + organic liquid (polymer gel); polymer + ionic liquid; polymer + inorganic solid electrolyte + ionic liquids; polymer electrolyte + ionic liquid; polymer electrolyte + ionic liquid + liquid organic electrolyte; ionic liquids + liquid organic electrolyte; polymer electrolyte + inorganic solid electrolyte.

The blends consisting of two and more mentioned components are used and studied for obtaining electroactive polymer materials (EPM) with combined merits of selected products.

Materials and synthesis

Electroactive hybrid **P**olymer **M**aterials (***EPM***) have been synthesized by joint polymerization of organic ($70\%_w$) and inorganic ($30\%_w$) components (Fig. 1).

Organic component was urethane oligomer (*UO*) with MW 4500 and reactivity R=0,036. Isocyanate-containing modifier (*IM*) with MW 450 and reactivity R=0,32 was used to improve stoichiometry and mechanical characteristics of EPM. For the present work the content of IM in EPM was varied from 0 to 80 wt.% changing the reactivity R of the organic component from 0,036 to 0,22. Inorganic component was metal silicate (***MS***) that exists in liquid oligomeric form.

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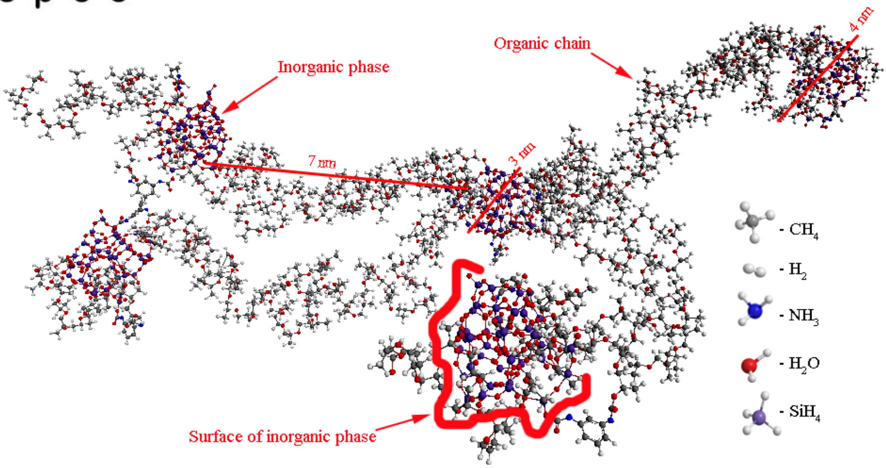

Figure 1. 3D structural model of the HOIS.

Joint polymerization of both components run due to reactions between reactive NCO-groups of organic components and OH-groups of inorganic component.

Two types of ionic liquids (*IL*), namely quaternary ammonium salts (*IL Q*) and diquaternary ammonium salts (*IL 2Q*) based on morpholine, were used (Fig.2).

The introduction of IL into the EPM bulk passed by adsorption and absorption processes.

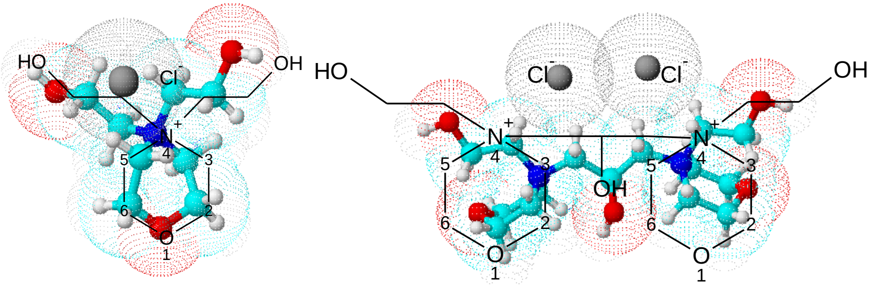

Figure 2. 3D structural models of the ionic liquids IL Q and IL 2Q.

Results and discussion

Relaxation spectra and activation energy of charge transport of the pure EPM

Fig. 3 represents the dielectric spectra of the lowly (with reactivity R of the organic part equal to 0,063) and highly (with R=0,22) cross-linked hybrid polymer system. It is obvious from electrical modulus M' that EPM with low values of R characterizes by higher electrical and dielectric properties having relaxation

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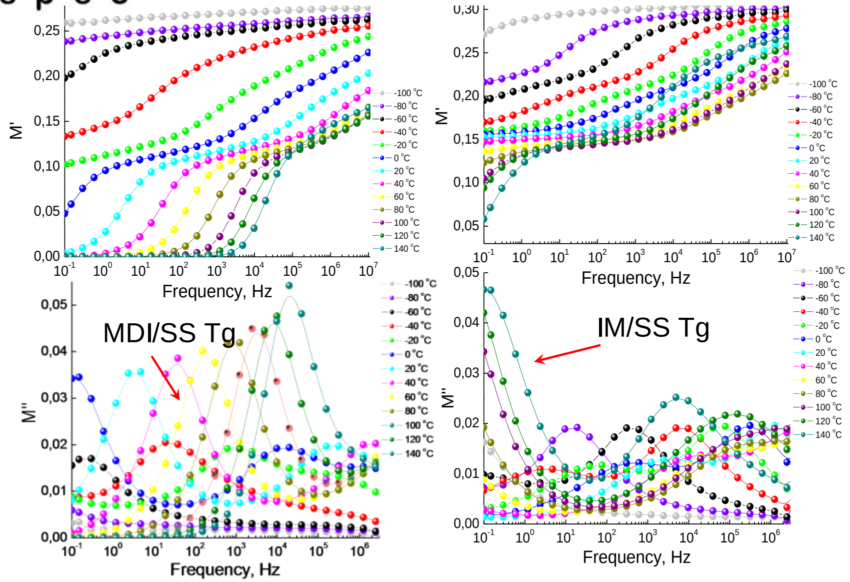

a) b)

Figure 3. Dielectric modulus spectra of lowly (a) and highly (b) cross-linked EPM.

processes at lower temperatures. That is the effect of structure transition from lowly cross-linked network MDI/MS that enables charge transport to the highly cross-linked network IM/MS that prevents mobility of the charge carriers. In addition with the change of the chemical structure of the dominant network in EPM it influences on the steady-state conductivity, in general, that has inverted view to the activation energy dependencies.

Activation energies of charge transport at glass transitions of the both networks were calculated from the dielectric spectra using Havriliak-Negami and Vogel-Fulcher-Tamman equations. With the rise of R the activation energy of charge transport through the volume of EPM increases because of the impact of growth of the potential barrier height.

With the idea to improve electrical and dielectric characteristics of the EPM synthesized the lowly cross-linked EPM with low R, glass transition temperature and activation energy were chosen for doping by ionic liquids.

Doping of the EPM synthesized by the pure ionic liquids

A high level of ionic conductivity and giant permittivity was obtained at sorption. IL plays a role of plasticizer for EPM that shifts the glass transition of EPM to higher frequencies at dielectric spectra (Fig. 4) and to lower temperature at calorimetric spectra (Fig. 5, a).

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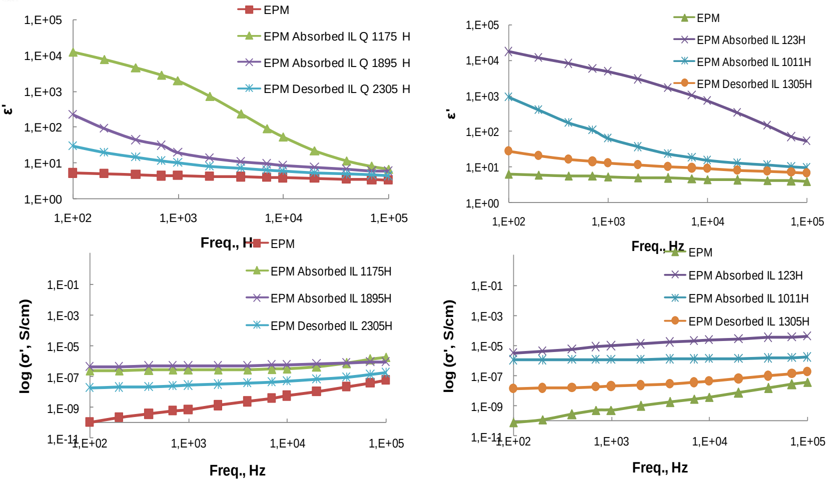
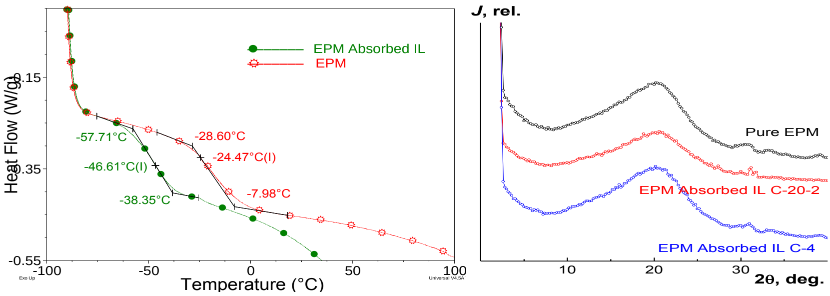


a) b)

Figure 4. Sorption/desorption processes of IL Q (a) and IL 2Q (b) in EPM by electrical and dielectric studies.



a) b)

Figure 5. Calorimetric (a) and WAXS (b) spectra of pure and doped EPM.

The decrease of conductivity and permittivity at sorption is due to reactions between molecules of ionic liquids and mineral phase of EPM, collapse with the simultaneous formation of new crystalline structures of ionic crystals (Fig. 5, b) due to MS/IL reactions. Because of that the number of charge carriers rapidly decreased.

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OPTICAL PROPERTIES OF THIN FILMS OF POLYAZOMETHINE WITH FLEXIBLE SIDE CHAINS

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The main aim of this work is to evaluate the effect of (2,5–bisoctyloxy) flexible side chains, linked to the polyazomethine PPI chain, on the optical properties, electronic transitions and conjugation, all being depended on the chemical structure and chain conformation.

Synthesis of a soluble derivative of a basic aromatic polyazomethine, i.e. poly(1,4-(2,5-bisotyloxy-phenylene-methylenenitrillo)-1,4-phenylene-nitrylomethelidyne) BOO-PPI, enabled us to prepare thin films of this polymer by spin coating technique. The BOO-PPI film has been characterized by X-ray diffraction, AFM studies, and UV-Vis-NIR spectroscopy and compared to un-substituted PPI thin film properties [1].

A better conjugation and planarization of the BOO-PPI polymer chain in relation to the PPI chain have been confirmed by the absorption edge parameters, obtained in the way typical for amorphous semiconductors and by other methods of investigations. Elastic side chains not only improve solubility but also affect the optical properties, important from the point of view of potential applications in layered systems as optoelectronic and photovoltaic devices.

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AMPHIPHILIC INVERTIBLE POLYMERS: SYNTHESIS, SELF-ASSEMBLY, AND APPLICATION

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Interest in nanomaterials derived from self-assembling amphiphilic polymers has dramatically increased over the past few years. The main challenge for scientists is to find new systems and materials that have enhanced properties and the potential to replace existing classic systems. These new materials have to face new and increasingly sophisticated demands of industry, where nanomaterials are finding wider niches. Nanosized micellar structures based on the macromolecules of amphiphilic polymers have been studied in a broad range of applications that include crystallization, surface modification for biocompatibility, control of particle aggregation in solution, and drug delivery.

We describe here new classes of amphiphilic invertible polymers (AIP) that form micelles and self-organize into micellar assemblies in response to changes in polarity of environment, polymer concentration and structure.

Figure 1 shows the synthetic route to amphiphilic invertible polyesters AIPE-1 *via* the polycondensation of PEGs (x = 6.4, 13.2 or 22.3) with aliphatic dicarboxylic acids (y = 8 or 10) that results in the formation of macromolecules with hydrophilic and hydrophobic moieties alternately distributed in the polymer backbone [1].

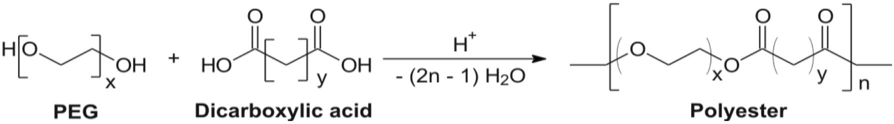

Figure 1. Reaction of the AIPE-1 synthesis.

Amphiphilic polyesters AIPE-2 with an alternating distribution of hydrophilic PEG (m = 6.4, 13.2 or 22.3) and hydrophobic PTHF (n = 3.2, 8.8 or 13.6) chains have been synthesized [2] as depicted in Fig. 2.

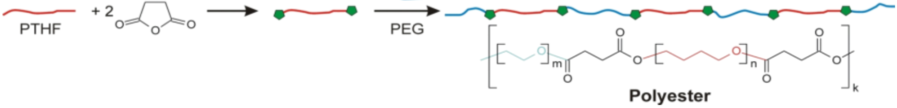

Figure 2. Scheme and reaction of the AIPE-2 synthesis.

Figure 3 shows a two-step procedure for the synthesis of amphiphilic invertible polyurethanes with either alternating or random distribution of the hydrophilic PEG (m = 6.4, 13.2 or 22.3) and hydrophobic PTHF (n = 3.2, 8.8 or 13.6) fragments in the macrochain [3].

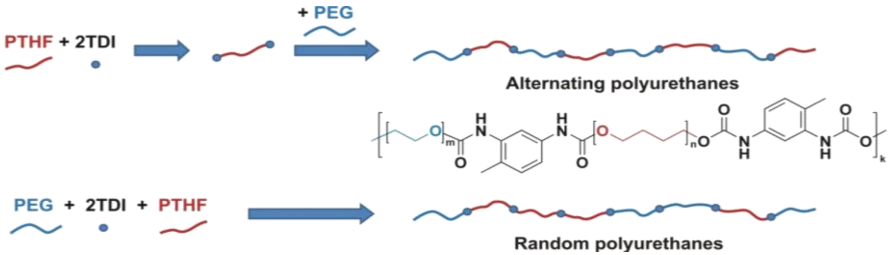

Figure 3. Scheme and reaction of the AIPU synthesis.

Hence, the synthetic approaches allowed both control of the macromolecular configuration and exact variation of the hydrophilic and hydrophobic fragments in the macromolecule, thus promoting polymer hydrophilic-lipophilic balance.

The developed amphiphilic polymers form monomolecular micelles (Fig. 4) due to the incompatibility of macromolecular fragments and different solvation of the hydrophilic and hydrophobic fragments by a solvent [4]. The monomolecular micelles self-organize into micellar assemblies (Fig. 4) in response to changes in polymer concentration [5].

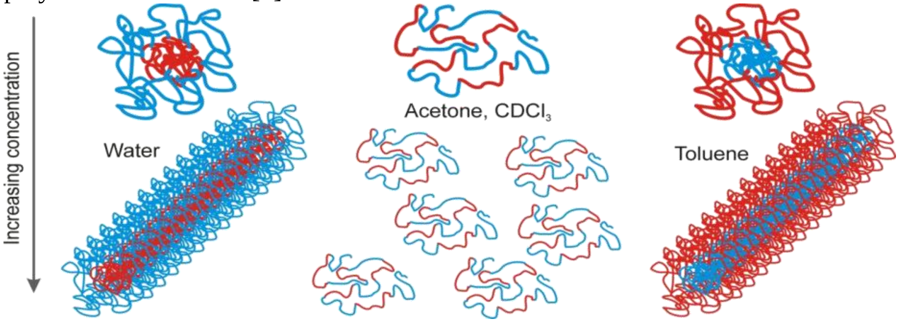

Figure 4. AIPs self-assembly by increasing concentration in aqueous and organic solutions.

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The synthesized AIP are capable of rapid reversible switching (*i. e.*, inverting) of their macromolecular conformation in response to medium polarity and encapsulating materials (soluble and insoluble) in monomolecular micelles and polymer micellar assemblies both in polar and nonpolar media.

Self-assembled AIP have been applied as nanoreactors for a size-controlled synthesis of metal nanoparticles (Fig. 5). The advantages of the employed methodology are in fast spontaneous formation of nanoparticles at room temperature, synthesis of a ready-to-use colloidal solution with an enhanced metal nanoparticle content, and formation of surface-modified nanoparticles dispersible in both polar and nonpolar media [6].

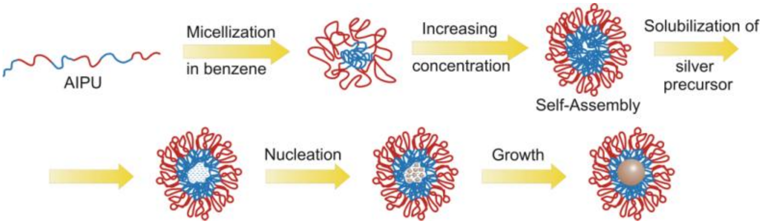

Figure 5. Preparation of metal nanoparticles inside micellar nanoreactors.

The unique ability of AIP to invert the molecular conformation depending on the polarity of the environment can be a decisive factor in establishing the novel stimuli-responsive mechanism of solubilized drug release that is induced just in response to a change in the polarity of the environment. The micellar assembly capability to solubilize lipophilic drugs and deliver and release the cargo molecules by conformational inversion of polymer macromolecules in response to a change of the polarity of the environment has been demonstrated by loading the micellar assemblies with a phytochemical drug, curcumin. It has been revealed [7] that micellar vehicles based on different AIP are capable of delivering the curcumin from water to an organic medium (1-octanol, which resembles the properties of lipid bilayer membranes) by means of unique mechanism: AIP conformational inversion in response to changing polarity from polar to nonpolar (Fig. 6).

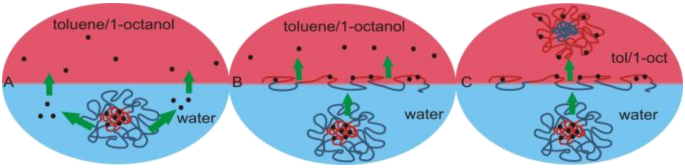

Figure 6. Possible mechanisms of a micellar assemblies-mediated curcumin delivery from water to an organic phase.

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The micellar assemblies have been shown to be nontoxic against human cells up to a concentration of 10 mg/L. On the other hand, the curcumin-loaded micellar assemblies are cytotoxic to breast carcinoma cells at this concentration (Fig. 7), which confirms the potential of micellar assemblies-based vehicles in controlled delivery of poorly water-soluble drug candidates and release by means of this novel stimuli-responsive mechanism. An additional advantage of micellar assemblies-based vehicles is their ability to stabilize curcumin molecules against chemical decomposition [7].

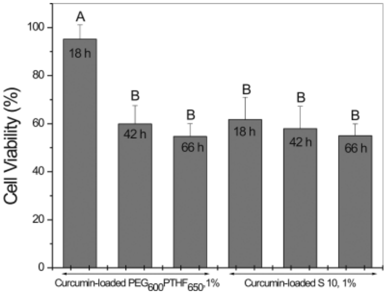

Figure 7. Cytotoxicity of curcumin-loaded AIPE micellar assemblies on breast carcinoma cells after 18, 42, and 66 h incubation.

In summary, amphiphilic invertible polymers composed of the PEG hydrophilic and PTHF/dicarboxylic aliphatic acid constituents in the main backbone build micelles and self-assemble in both aqueous and organic media by increasing concentration. The resulting micellar assemblies undergo inverse conformational changes and are functional in both polar and non-polar environments, giving them potentially broad use in many applications including pharmaceutical industry, cosmetics, nanoparticle synthesis, and so forth.

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P30

NITROXY PROBE DYNAMICS IN ORGANIC-INORGANIC COMPOSITES BASED ON POLYIMIDE DIFFERENT CHEMICAL STRUCTURE

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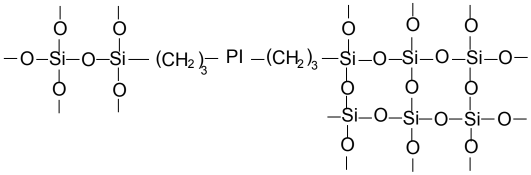
Polyimides (PIs) are a class of high performance polymers because of their high-temperature stability, excellent electrical and mechanical properties, and good chemical resistance [1].Most PIs are often insoluble and hard processible. In order to improve the process ability of polyimides many attempts have been made to modify their melt processing properties and/or solubility in organic solvents. The common ways to improve the process ability are to introduce flexible bridging groups and/or bulky units into the rigid PIs backbones, or to attach bulky side groups [2]. These structure modification have also resulted in a decrease of the rigidity of the polymer backbones so that their thermal properties may be reduced. In the last years many attempts were devoted to development of PI-based organic-inorganic composites using PI of various chemical structure.

In the present study, the influence of bulk card substituents in the polyimide chain on the dynamics of the organic matrix of organic-inorganic nanocomposites based on PI and tetraethoxysilane (TEOS) compared with PI-composites that such substituents do not have are investigate using EPR spectroscopy with nitroxy paramagnetic probe TEMPO. Analysis of a polymer system using nitroxy spin probe SP (TEMPO in our case) uses dependence of EPR spectrum of the probe on its rotational and translational mobility in polymer. The last characteristics in turn are determined by structure and mobility of polymer matrix surrounding the probe [3].

As described in detail elsewhere [4] the preparation of PI-based of organic-inorganic nanocomposites involved the following steps: synthesis of polyamic acid with ethoxysilane end-groups based on 4,4’-diaminodiphenyl ether (series 1) and

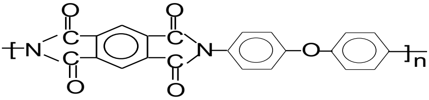
9,9- bis-(4-aminophenyl)fluorone (aniline fluorone) (series 2), and pyromellitic dianhydride and 3-aminopropyl triethoxysilane; preparation of nanocomposite precursor by addition of the required amount of tetraethoxysilane (5, 20,50 wt.%); casting of a homogeneous solution on a glass slide and storage under humid conditions to ensure water absorption and TEOS hydrolysis and finally, imidization of the polyamic acid to the corresponding polyimide. The two nanocomposites series studied in this paper : PI-0, PI-5, PI-20, PI-50 (series 1) and PI_c-0, PI_c-5, PI_c-20, PI_c-50 (series 2).

The anticipated structure of final product can be represented schematically as follows:

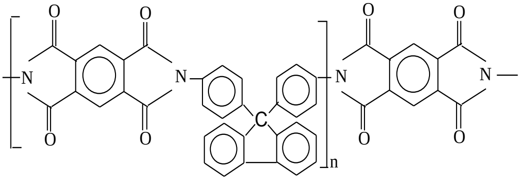


,

where PI (series 1):



(series 2):



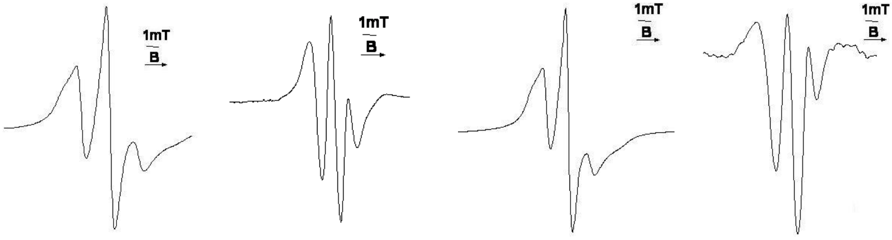
EPR spectroscopic studies were carried out at 20°C using a 3-cm radio spectrometer PE-1306 (AnalitPribor). The fields calibration was performed using 2,2-diphenyl-1-picrylhydrazyl (DPPH) with g=2.0036 and Mn(2+) doped MgO matrix with g=2.0015. Stable nitroxide radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) was used as paramagnetic spin probe (SP). Nitroxide spin probe 2,2,6,6-tetramethyl-1-piperidinyl-oxy (TEMPO) was introduced into PI films via diffusion of its 0.02M solution in dichloromethane at 35°C for 2 hours with subsequent vacuum drying till constant weight at 20°C.

The X-band EPR-spectra were recorded at temperature 20°C using radio spectrometer PE-1306 equipped with frequency meter ChZ-54. The magnetic field was calibrated using 2,2-diphenil-1-pycrilhydrazyl (DPPH) (g=2,0036) and ions of Mn(2+) in MgO matrix (g=2,0015). Correlation time (τ) of SP rotational diffusion in the range of its fast motion ($10^{-11}<\tau<10^{-9}$s) was calculated according [3] as follows:

$$\tau = 6{,}65\Delta H_{(+1)}\left(\sqrt{(I_{(+1)}/I_{(-1)})}-1\right)10^{-10}\,c \qquad (1),$$

where $\Delta H_{(+1)}$ - is width of the central component of TEMPO EPR-spectrum, I_{+1} and I_{-1} - are intensities of low-field and high-field components of the spectrum, respectively.

The densities (*ρ)* were measured by hydrostatic weighing in isooctane. Figure 1 illustrates the EPR spectra of PI nanocomposites series 1 (a,c) and series 2 (b,d) for initial PI (a, b) and containing 50 wt% TEOS.



a b c d

Figure 1. SP EPR spectra in PI nanocomposites series 1 (a,c) and series 2 (b,d) for initial PI (a, b) and containing 50% wt of TEOS (c,d).

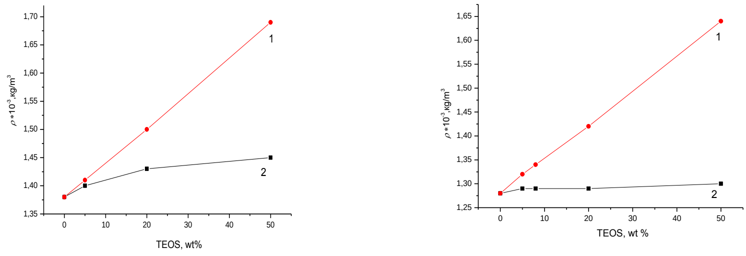
The EPR spectra of TEMPO in PI are of complex structure and have asymmetric shape (Fig.1). In some cases the visible splitting of spectra low field component occurs. The complex structure of EPR spectra of the probe in PI matrix are most likely the result of signal superposition of “fast” and “low” probes located in polymer regions with different mobility. The calculated using formula (1) τ values are listed in Table:

Table. Selected properties and calculated spin probe correlation times

Series 1			Series 2		
Sample	$\rho\times 10^{3}$, kg/m^3	$\tau\times10^{9}$, c	Sample	$\rho\times 10^{3}$, кg/m^3	$\tau\times10^{10}$, c
PI-0	1,38	29	PI_c-0	1,28	69
PI-5	1,40	42	PI_c-5	1,29	25
PI-20	1,43	41	PI_c-20	1,29	22
PI-50	1,45	37	PI_c-50	1,30	50

As it can be seen from table, introduction of card substituent in composite is accompanied by an essential increase in the mobility of probe (in the order) for all the samples of series 2 (value $\tau\times10^{-10}$) as compared with probe mobility for samples of series 1. This correlates with the density decrease for samples of series 2 (see table) (1.29-1,30 compared 1,38-1,47).

In both series density change with the introduction of inorganic component is not additive. (Fig.2). As it is shown in Figure 2 for series 2 density almost not depends on the composition of the system. This is opposed to density changes of series 1 composites. Deviation from additivity density composites series 1 is two times less than the corresponding values for series 2. This can be associated with the presence of bulk card substituents in PI.



a b

Figure2. Density versus TEOC content dependence for PI composites of series 1 (a) and series 2 (b). Additive (1) and experimental (2).

Mobility of nitroxide in PI composites series 1 correlate with the amount of inorganic component whereas the mobility does not correlate with the amount of inorganic component in PI composites of series 2. It has extreme character. This significantly distinguishes the PI composites of bulky card substituents from the composites of series 1, for which the introduction TEOS is always accompanied by a decrease in mobility.

The EPR spectra of TEMPO for organic PI matrix containing bulky card substituents correspond to the superposition of signals “fast” and “low” probes ". Introduction of tetraethoxysilane into polyimide with card substituents in all cases is accompanied with decreasing of inhomogeneity of the polyimide component in composite. This distinguishes them from composites based on polyimide, which do not contain such substituents. The introduction of card substituent in PI is accompanied by an increase of the mobility of probe in order for all composites.

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P31

RESEARCH ON COMMERCIAL SBS RUBBERS, WITH DIFFERENT CONTENT OF CARBON BLACK, MODIFIED BY COLD PLASMA

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Literature shows the possibility of improving the adhesion properties of SBS rubbers using low-temperature plasma.

To better characterize the plasma treatment process, it is necessary, however, to determine the role of the rubber additives in the process.

In this work, the influence of carbon black content on the adhesion of plasma-treated SBS rubbers to solvent based and dispersion polyurethane adhesives was studied. The carbon black content was changed from 30 to 60 % w/w. The plasma-treatment was performed using plasma generated by an RF discharge (13.56 MHz) in argon (Ar), oxygen (O_2) or carbon dioxide (CO_2). The 180°-peel test, analysis of surface energy and scanning electron microscopy (SEM) with EDX microanalysis were employed to investigate the surface properties.

The obtained results indicate that the increase in carbon black content in the SBS rubber significantly deteriorating the adhesive properties of its plasma-treated surface.

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MODIFIED POLY(VINYL CHLORIDE) PLASTICATES AND COMPOSITES BASED ON THEM

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The wares from polymeric materials with necessary elastic-plastic, strength and thermo-physical properties are of great importance. It was established [1] that it is possible to directionally control the properties of materials plasticized by poly(vinyl chloride) (PVC) within a wide range by their combination with other thermoplastics and polymer-silicate composites. It was proved [2] that among procedures of modified materials obtaining the thermoplastic (polystyrene (PS), ABS plastic) preliminary dissolution in the plasticizer followed by introduction of fine-dispersed PVC and composite are the most rational and economically grounded method.

The introduction of polystyrene modifier preliminary dissolved in the plasticizer increases PVC wetting by the plasticizer (fig. 1) and improves the components compatibility (fig. 2) and technological effectiveness of compositions preparation.

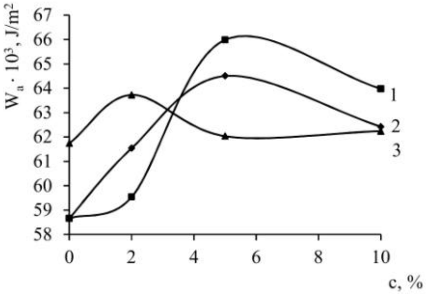

Figure 1. Effect of polymer-modifier content on the adhesion between PVC-plasticizer: 1,2 - dibutyl phthalate (DBP); 3 - di-2-ethylhexyl phthalate (DEHP); 1,3 - PS; 2 - ABS

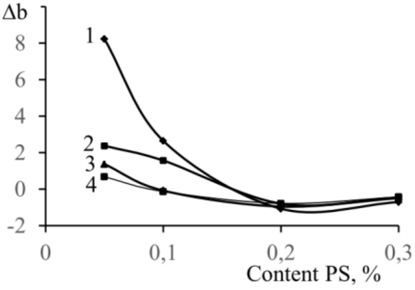

Figure 2. Dependence of compatibility parameter Δb of polymer concentrations in DBP, g/100ml:
1 – 0,4; 2 – 0,6; 3 – 0,8; 4 – 1,0.

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The quantitative estimation of polymer-containing ternary system is based on the assumption that macromolecules packing may be the reason of their mutual repulsion [2]. At the same time the polymeric mixture viscosity is lower than values of pure components calculated in accordance with additivity rule. If there is an interaction between polymers, the macromolecule associates of both types are formed and viscosity increases. The estimation of interaction between different macromolecules was carried out on the basis of comparison between parameters of molecular interaction determined from experimental data on viscosities (b_{12exp}) and theoretically calculated data ($b^*_{12theor}$). Thus Δb_{12} allows to consider the prior interaction between dissimilar macromolecules, i.e. the presence of mixed associates in the solution (positive value) or between similar ones, i.e. the presence of homoassociates (negative value).

It should be noted that the most essential interactions in PVC-PS-plasticizer system are observed at polymer low concentrations in the plasticizer solution and at the small amount of one polymer relative to another. In the compositions with PVC content 90-95 % the values Δb is positive. This fact testifies to the attraction between dissimilar macromolecules of PVC and PS and existence of mixed associates and hence, to greater compatibility between system components. At the same time the nature of diester phthalate plasticizer have minor effect on PVC and PS compatibility in the solution.

The highest value of hardness (95,57 MPa) is observed (table) for plasticized PVC based on diisononyl phthalate (DINP). Obviously it is connected with specific interactions between components and their effect on composite morphology. While using dibutyl phthalate (DBP) and DINP the elasticity essentially decreases (49,6 %) but hardness is almost the same.

Table. Effect of plasticizer and modifier nature on strength properties of PVC

Composition*, wt parts					Elastic-plastic properties		Vicat softening point, °C
Plasticizer			Modifier		Hardness H, MPa	Elasticity S, %	
DBP	DEHP	DINP	PS	ABS			
30	-	-	-	-	7,14	42,5	~22
-	30	-	-	-	62,19	40,6	40
-	-	30	-	-	95,57	68,4	52
15	-	15	-	-	93,52	49,6	40
30	-	-	-	2,8	22,22	52,5	36
30	-	-	2,8	-	13,08	48,3	35
30	-	-	4,2	-	19,60	84,6	-
90	-	-	13,4	-	6,29	80,1	-
120	-	-	17,6	-	4,60	81,3	-
-	30	-	2,8	-	101,15	59,0	38

* - per 100 parts by weight PVC.

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It should be noted that elasticity of PVC materials increases with the increase of modifier content. The hardness increases as well. It is observed most of all at high content of plasticizer. Thus, for the compositions based on DBP the increase of PS content by 1,5 times increases the hardness from 13,08 to 19,60 MPa and elasticity from 48,3 to 84,6 %. The same regularity is observed while using ABS plastic as the modifier.

The increase of modifier content allows to support elastic properties of plasticized PVC at high level (elasticity is 80-84 %) even at the considerable (by 4 times) increase of plasticizer content. At the same time the nature of plasticizer and polymeric modifier also affects the thermo-physical properties of plasticized PVC which are estimated by Vicat softening point. The increase of softening temperature is observed while using plasticizers in the row DBP– DEHP–DINP. The DBP+DINP mix averages the softening temperature values. Polystyrene modifier increases softening temperature of plasticized PVC based on DBP by 15-20 °C.

The introduction of polystyrene modifier and polymer-silicate composite allows to directly control the elastic-plastic properties of plasticized PVC, increases the surface hardness, tensile strength and Vicat softening point (fig. 3).

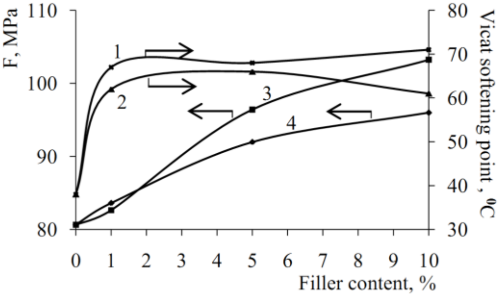

Figure 3. Effect of filler content of polymer-silicate composite on surface hardness and Vicat softening point. 1, 3 - polymer-silicate composite modified by polyvinylpyrrolidone; 2,4 - polymer-silicate composite.

Due to the direct selection of components and the morphology of (nano)composites and the kind of the polymer matrix, the required set of performance properties (durable, elastic-plastic, thermal, electrical, etc) of special-purpose composite materials has been achieved.

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ORGANIC-INORGANIC NANOSTRUCTURED POLYMER BLENDS

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Recently the fundamentally new materials – organic-inorganic polymers (OIP) and organic-inorganic polymer blends or nanocomposites – with organic and inorganic structural elements combined at the molecular level [1,2] have attracted more and more attention. Nanocomposites belong to the class of composite materials characterized by nanometric sizes of their structural elements. The organic phase may entrap metal-containing particles into a kind of trap, co-polymeric network or polymeric link. Oxides of silicon, aluminium, titanium, zirconium and vanadium, metal phosphates and chalconides, iron oxychloride and graphite are used as inorganic compounds-precursors. Carbon-chain or hetero-organic polymers (usually organosilicon polymers) are used as polymeric component [3]. As a rule the hybrid nanocomposites show synergism of initial component properties.

Experimental results and discussion

In this report we submit the results of our works in the field of manufacturing the hybrid ≡Si–O–Si≡ organic compounds produced by the sol-gel process and characterization of their properties. Silicon alkoxide – tetraethoxysilane $(C_2H_5O)_4Si$ and functional organosilicon oligomers, containing OH- and Cl- end groups have been used as initial compounds for the sol-gel process. The scheme of reactions may be presented as follows:

$$\text{Hydrolysis} \qquad \equiv\text{Si–OEt} + H_2O \xrightarrow{H^+ \text{ or } OH^-} \equiv\text{SiOH} + \text{EtOH}$$

$$\text{Condensation} \qquad \equiv\text{SiOH} + \text{HOSi}\equiv \longrightarrow \equiv\text{Si–O–Si}\equiv + H_2O$$

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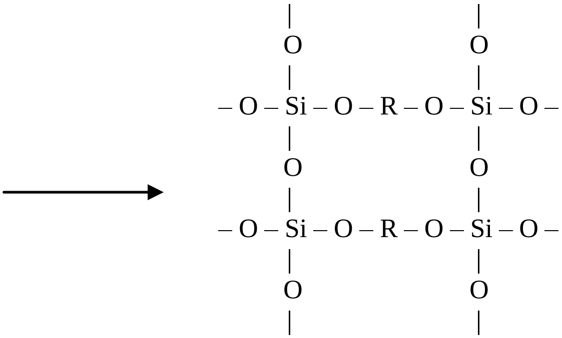
Silanolysis $\equiv SiOH + SiOEt \xrightarrow{H^+ \text{ or } OH^-} \equiv Si–O–Si\equiv + EtOH$

General scheme reaction $n\ Si(OEt)_x \xrightarrow[H^+ \text{ or } OH^-]{H_2O} [–SiO_2–]_n$

General scheme of reaction in the presence of oligomers

$n\ Si(OEt)_4 + HO–(R)_m–OH \xrightarrow{H_2O,\ kat.}$



$$\longrightarrow \begin{array}{c} \quad | \qquad\qquad\qquad | \\ \quad O \qquad\qquad\quad O \\ \quad | \qquad\qquad\qquad | \\ –O–Si–O–R–O–Si–O– \\ \quad | \qquad\qquad\qquad | \\ \quad O \qquad\qquad\quad O \\ \quad | \qquad\qquad\qquad | \\ –O–Si–O–R–O–Si–O– \\ \quad | \qquad\qquad\qquad | \\ \quad O \qquad\qquad\quad O \\ \quad | \qquad\qquad\qquad | \end{array}$$

R--- $R'OOCHNCH_2(CH_3)_2Si—O—Si(CH_3)_2CH_2NHCOOR'—$ (1)

R' — $(CH_3)_2Si—O—[CH_2—CH(CH_3)—O]_n—Si(CH_3)_2$--- (2)

The compounds of type (1) have been obtained by the ecologically safe isocyanateless method developed in the Institute of Macromolecular Chemistry of National Academy of Sciences of Ukraine of High-Molecular Compounds. This method of manufacturing of organosilicon carbon-functional oligourethane with end hydroxyl (OSOUD) isocyanate groups [4,5] is based on the interaction between 1,3-bis(chloromethyl dimethyl) disiloxane and potassium cyanate in the presence of organic and OS hydroxyl-containing compounds in the twofold excess of the latter. It follows the scheme:

$Cl—CH_2—Si(CH_3)_2—O—Si(CH_3)_2—CH_2—Cl + KOCN \xrightarrow{\text{DMFA, KJ}}$

$\rightarrow OCN—CH_2—Si(CH_3)_2—O—Si(CH_3)_2—CH_2—NCO + KCl\downarrow \xrightarrow{HO—[R']_n—OH,\ \text{DMFA, } 100°\ C}$

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$\rightarrow HO—R'OOCHNCH_2(CH_3)_2Si—O—Si(CH_3)_2CH_2NHCOOR'—OH$ (OSOUD)

R' – organic or organosilicon radicals:

(polyoxypropylene glycol – POPG, polyoxyethylene glycol – POEG, polyoxytetramethylene glycol – POTMG, organosilicon diols (α, γ–diols), hydroxyl-containing oligosiloxanes (ODOL).

OSOUDs are stable in time, light-brown viscous products, easily soluble in the most of organic solvents (benzene, xylene, chlorobenzene, dimethyl formamide and others).

Table 1 shows that the oligomers differ by the length and structure of oxyalkylene and siloxane block, content of ≡Si–O–Si≡ fragments and hydroxyl functionality.

Table 1. Properties of hydroxyl-containing organosilicon oligourethane diols

Oligomer	MW		Group content (%), ±0,3				n_D^{20}, $\pm 10^{-3}$	ρ^{20}, g/cm3 ±0,01
	Found	Calculated	-OH found	–OH calculated	–SiO–	Urethane		
OSOUD-POEG	820	1045	3.3	3.4	7.7	10.9	1.4104	1.120
OSOUD-POPG	2245	2200	2.4	2.8	3.4	8.5	1.4608	1.080
OSOUD-POTMG	2100	2200	2.5	2.7	3.7	5.0	1.4621	1.090
OSOUD - γ–diol	600	532	2.7	3.0	22.0	15.8	1.4701	0.995
OSOUD–ODOL	5020	4982	8.8	4.0	45.0	9.40	1.4780	0.984

The following initial compounds have been used for synthesis of chlorine-containing organosilicon oligomers (type 2 compounds):

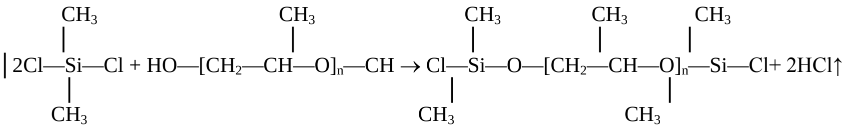
dimethyl–dichlorosilane,

polyoxypropylene glycol (L–1052, MW 1000),

polyoxypropylene triol (L–1003C, MW 1000)

polyoxypropylene triol (L–3003C, MW 1000).

Dimethyl–dichlorosilane is related to very reactive silicon compounds. Its interaction with diols and oligopropylene polyols (OPPO)follows the following scheme:



$$2Cl\!-\!\overset{CH_3}{\underset{CH_3}{Si}}\!-\!Cl + HO\!-\![CH_2\!-\!\overset{CH_3}{CH}\!-\!O]_n\!-\!CH \rightarrow Cl\!-\!\overset{CH_3}{\underset{CH_3}{Si}}\!-\!O\!-\![CH_2\!-\!\overset{CH_3}{CH}\!-\!O]_n\!-\!\overset{CH_3}{\underset{CH_3}{Si}}\!-\!Cl + 2HCl\uparrow$$

As the reaction proceeds HCl is blown off (with the use of neutral gas or by evacuation with the use of a water jet pump). On completion of the reaction the resultant products have been deaerated. IR spectra have been registered for synthesized chlorine-containing oligomers. The strong absorption lines have been registered in the following regions:

2964 cm^{-1} — CH (—CH_3),
1408 cm^{-1} — H—C—H,
1260 cm^{-1} — Si—CH_3,
1080 cm^{-1} — Si—O—Si,
1024 cm^{-1} — C—O—C,
844 cm^{-1} — Si—(CH),
804 cm^{-1} — Si—(CH) ,
692 cm^{-1} — Si—Cl

The resultant products differ by their structures (linear, branched) and molecular weights (Table 2).

Table 2.Physical and chemical indices of chlorine-containing organosilicon oligomers

Designation of hydroxyl-containing component	**Functionality by –Cl**	**Refraction index, n_D^{20}**	**Specific gravity, g/cm^3 ±0,0005**
Polyoxypropylene glycol (MW 1000)	2	1.4062	1.008
Polyoxypropylene triol (MW 1000)	3	1.4065	1.030
Polyoxypropylene triol (MW 3000)	3	1.4455	1.003

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The synthesis of organic-inorganic polymers has been carried out by the hydrolysis-condensation reaction of tetraethoxysilane in solvents at (20-50) °C in the presence of the above-mentioned OSOUD and acid catalysts.

At first the 20 % solution of silicon-containing oligourethane diols (OSOUD compounds of type 1) in benzene or chlorine-containing oligomers (type 2 compounds) in dioxane. Tetraethoxysilane and acidified water have been added to this solution. The reaction mixture has been maintained under agitation for 16 hours at the temperature of 20 °C. In the process of synthesis the gel sediment has been produced. On complete reaction the gel has been isolated, washed from benzene or dioxane and dried in the vacuum-desiccator until the constant weight. The organic-inorganic polymers obtained by the hydrolysis-condensation reaction with the use of OSOUD are solid products of brittle glass type. Organosilicon – polymers of the second type based on chlorine-containing oligomers are amorphous and powder-like. For the purpose of their identification the IR spectrum analysis and derivative DTA have been used. The IR spectra have been registered within the region of 4000–300 cm^{-1} on the specimens in the form of tablets containing KBr. The IR spectra for composites are characterized by the presence of bands peculiar to $\equiv$Si–O–Si$\equiv$, –CH_2–CH_2–, –CO–, NH–bonds. The studies by derivative DTA have shown the presence of silicon composites in the specimens. The content of silicon composites depends on the content of organic phase in the initial oligomers and is up to (60-80) %. The temperatures at which they begin to decompose are in the range from 220 °C to 280 °C.

The hybrid organosilicon composites have been successfully used as modifier-fillers for film-forming polyurethane network polymers.The next report is to be dedicated to investigation of organic-inorganic polymer blend structure.

Summary

The new organosilicon oligourethane diols and chlorine-containing oligomers of various structures and molecular weights have been synthesized. The hybrid organosilicon composites have been produced. They have been successfully used as modifier-fillers forfilm-forming polyurethane network polymers. Film-forming polyurethane nanomaterials are characterized by increased tensile strength, relative hardness, adhesion, etc.. They can be recommended as adhesives, sealants, anti-corrosion materials, materials for special purposes

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P34

RELAXATION PROPERTIES OF CROSS-LINKED POLYURETHANES, MODIFIED WITH CARBONE NANOTUBES AND METAL COMPLEXES

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Immobilization *in situ* in polymers, including polyurethanes (PUs), of low quantity of carbon nanotubes (CNTs) strongly improves the electrical, thermal and mechanical properties of the composites [1]. Introduction of metal compounds in polymers, including PUs, provides the material with specific properties. For example, the simultaneous addition in the PUs the modifiers with different structure and properties (CNTs and metal complexes) enables to control the performance characteristics of obtained composites.

On the Fig. 1 the frequency dependences of the imaginary part of the complex modulus (M”) at the room temperature for unmodified CPU-0 and CPU-KNT are shown.

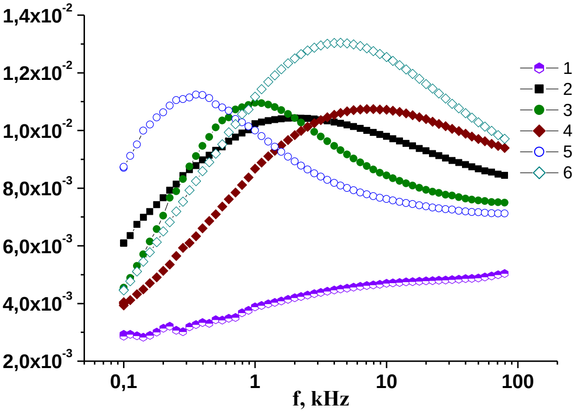

Figure 1. Frequency dependences of M” for the unmodified CPU-0 (1) and CPU-KNT, modified with 1% wt. of $Cu(acac)_2$ (2), $Co(acac)_3$ (3), $Cr(acac)_3$ (4), $[Cu_3Mn(L)_4(CH_3OH)(H_2O)_3]Br \cdot 3H_2O$ (5) and $[Cu_3Mn(L)_4(CH_3OH)_3]I_3$ (6), where L is the product of condensation of salicyl aldehyde with ethanolamine.

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The maxima are observed for CPU-KNT, modified with metal complexes (fig. 1). These maxima associated with segmental relaxation of the soft segments in polyurethane macromolecules for CPU-KNT with metal complexes. This effect pointed on segmental mobility of the soft segments in polyurethanes, modified with metal complexes. In addition, such complex formation occurred mainly of urethane component of polyurethane hard segments. As a result, the flexible components of CPUs with metal complexes, which involved in the relaxation process were free from hydrogen bonds and became more mobile.

The presence of $[Cu_3Mn(L)_4(CH_3OH)_3]I_3$ and $Cr(acac)_3$ in CPU leads to significant shift of the maxima towards higher frequencies, compared to the another CPUs. This effect was observed because of such modifiers have formed more strong coordination nodes with functional polyurethanes groups. The distinguishable increase in the maxima' intensity indicated on the increasing of the quantity of the segments, which involved in relaxation.

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P35

PRELIMINARY STUDIES AND PROPERTIES EPOXY POLYURETANE COMPOSITE MATERIAL FILLED WITH POLYHYDROXYBUTYRATE AND DOXORUBICIN

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Increase quality of patients with abnormalities of bone tissues cause need the development of new biocompatible and bioactive materials with therapeutic cytostatic effect. The creating such materials allow obtaining effective remedies for bone grafting.

The aim of this work is to develop of the new epoxy polyurethane (EPU) implanted polymeric materials containing cytostatic agent doxorubicin (DOX) and poly-3-hydroxybuytrate (PHB), the study of their structure and properties [1].

Synthesis EPU was performed in a 3 stage. The first stage is synthesis of prepolymer isocyanate (PI) based POPG 2000 and TDI 80/20 in molar ratio of 1:2,2. In the second stage EPU copolymer obtained by reaction of isocyanate groups PI and secondary hydroxyl groups of epoxy oligomer ED-20 (M = 420, epoxy number 21.6) with molar ratio of 1:5. The third stage is synthesis EPU basis. The macro chain extender 1,4-butanediol was injected into the reaction mixture [2, 3]. As a result, the reaction mixture was treated with EPU copolymer, linear polyurethane and ED-20. Composite materials have been received by the introduction into the EPU basis of PHB in the amount of 0,1-3,0 wt. %. Quantity of DOX in the composition does not exceed its therapeutic dose and was 0.29 wt. % (40 mh/14 g) [4]. Cured composition amine hardener L-20 (65 ± 5) ° C for 3 days.

The chemical immobilization DOX opportunity to EPU matrix by using a model reaction of the drug with phenyl glycidyl ether (PhGE) was investigated by methods IR-, NMR spectroscopy. The possibility of chemical immobilization DOX on EPU carrier by interaction NH_2-group of amino sugar daunozamine DOX with of ED-20 was confirmed.

As result of physical and mechanical testing the input PHB into EPU at concentrations of 0.1 wt. % and 0.3 wt. % is the best in terms of developing new compositions for the manufacture of bone implants that would have sufficient strength and elasticity.

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To according of the IR spectroscopic studies the introduction into epoxy polyurethane of PHB and DOX leads to changes in the structure of the polymer through the redistribution and the formation of new intermolecular hydrogen bonds and covalent binding of DOX with polymeric matrix, that in turn affects on the final physical and mechanical properties of the composite.

Conducted histological studies of the obtained composites proved its biocompatibility. Thus, on the properties the studied EPU composites containing in its structure DOX and PHB can be used to create new bioactive bone implants.

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P36

PERCOLATION BEHAVIOR IN POLYETHYLENE GLYCOL-CARBON NANOTUBES SYSTEM

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The study of the critical phenomena is one of important questions in fundamental physics. Mostly, the critical phenomena are observed in the systems at the second order phase transitions. In such systems, large fluctuations with the infinite correlation radius are show up. Thus, the system is nonlinear. The analogue of the critical phenomena is the phenomenon of percolation. Unlike temperature phase transitions, where a transition between two phases takes a place at a critical temperature, a percolation transition is a geometrical phase transition. The percolation threshold, or a critical concentration, divides two phases: in one phase there are clusters of certain length, in other there are clusters of infinite length [1].

As result of the swift development of nanotechnologies, wide attention of researcher is spared to the nanofilled systems. The oxides of metals, layered silicates, aerosils and others are used as nanofillers in such systems. Carbon nanotubes (CNT) are one of perspective nanofillers. CNT and nanofibers cause enhanceable attention of researchers because with perspective of their application in the different areas of science and technology. Their property of semiconductor conductivity allows to utillize them in quality emission displays, facilities of information storage and other electric devices [2]. In addition CNT have considerable elasticity, hardness and resiliency, that allows to utillize them in composition different nanocomposites. The adding of CNT to polymeric material substantially changes some its properties (conductivity, heat conductivity, mechanical hardness), that it is related to formation of continuous (percolation) cluster [1]. There are many factors, that can influence on percolation transition. The purpose of this work is studying the features of percolation threshold of the model system based on polyethylene glycol and carbon nanotubes.

Influence of the crystallinity of polymeric matrix on percolation.

Nanocomosites based on polyethers and carbon nanotubes are investigated using the method of impedance spectroscopy. It is set that the crystallinity of polymer matrix considerably influences on electric and dielectric descriptions of nonofilled polymer materials: the values of percolation thresholds are inverse proportional to the degree of cristallinity. The mechanism percolation cluster formation is offered for the systems with a high cristallinity. It is shown that the dielectric permittivity of nanofilled polymer materials depends on the structure of percolation clusters. It is set that the topology of polymeric matrix does not influence on the percolation behaviour of nanocomposites based on polyethers.

Influence of the filler's size on percolation. The research of electric properties of the systems based on polyethylene glycol and carbon nanotubes near-by the percolation threshold is done using the method of impedance spectroscopy. It is set that the percolation threshold for these systems substantially depends on the sizes of nanotubes. It is discovered that with the increase of CNT diameter, the percolation threshold is increased. The dispersion parameters on nanotubes was expected using theoretical model. The results of calculations and microphotographs testify to the high level of CNT aggregates in the polymer nanocomposites based on polyethylene glycol.

Influence of the temperature on percolation. The research of electric properties and percolation behavior of the systems based on polyethylene oxide and carbon nanotubes is done using the methods of impedance spectroscopy and optical microscopy. It is discovered that with the increase of temperature the percolation threshold is increased from 0,35% to 0,38%, and the critical index of conductivity changes from 1,44 to 2,36. It is set that there are two types of conductivity in the investigated systems: ionic and electronic. It is rotined that under reaching the percolation threshold, when nanotubes which are dispersed in a polymeric matrix have the most specific surface, the activating energy of the system has a minimum value. It is discovered that the systems of polyethylene oxide-carbon nanotubes have the negative temperature coefficient of resistivity.

Influence of the filler's surface functionalization on percolation. The research of microstructure, electric and dielectric properties of the systems based on polyethylene glycol and carbon nanotubes is done using the methods of impedance spectroscopy and optical microscopy. It is set that the probed systems show the percolation behavior. It is discovered that the threshold of electric percolation is increased from 0,44 % to 0,55 % after the use of functionalizated nanotubes. It is set that the threshold of dielectric percolation grows after the use of OH-functionalizated nanotubes.

Influence of the preparation method on percolation. The research of microstructure and electric properties of the systems based on polyethylene oxide and carbon nanotubes, prepared by different methods is done using the methods of impedance spectroscopy and optical microscopy. It is set that the probed systems show the percolation behavior. It is discovered that using the method of ultrasonication in melt, the threshold of electric percolation is 0,4 %, and for the system, prepared by the method of ultrasonication in polymer solution – 0,52 %. It is set that in the system, prepared by the method of ultrasonication in polymer solution, the large aggregates of nanotubes was formed via the long time of solvent evaporation. The method of ultrasonication in melt is the most perspective for preparation of polymer nanocomposites with low percolation threshold.

Influence of the electric field on percolation. Thermophysical properties and percolative behavior of the systems based on polyethylene glycol and carbon nanotubes, formed at normal terms and under the action of permanent electric field are investigatied by the methods of differential scanning calorimetry and impedance spectroscopy. It is rotined that the electric field substantially influences on the behavior of nanotubes, dispersed in the polymer matrix. Supposition is done, that at imposition of the field three basic types of nanotubes' motions (rotation, translation and migration) are carried out and characteristic times are calculated for each to the type. It is discovered that at forming of the nanofilled systems in the electric field the percolation threshold decreased from 0,42% to 0,1%, that testifies to the substantial orientation of nanotubes in polymer matrix.

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P37

SPECIAL POLYMERIC MINERAL COMPOSITES WITH INCREASED SORPTION ACTIVITY TO THE TRANSITION METAL IONS

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Polymer mineral composites (PMC) represent the volume polymeric mesh cells, which can be filled with particles of minerals of different fineness. Polyacrylamide or polyacrylate alkali metals are often used for the formation of polymer networks. Mineral particles, such as bentonite, palygorskite, zeolite and other minerals can be used as fillers. Sand, cement, and magnetite may also be used as functional fillers. Properties of the resulting PMC are determined by the following factors: type of polymer, the polymerization conditions, the composition and amount of mineral filler, the ratio between the polymer and mineral components and so on.

The obtained PMC have not only good sorption of heavy metals and radionuclides, but also the catalytic properties in relation to the polymerization process. A low coefficient of PMC filter having order 10^{-10} m/s and the lowest porosity of the air-dry (about 1%) are also commonly used properties for practical applications.

Water molecules introduce inside the composite particles while they contact with water. Communication between polymer chains is reduced; they have the ability to change conformation, whereby the distance between the chains increases forming channels, which may include hydrated cations from the solution. These cations penetrate into PMC volume and further they are fixed on the surface of the active centers of the mineral particles. This property of PMC is quite clearly manifested upon contact with aqueous solutions, which contain various cations.

The aim of the presented work was to study the absorption of Cs, Sr and Co cations by PVC with a concentration of 4-14 mg/l of the solutions in the presence of sodium tetraborate, the content of the sulfanol, Trilon B, and citric acid was about 800 mg/l.

For experimental studies the composites K-1 (t_{max} polymerization 61^0C, the degree of swelling in water 83,4 g/g) and K-5 (t_{max} polymerization 78^0C, the degree of swelling in water of 130,6 g/g) were synthesized (Table 1).

Table 1. Composition of composites, %

Component	K - 1	K - 5
sodium acrylate	25,23	18,2
zeolite	-	27,86
ammonium persulfate	0,39	0,28
N, N-methylenebisacrylamide	0,26	0,19
ascorbic acid	0,13	0,10
water	74,0	53,39

Photos of samples K-1 and K-2 made by scanning electron microscopy are shown in Figure 1. It is seen that the composites have pores and cracks where the solutions penetrate. While filling the cracks solution was partitioned between particles in a polymeric matrix, as clearances are present between the individual particles.

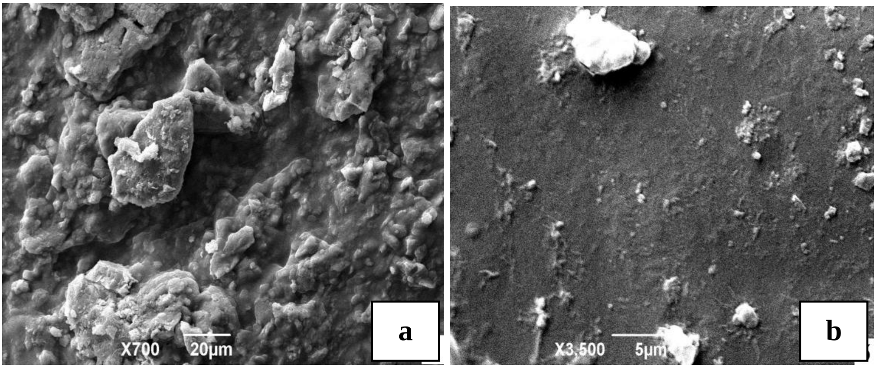

Figure 1. SEM photos of the PMC samples K-1 (a) and K-2 (b).

Studies have shown that the degree of swelling of the samples depends on the composition of the model solution (for K-1 it decreases from the solution A to the solution D) and increases as a whole after the water washing. The degree of swelling of the sample K-5 of the same nature, however, higher sorption characteristics which can be related to varying amounts of zeolite incorporated in the PMC structure.

Cations sorption of cesium, strontium, cobalt occurs in the course of swelling of the polymer matrix on the background of increased content of Na^+ ions in the sequence $Cs^+ \geq Sr^{2+} \geq Co^{2+}$. In this case it decreases from the solution A to the solution D, which can be explained by the presence of surfactants and complexing agents. At the same time, the introduction into the polymeric matrix of the zeolite particles (<14 mm), significantly alters the behavior of a composite of the test solution expressed in increasing the amount of absorbed cations present in solution. The sequence $Cs^+ \geq Sr^{2+} \geq Co^{2+}$ is fair, however, the amount of absorbed cations Co^{2+} significantly increased in comparison with the sample K-1.

It should be noted that the ratio of sorption of Cs^+ is practically independent from the composition of the solutions since absorbed cations are weakly immobilized in the PMC. At the same time, Sr^{2+} cations absorbed from solutions A are significantly better held in the hydrogel, than absorbed from solutions C and D. Such a behavior is typical for the Co^{2+} cations, but with a slightly smaller refractive C_d. Addition of zeolite (sample K-5) significantly increases retention of cations in the hydrogel regarding to the composition of the solution in which the swollen hydrogel exists.

Thus, mineral polymer composites can be considered as promising materials for sorption of Cs, Sr, Co under conditions of high salt background, creating sodium tetraborate, as well as for the localization of drain water and transfer them into a gel-like form. Improvement of rheological and sorption properties of the PMC obtained due to the properties of the filler (zeolite). The polymer matrix allows cations migrate to the surface sorbent and fixed at its active sites. Additional cations absorption occurs and the polymer mesh by replacing the cations Na, ruptures the polymer chains and mesh deformation arising due to uneven polymerization in volume of the sample. Subsequent work in this area should be aimed at finding more effective sorbents and their use in finely divided form.

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BIOACTIVE FOLATE-FERROCENE CONJUGATE

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Ferrocene is one of the most well-known metal-organic compounds, which is unused in catalysis, organic synthesis, industry [1, 2]. Thermostability, chemical resistance, physical properties of ferrocene determine its use in many fields of science. Its properties related to biological activity attract the interest, namely the antitumor activity by immune system stimulating [3].

Since folate receptors are expressed in some tumors, the receiving of folate-ferrocene conjugate as magnetosensitive material in malignant tumors hyperthermia is topical [4,5]. Conjugation of folic acid will secure efficient selective transport of magnetosensitive particles to cancer cells in the presence of normal cells, thereby improving the efficiency of guided local hyperthermia of cancer. Conjugation of folic acid to the ferrocene will allow receiving a new material that can be used for both direct delivery and the development of new bioactive polymer implantation materials.

To this purpose we have developed a method of folate-ferrocene conjugate synthesis and studied its biological activity by tissue culture method.

Chemical structure of the synthesized compounds was investigated by IR- and ^{1}H NMR spectroscopy. IR-spectra were recorded by «Bruker» IR-spectrometer with the Fourier transform «Tensor-37» in 400 – 4000 cm^{-1} range.

^{1}H NMR spectra were recorded by «Varian VXR-300» spectrometer in the solution of fully deuterated DMSO-d6, internal standard - tetramethylsilane.

Biological activity of folate-ferrocene conjugate was investigated by tissue culture .

Folate-ferrocene conjugate (FFC) was synthesized across stage synthesis of ferrocene carboxylic acid (FCA). FCA was conducted in two stages [6]. The first stage is the synthesis of 2-chlorobenzene ferrocene. Synthesized 2-chlorobenzene ferrocene as red needles, soluble in organic solvents at Tm = 364–368 K. The output of the product is 68.3 %.

In the second stage, the ferrocene carboxylic acid synthesis is carried out. FCA was derived as a yellow powder, soluble in organic solvents (DMSO, DMFA, DMAA) at t_m = 455 – 471 K, Mr = 230,04. Found (%): C 56.92, H 4.33. Calculated

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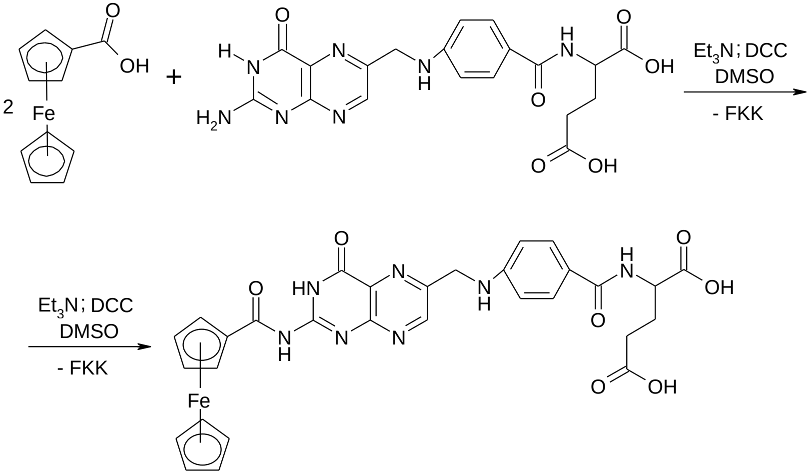
(%): C 57,42; H 4,38. ^{1}H ЯМР (δ, ppm): 4,4 (2H, t, Cp_1), 4,6-4,7 (2H, t, Cp_1); 4,3 (5H, s, Cp_2), 12,1 (1H, s, -COOH). FCA was recrystallized from toluene. The yield is 52.4 %.

Synthesis of FFC was carried out in accordance to scheme:



FFC was obtained as a brown powder with t_m 449 – 455 K, with practical yield 67.2 %. The chemical structure of the reaction products confirmed by inftared method and 1H NMR-spectroscopy.

In the ^{1}H NMR spectrum FFC there are signals of ferrocene carboxylic acid: 4.4 ppm (2H, t, Cp_1), 4,6-4,7 ppm (2H, t, Cp_1); 4,3 ppm (5H, s, Cp_2), the disappearance of the signal of carboxyl group of ferrocene carboxylic acid is registered at 12.1 ppm (1H, s,-COOH) and the reduction of signal intensity of amino group of folic acid (1H, s,-NH-) at 6,8-7,0 ppm. The signals of protons of other functional groups experienced a slight enlargement associated with presence of solvents (diethyl ether, dimethyl sulfoxide).

To establish the biological activity of FFC a study of this compound was performed by means of tissue culture. As the main mode of cultivation the method of explantation in plasma clot (solid phase) in Carrel vials with nutritional mixture (liquid phase) adding was used. Subcutaneous tissue of white laboratory rats, males of three month age, served as the explantation material. Cultures were incubated at 310 K. The replacement of the liquid phase of nutrient medium was performed every 3 days.

On the third day after explantation the migration of rare fibroblastic elements that were mainly fusiform started, and in some areas formed bands, composed of 3-4 cells (Fig. 1a). During this period there was also quite active migration to the nutrium medium of isolated macrophage items presented by cells bigger than fibroblasts, of mostly irregular polygonal shape. Some have shifted to a considerable distance from the explants, while others placed closer to it. Typically, the growth and migration of fibroblasts and migration of histocytic elements occured with approximately the same intensity along the entire perimeter of the explants. However, in some cases, the growth of cellular elements was observed only from one side of the cultivated tissue.

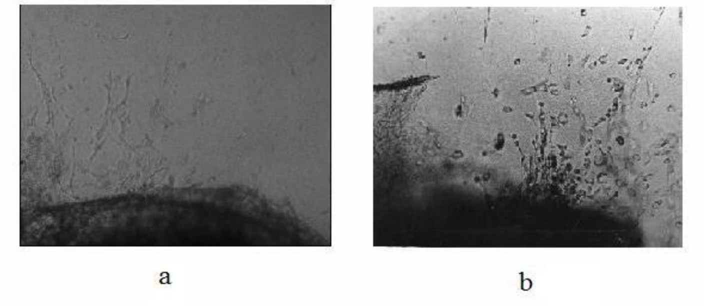


Figure 1. Migration of fibroblastic elements on day 3 of cultivation: in control, microphoto 100^x (a) and at entry to the medium folate-ferrocene conjugate, microphoto 100^x (b).

On day 7, the growth area is clearly divided into three: compact, reticular, and area of single migrating cells. The structure of the first two so far has not significantly changed, only the number of cells has increased. Unlike the previous period most cells to be divided, was observed in the third area.

On day 14, the cell population entered a stage of severe degeneration, which appears in acute vacuolization of cytoplasm and its granular degeneration (Fig. 2a). The number of histocytic elements that have lost their normal structure has significantly increased. Besides, architectonic of compact and reticular growth area finally disturbes.

Available data on the nature of growth and transformation of cellular elements of subcutaneous connective tissue of white outbred rats is generally similar to results obtained by other authors by using of other variants of nutrient media, cultivation conditions and animals of all ages.

Folate-ferrocene conjugate was contributed to the liquid phase of culture media during explantation at early cultivation in the amount of 0.1%. Observations on tissue cultures with FFC showed that migration of fibroblastic elements, the same as in control, begins from the third day in the form of strands and single cells located at the base perpendicular to the surface of explants. It is worth noting the greater variability of cell forms from spindle to polygonal, and bigger amount of isolated cellsof polygonal shape that lie in the distance from the explants (Fig. 1b).

On days 7 of cultivation in Carrel vials, as well as in control, three areas of growth are formed: compact, reticular and individual migrating cells. So called tissue-like growth is also present. Growth area of individual migrating cells is broader than in control and differs with bigger variety of cellforms.

On the 14th day of cultivation the growth areas of cellular elements in vials with folate-ferrocene conjugate significantly differ from control cultures. Growth areas are represented by wide fields of cells of polygonal shape mainly macrophage elements. Growth area of individual migrating cells in the form of fibroblasts of fusiform is marked.

After 21 days there is complete degradation of growth areas in the control, while in the experimental vials only degradation phase occurs in the compact growth area, in parallel with the migration of fibroblastic elements in the growth area of single migrating cells (Fig. 2b).

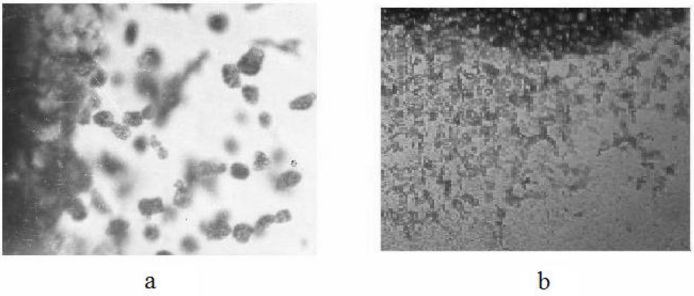

a
b

Figure 2. Grainy degeneration of cytoplasm of the cells on day 14 in control, microphoto 150^x (a), the beginning of degenerative changes in the compact growth area at entry to the medium folate-ferrocene conjugate, microphoto 100^x (b).

Thus, as a result of the studies folate-ferrocene conjugate was synthesized through the stage of ferrocene carboxylic acid synthesis. The conjugate was characterized by IR and ^{1}H NMR spectroscopy. Studies of biological activity evidence that folate-ferrocene conjugate, introduced in tissue culture, stimulates the growth of fibroblastic and histocytic elements at all stages of cultivation. In the later stages of cultivation a significant growth of macrophage and histocytic elements occurs, confirming the biological activity of the synthesized compounds in tissue culture.

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ANISOTROPY OF PHYSICAL AND MECHANICAL PROPERTIES OF EPOXY SYSTEMS FORMED IN A MAGNETIC FIELD

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Thesis is dedicated to the influence of a constant magnetic field on the structure and properties of epoxy systems during curing.

The results of investigations of the optical, mechanical, and thermal relaxation properties solidified epoxy systems with the hardener of different chemical structure and isomerism, and nanocomposites based on them, formed in a constant magnetic field have been represented [1-4]. The structural changes have been investigated by methods of thermomechanical analysis (TMA), the mechanical relaxation spectroscopy (MRS), differential scanning calorimetry (DSC). The regularities in origin and manifestations of anisotropy of physical properties have been studied. The explaination of the effect of the magnetic field at various levels of structural organization of epoxy systems has been suggested.

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3. *N. I. Shut, T. G. Sichkar, P. M. Malezhyk* The investigation of the kinetics of curing of epoxy oligomer in magnetic field // Physics and Chemistry of Solid State Vol. 13, № 1 (2012) P. 234-237.

P40

NANOSTRUCTURED POLYURETHANE ELASTOMER – POLY(VINIL CHLORIDE) BLENDS

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Extensive studies of interfacial interactions and features of a formation of nanoheterogeneous structure in polymer/polymer systems are conducted during last years to obtain the composites with novel functional characteristics. It is well-known fact that bonding at the interface determines the structure of interfacial region, supramolecular structure and mechanical properties of the composites. Relatively high polarity of both polyurethane and poly(vinyl chloride) (PVC) macromolecules allows to obtain the mixed-type materials with valuable properties. The chemical structure of soft and hard segments of polyurethane block copolymers has a great impact on phase separation processes, compatibility with chlorinated polymer and properties of composites.

An influence of chemical structure of hard segment in poly((urethane-urea)s (PUU) on intra- and intermolecular interactions in PUU/PVC systems by FTIR, as well as their morphology and mechanical properties has been studies. Generally, soft segments of elastomers consist of ether oligomeric fragments of poly(propylene glycol) and poly(tetramethylene glycol), M_n = 1000 are immiscible with PVC macromolecules. However, their immiscibility could be overcomed by introducing in to PUU structure highly polar urethane-urea segments. Morphology studies of the composites by SEM show a formation of nanoheterogeneous structure with averaged size of PVC phase of 20 – 40 nm, which dispersed in elastomer matrices. Thus, results shown that chemical structure of poly(urethane-urea) and cohesion energy of hard domains have a great impact on the intermolecular interactions between PUU macromolecules and chlorine of PVC. Structural asymmetry and weakening intermolecular interactions in PUU promotes an increasing energy of interfacial H-bonds in PUU/PVC blends, formation of nanogeterogeneous structure and improves the tensile properties of the composites.

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AN INFLUENCE OF SODIUM SILICATE MODIFIED BY POLYACRYLIC ACID ON THE PROPERTIES OF ORGANIC-INORGANIC COMPOSITES

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Over the last years organic-inorganic system (OIS) consisting of a polyurethane organic phase and a mineral inorganic phase are studied because of the possibility of obtaining composites with novel functional characteristics.

The aim of this work is the study of influence of sodium silicate (SS) modified by polyacrylic acid on the structure and mechanical properties of OIS. Hybrid polymer composites were prepared by the joint polycondensation of the organic macrodiisocyanate which has free isocyanate groups with water solution of sodium silicate. It is stated that curing of reactive components of the systems in a presence of modified sodium silicate increases the molecular mass and decreases branching degree of macromolecules polymer in organic phase due the increasing interface area. The increasing of interface interactions between isocyanate groups of organic phase and silanol groups of inorganic phase is confirmed by FTIR. Morphology studies of the OIS containing 40 wt % unmodified sodium silicate by SEM show a formation of nanoheterogeneous structure of the composite in which inorganic phase is dispersed in continuous elastomer matrix. Modification of SS allows to obtain the composites with well-defined microheterogeneous structure.

Thus, sodium salt of polyacrylic acid playing a role of surface-active substance and assists the rapid emulsification of components. Increasing interface area, chemical interactions at the interface and molecular mass of organic polymer cause to growing tensile strength at break, modulus E_{100} and water soption ability OIS. Formation of low branching structure of polymer macromolecules and increasing interfacial urethan-silicate layer content enhance deformation characteristics of the composits.

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METHODS OF OBTAINING AND PROPERTIES OF FUNCTIONAL POLYMER-SILICATE COMPOSITES

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Composite materials are widely used in all branches of industry due to the set of their valuable performance properties. Among them a special place is occupied by polymer-silicate composites.

As a result of practical investigations, the basic methods of producing materials for various purposes based on polymer-silicate composites have been developed. Depending on the nature of the polymer matrix, they are rigid or elastic composites in the form of fine powders, films, sheets, coatings, and materials for constructional purposes.

It has been found that functional surface-active polymers, such as polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP), increase technological compatibility between silicate filler and a thermoplastic or thermosetting polymer matrix [1]. At the same time, they provide a set of functional characteristics of composites: selective sorption capacity, regulated permeability, adhesion strength, required electrical conductivity, etc.

Modification was performed under polymer compatible precipitation and sodium liquid glass (Na-LG) under the influence of metal chloride (Cu, Ba, Zn, Fe, Co, Ni) or hydrochloric acid. The concentration of Na-LG and metal chloride reaches 15-20 wt%. As a result of reaction the fine colloidal precipitate has been formed. Then it was washed with the distilled water to remove ions Na^+ and Cl^-. The reaction time of deposition is 40-60 min. On the basis of gravimetric, potentiometric and photocolorimetric studies the physical-chemical and technological regularities of obtaining polymer-silica composite have been determined.

It was established (Fig. 1a) that for the effective modification of silicate structures the PVP must be in Na-LG previously and PVA must be dissolved in solution of metal chloride due to the peculiarities of interaction between the components (Fig. 1b).

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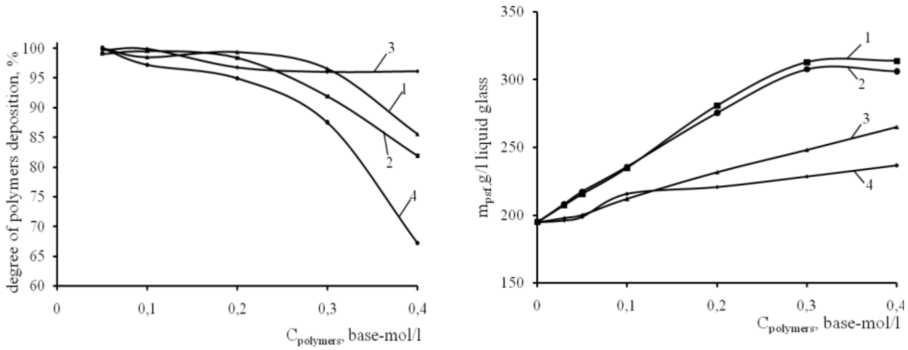

a) *b)*

Figure 1. The influence of polymer concentration and the method of his addition (1, 4 - into the liquid glass, 2, 3 -into the solution $CuCl_2$) on the degree of his deposition (a) and on the change of weight of polymer-silicate formations (b). 1, 2 - PVP; 3, 4 – PVA.

The concentration of polymers are 0.15-0.2 base-mol/l, and the optimal ratio of metal chloride - Na-LG (mol/mol) is in the range 0.8-1. But the influence of the metal cations nature on the precipitation process is negligible (Table 1).

Table 1. The influence of cation nature and the method of addition PVP on the change of weight of polymer-silicate formations (C_{pvp} = 0,2 base-mol/l)

The method of polymer modifier addition	Precipitator				
	$CuCl_2$	$FeCl_3$	$CoCl_2$	$ZnCl_2$	$BaCl_2$
	Change of weight of polymer-silicate formations, g/l liquid glass				
without PVP	194,92	181,93	184,71	178,61	167,17
PVP+precipitator *	276,52	268,18	251,44	234,43	278,14
PVP+liquid glass **	279,73	272,51	254,53	234,73	294,57

* PVP pre-dissolved in the metal chloride
** PVP pre-dissolved in sodium liquid glass

The obtained modified polymer-silicate material were observed by decrease of sorption capacity relative humidity in 1.5-2 times (Fig. 2).

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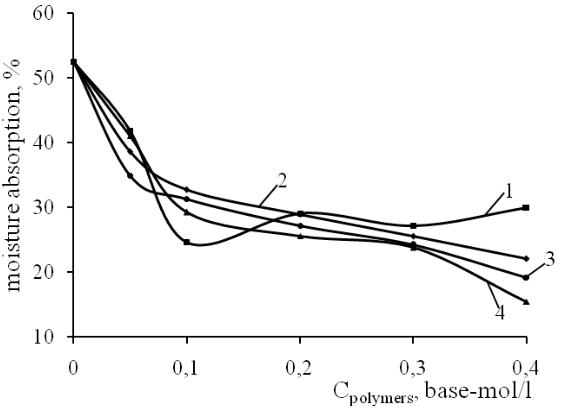

Figure 2. The influence of polymer concentration and the way of his addition (1, 4 - into the liquid glass 2, 3 - into the solution $CuCl_2$) on the moisture absorption of polymer-silicate materials; 1, 2 - PVP; 3, 4 – PVA.

These results confirm the presence on the surface of the polymer-silicate particles of functional active hydrophobic groups.

Found that the process of compatible precipitation is affected of the concentration of reactants, their ratio and the method of adding a polymer modifier. The conditions and rational technological parameters of compatible precipitation of soluble silicates and functional active polymers under the influence of metal chlorides have been well-grounded.

The technology of obtaining of modified polymer-silicate materials that can be used as fillers for creating polymer composites for special purposes with high physical-mechanical, thermal and sorption properties based on research has been developed [2, 3].

Depending on the type of products, the physical and chemical basics of a number of technologies for polymer-silicate composites have been developed, as well as materials based on them: for fine powders it is the compatible deposition of soluble silicates and surface-active polymers under the influence of metal chlorides or mineral acids; for different coatings – the combination of finely dispersed polymer-silicate composites with a thermosetting matrix based on epoxy resins, or polyester and organosilicone ones; for films and sheets – combining (by rolling and calendering with polyvinyl chloride and its mixtures) with other thermoplastics; for products for constructional purposes – the injection molding of thermoplastics filled by the polymer-silicate composite of different nature (polyolefin, polyvinyl chloride, polystyrene, polycaproamide).

It was established (Table 2) that the nature of the modifier significantly influence on the physicomechanical properties of polycaproamide (PA-6) and polypropylene (PP): tensile strength (σ_b), tensile elongation (ε_s), surface hardness to (F) and after (F_h) heat treatment and thermal stability by Wick (T_a), heat resistance by Schram-Tsymbovsky (IR) and the degree of crystallinity (S_c).

Table 2. Physicomechanical and thermophysical properties of modified PP and PA-6

Modifier	σ_b, MPa	S_c, %	ε_s, %	T_a, ^{0}C	F, MPa	F_T, MPa	IR
PA-6							
Without modifier	53,4	41,1	40	202	290,2	296,9	1,71
Precipitated Na-LG	63,9	55,9	17	210	313,5	317,7	2,92
Coprecipitated Na-LG and PVP	75,3	64,9	23	218	330,4	339,8	3,30
Physical mixture PVP and precipitated Na-LG	59,1	48,2	15	204	291,2	299,0	2,25
PP							
Without modifier	31,6	43,9	449	104	173,6	179,5	1,52
Precipitated Na-LG	50,8	47,1	168	105	196,9	199,2	1,73
Coprecipitated Na-LG and PVP	54.7	58,7	123	124	209,1	218,3	1,86
Physical mixture PVP and precipitated Na-LG	45.7	48,1	86	121	201,6	206,6	1,67

The principles of the directed control of morphology and properties of thermoplastic and thermosetting polymeric materials being in thick-flowing and highly elastic state or in solution have been developed as a result of their physical and chemical modification by multi-component polymer-silicate (nano)composites of different nature and structure with increased thermodynamic or technological compatibility with the polymer matrix.

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SOLID ION-CONDUCTIVE ELECTROLYTE BASED ON EPOXY OLIGOMER AND LiClO$_4$ AT ELEVATED TEMPERATURE

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Nowadays, one of the most important research directions in development and creation of functional polymeric materials is the search of new solid electroactive polymers with high ionic conductivity at elevated temperatures. Particularly, widening of the range of materials, which can be used for this purpose, is relevant [1]. For example, composite materials based on polymers and inorganic components are used for ion-conductive membranes production and further application in batteries, electrolysers and fuel cells [2, 3].

It is known that the use of organic compounds such as oligoethylene oxide makes possible an existence of ionic conductivity at anhydrous conditions that widens the range of operating conditions and, accordingly, the sphere of their practical application. The choice of polyethylene oxide PEO was caused by significant ability to solvate inorganic salts and, as a consequence, the presence of high ionic conductivity in materials on its basis [3]. As charge transport in polymer electrolytes passes mainly through the amorphous regions [2-4], a high molecular weight of the crystalline PEO and complexes formation with alkali metal salts greatly reduces the ionic conductivity at room temperature [3], but provides opportunities of sufficiently high conductivity at elevated temperatures.

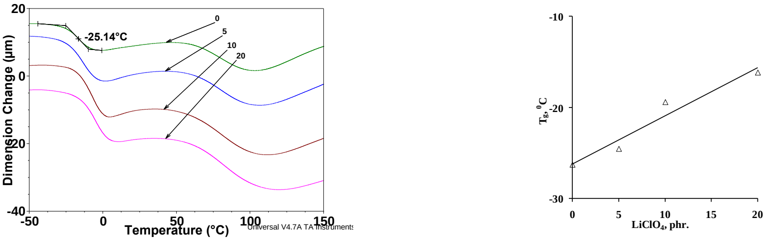
Besides polyethylene oxide epoxy oligomer of diglycide aliphatic ester of polyethylene glycol (DEG) also contains fragments with ether oxygen in the polymer chain. Its chemical structure is similar to the structure of PEO that makes possible to assume the possibility of transfer mechanism of lithium ions similar to polyethylene oxide. However DEG has good mechanical properties and heat resistance comparing to PEO. Also, an amorphous structure of DEG allows the charge transport even at ambient conditions, while a high crystallinity of the PEO prevents achieving high ionic conductivity [3].

High ionic conductivity can be achieved by dispersing various salts in a polymer matrix at molecular level, wherein conductivity is provided by mobility of the metallic ions [4]. In general, the lithium salts are often used for creating the ion-conducting systems due to the smallest size of lithium ions, low-potential energy and, correspondingly, low activation energy of the charge transfer.

The epoxy oligomer of diglycide aliphatic ester of polyethylene glycol (DEG) and salt of lithium perchlorate $LiClO_4$ were used for synthesis of ion-conductive epoxy polymer composites. DEG-$LiClO_4$ solutions were prepared with content from 0 to 20 phr on 100 phr of DEG. Polyethylene polyamine hardener (10 phr) as a curing agent of DEG was used.

The effect of $LiClO_4$ content on electrophysical properties of epoxy polymers has been studied by Thermomechanical analysis (TMA), the Broadband Dielectric Spectroscopy (BDS) and Thermogravimetric Analysis (TGA).

The results of TMA (the first heating) are shown in Fig.1a. The values of the glass transition temperature derived from the curves of the obtained composites depending on the content of lithium perchlorate in the reaction mixture are shown in Fig. 1b. It is obvious that the increase of $LiClO_4$ amount in reactive mixture from 0 to 20 phr leads to linearly increase of glass transition temperature from -26 to -16 °C.



a) b)

Figure 1. TMA curves (a) and dependence of the glass transition temperature of the epoxy system based on DEG obtained on contents of $LiClO_4$ (b).

That can be a result of electrostatic interactions between lithium cations Li^+ and the macromolecular chain of DEG with immediate forming of coordinative complexes, such as {ether oxygen - lithium cations - ether oxygen} (Fig.2), which are accompanied by displacement of electron density of the oxygen atoms and their partial polarization [3]. The result is a substantial reduction of segmental mobility of DEG chains within the complexes formed, that shows up in a glass transition temperature rise of polymer matrix.

The frequency dependences of the impedance of the systems studied on temperature were also analyzed. Figure 3, a shows the isothermal spectra of

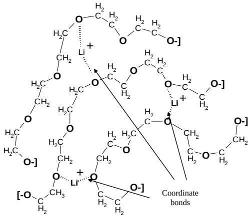
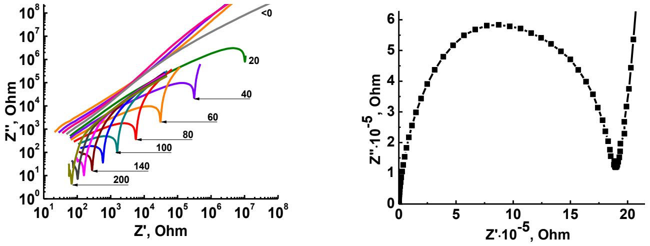


Figure 2. Scheme of coordinate bonds between the lithium cations and the polymer chains containing ether oxygen.

$Z''=f(Z')$, where $Z'=M''/(\omega\cdot C_o)$ is the real part of the complex impedance, $Z''=M'/(\omega\cdot C_o)$ is the imaginary part of the complex impedance, M' and M'' are the real and the imaginary parts of electrical modulus, C_0 is cell capacitance without the sample in vacuum, in double logarithmic coordinates for the DEG system containing 5 phr lithium perchlorate in the temperature range from -60 to +200 °C. It is evident that the nature of the isotherms at temperatures below the glass transition temperature Tg corresponds to the character of the open Warburg diffusion impedance (direct linear relationship) that describes a semi-infinite diffusion process, and due to the "frosting process" of charge transfer in such systems. The bulk resistance of the systems is represented by minimums on isotherms, which appears when the temperature passes the glass transition temperature of the systems. Curves acquire the form of a finite (closed) Warburg diffusion impedance that describes the linear diffusion process in a homogeneous layer of finite thickness, i.e. the charge transfer through the bulk of the systems becomes "unfrozen"[5].

Cola-Cola plots ($Z''=f(Z')$) were built for calculating the DC conductivity σ_{dc}. Figure 5 shows the classical Cola-Cola plots built for the composite of DEG with 5 phr $LiClO_4$ at temperature 30 °C. The dependence $Z''\sim Z'$ forms a clear minimum at a certain value of Z' in Cola-Cola coordinates.



a) b)

Figure 3. Z''/Z′ plots of the epoxy system with 5 phr $LiClO_4$ at temperature range from -60 to +200 °C in double logarithmic coordinates (a) and in the coordinates Cola-Cola at temperature 30 °C (b).

Conductivity values were calculated from the equation: $\sigma_{dc}=\frac{1}{R_{dc}}\frac{l}{S}$, where R_{dc} is a bulk resistance of the system (Ohm) that equals the value of Z' on the minimum of the Cola-Cola plot; l is a thickness of the sample (cm), S is an area of the sample (cm^2). The right part of the curve corresponds to surface polarization effects, which are observed in the low-frequency region. The left part of the curve corresponds to volume polarization effects in the high-frequency region. The calculated values of the conductivity σ_{dc} are presented in Table 1.

Table 1. Characteristics of epoxy polymers with different content of $LiClO_4$

Conductivity	**Content *$LiClO_4$* *phr.***			
σ_{dc}, (S/cm)	**0**	**5**	**10**	**20**
60 °C	**$1,52\cdot10^{-7}$**	**$5,1\cdot10^{-7}$**	**$6,5\cdot10^{-7}$**	**$1,48\cdot10^{-7}$**
100 °C	**$1,47\cdot10^{-6}$**	**$1,01\cdot10^{-5}$**	**$2,08\cdot10^{-5}$**	**$1,17\cdot10^{-5}$**
200 °C	**$1,21\cdot10^{-5}$**	**$2,3\cdot10^{-4}$**	**$1,01\cdot10^{-3}$**	**$1,17\cdot10^{-3}$**

These data suggest that ion-conductive systems based on DEG and $LiClO_4$ are of interest as a solid polymer electrolyte able to operate at high temperatures (up to 200 °C). According the TGA results the weight loss at this temperature is negligible, thus their usability at high temperatures is possible.

Thus, the synthesis of epoxy polymers in the presence of lithium perchlorate made possible to obtain an ion-conductive polymeric material with a high level of ionic conductivity (~10^{-3} S/cm) at elevated temperatures (200 °C). The presence of ether oxygen atoms in polymer chains of the aliphatic epoxy DEG makes its structure similar to the polyethylene oxide structure and provides the possibility for lithium cations transfer throughout the ether oxygen atoms. Contrariwise epoxy polemer DEG has a higher heat resistance comparing to PEO, thus it is of interest as a solid polymer electrolyte able to operate at high temperatures.

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EPOXYPHOSPHOTUNGSTIC POLYMER: STRUCTURE FORMATION

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Epoxy materials possess wide range of valuable properties which are determined by peculiarities of their chemical structure and convenience of their industrial application. In general, characteristics of the epoxy polymers somewhat depend on type of the hardener used [1]. For example, heteropolyacids cause the reaction of the homopolymerization of epoxy oligomers and allow obtaining of electroactive proton-conductive polymer materials [2, 3]. Properties of such polymer materials are formed during the process of their structuring that is not studied enough.

The aim of the research is studying the process of structure formation of epoxyphosphotungstic polymers (EPTP) at homopolymerization of the epoxy resin ED-20 in catalytic reaction with phosphotungstic heteropolyacid PTA with different content of water in the reactive mixture.

PTA was taken in a form of water solution. Crystal heteropolyacid PTA mixed with water and the solution of necessary concentration (from 33 to 10% that corresponds the weight ratio PTA/water from 1/2 to 1/9) has been prepared. Afterwards water solutions of PTA with different concentrations put at epoxy resin in such a way, that ratio ED-20/PTA was 99/1 in all cases and therefore water content was varied from 2 to 9 weight parts.

Process of the structure formation of epoxyphosphotungstic polymer due to the reaction of homopolymerization of the epoxy resin ED-20 under the catalytic effect of water solution of heteropolyacid PTA has been studied by electrometric method and termomechanical analysis.

Received results are shown at the Fig.1. There are three regions for the systems, that contain 2-7 weight parts of the water at the polymer mixture: the level of conductivity of polymer material is slowly decreases at the first region, it strongly decreases (several orders of the magnitude) at the second region, and it stabilizes at the third region.

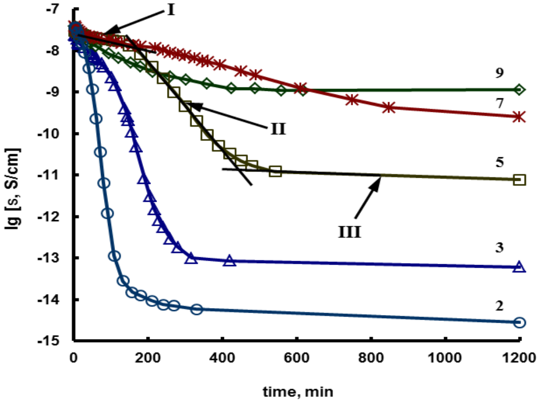

Figure 1. Kinetics of the hardening process of the EPTP systems studied by electrometric method. Numbers near curves show water content in the reactive mixture.

For explanation of the structure formation kinetics it can be proposed such structural model that represents the morphological changes during hardening. Heteropolyacid molecules are the catalyst for the reaction of the oligomer homopolymerization and correspondingly they are the centers around which this reaction starts. Thus, some heterogeneity appears in the viscous mixture, which are the zones of partially hardened oligomer around catalytic center. Under upplied voltage the proton is released from PTA anion and moves to negative electrode through the polymerized substance (Fig. 2a). At this initial stage of polymerization the conductivity slightly decreases (region I in Fig.1). When the cross-linked phases of the hardened polymer around PTA anion overlap, one can consider such a structure as interpenetrating phases polymer/oligomer (Fig. 2b). This causes sharp decreasing of the conductivity level (region II in Fig. 1).

Further polymerization causes the phase inversion and after that the main phase is phase of the hardened polymer. Part of the non-hardened oligomer reserves as inclusions (Fig. 2c). Completely hardened polymer can “carry the memory in it” about heterogeneous structure, which was existed during hardening (Fig. 2d), i.e. polymer can have zones with less and large density.

Reactive mixture of the system with 9 weight parts of water behaves another way. The level of the conductivity starts to decrease fast at the beginning of the homopolymerization reaction). Then the constant level of the conductivity appears without second region (it is not observed sharp decreasing of the conductivity). It can be because of higher content of the water molecules, which react with growing epoxy chain and break this one [4]. It leads to the rarely cross-linked structure of the epoxy oligomer (average molecular mass between sites of the network for polymer with 9 weight parts of water is one order in magnitude higher than for 2 parts of water [4]. contrarily 2 parts [4]). So, higher content of water in the reactive mixture prevents appear of globules at the first stage of polymerization and causes creating of more homogeneous structure at volume of polymer.

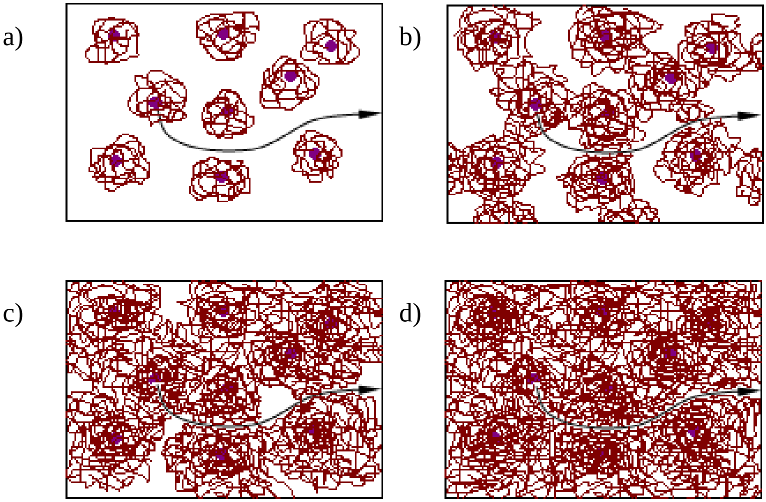

Figure 2. Morphological model of the creating process of the polymer structure of the epoxy resin hardened by heteropolyacid due to the homopolymerization mechanism. The arrows show proton movement under voltage to the negative charged electrode.

Thus, it is assumed some heterogeneity of the polymer material (polymer network is more dense around PTA molecules, than in the distance from them from them) in the case of the water content less 7 of water parts. The polymer is more homogeneous in the systems with 9 weight parts of water. Such assumption is confirmed nicely with termomechanical analysis (TMA) data.

The TMA curves show the deformation of polymer under load at temperature increase L=f(T). The differential TMA curves (DTMA) reflect the rate of deformation with temperature dL/dT=f(T). Latter method is much more sensitive to the change of deformation that corresponds to the transformation of the polymer structure. Fig.3 demonstrates the DTMA curves for polymer hardened by PTA with 2 and 9 weight parts of water. First polymer has two values of glass transition temperature T_{g1}=103°C and T_{g2}=117°C whereas second polymer (with 9 parts of water) has one glass transition at T_g=64°C. Such a behavior is evidence of inhomogeneous structure in first case and homogeneous one in second case. Lower value of T_g for the polymer with homogeneous structure is causes by higher molecular weight M_c between sites of polymer network and consequently higher molecular mobility.

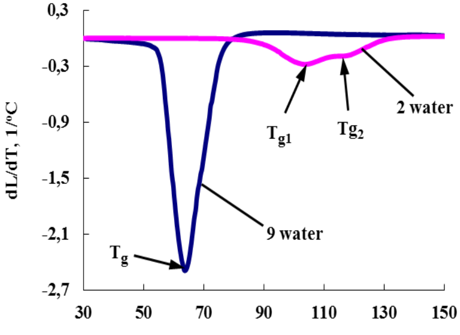

Figure 3. Differential TMA curves of polymers hardened by PTA with 2 and 9 weight parts of water in the reactive mixture.

Thus, it is found that the structure formation process is more energetic near the catalytic molecule in the case of small content of water in the reaction mixture. It causes creation of two regions into polymer volume: with more dense structure round the PTA anion and with less dense structure in the rest of volume that causes two glass transition temperatures. In the case of high water content in the reactive mixture the EPTP network structure is homogeneous with one T_g value.

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FACILE SYNTHESIS OF TITANOSILICATE COMPOSITES FOR CATALYTIC EPOXIDATION OF ALKENES

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Nowadays technology of epoxidation of unsaturated substances is required to be redirected to ecological and human friendly way. To the date for transformation of alkenes into epoxies in industrial processes the highly dangerous and toxic (hydro)peroxides [1] or oxygen in specific conditions (elevated temperature and pressure) [2] are widely used. However very prospective processes were recently elaborated and include photo-induced oxidation of alkenes by oxygen (air) in mild conditions [3] or chemical oxidation by aqueous hydrogen peroxide [4]. In both processes titanosilicate catalysts which could be synthesized by convenient methods are applied.

Recently a variety of titania-containing silicates are developed and tested as catalysts of epoxidation of unsaturated substances [3-4]. Synthesis of the titanosilicates is relatively simple and includes deposition of titania on a surface of silica carrier. There are many approaches to regulate the structure (architecture, phase composition, porosity) and properties ((photo)catalytic activity, selectivity) of prepared catalysts before their application in industrial processes. Among them the most applicable methods for modifying characteristics of titanosilicates include a selection of type of silica substrate, changing SiO_2/TiO_2 ratio, coating technique as well as pre- or post treatment conditions.

In spite of general effect of bulk structure of the catalyst on their activity the main impact have a structure and a nature of surface active sites [6]. According to last progress in this field the tetrahedral titanium sites on the surface of titanosilicates have main effect on efficacy and selectivity of epoxidation of alkenes [5]. Because of high concentration of octahedral titanium moieties in titanosilicates and minority of tetrahedral structures a determination of tetrahedral titanium sites content seems to be very difficult and requires precise and highly sensitive techniques. UV-vis diffuse reflectance spectroscopy (DRS) of titanosilicate samples in far UV region is mostly preferred and applicable method to determine the existence and relative content of highly active tetrahedral titanium sites at the surface of the catalysts produced.

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In this work we have developed a facile method of the preparation of titanosilicate catalysts and studied their surface properties. Exhaustive determination of characteristics of the catalysts is very necessary for elaboration economically and ecologically attractive technology of epoxidation of unsaturated compounds into epoxy monomers and oligomers.

Catalysts were synthesized via wet chemical method using natural mineral wollastonite (calcium silicate, 49.2 % by weight SiO_2) as a silica source and titanium (IV) chloride as a titania source. Briefly, in aqueous dispersion of wollastonite a solution of $TiCl_4$ was slowly added. TiO_2 content in catalysts is varied within a wide concentration range. Mixing of the components under elevated temperature (up to 90 ^oC) for an hour gives a dispersion of white powder. The catalysts was separated by filtration of the powder from supernatant and dried in vacuum. Phase composition of the samples was determined by X-ray diffraction scattering technique (XRD). Surface state of the catalysts has been evaluated by DRS.

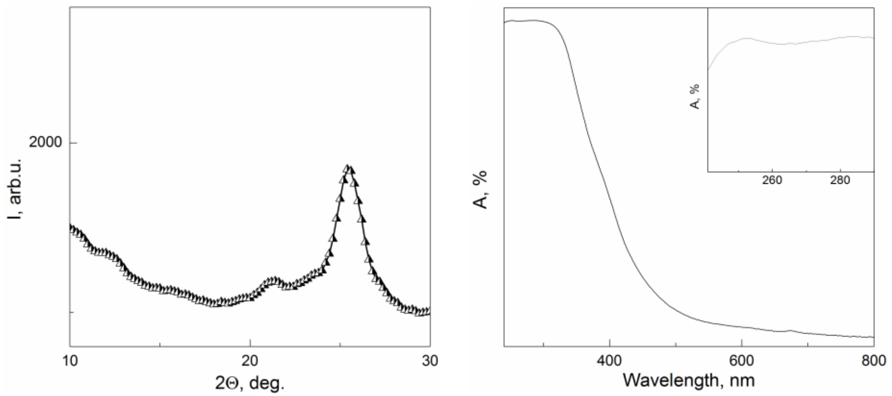

Figure 1. XRD pattern (a) and UV-DRS curve of catalyst with TiO_2 content of 50 % (by weight).

Structural characteristics of obtained titanosilicate catalyst with TiO_2 content of 50 % (by weight) were studied and the results are presented in Fig. 1. XRD results shown that composite is characterized by low-intensity reflection of anatase crystalline modification of TiO_2 constituent centered at 25.5 degrees. Relatively low level of crystallinity of the sample is due to effect of surface properties of substrate and the treatment conditions. Analysis of UV-vis DRS spectrum of the catalyst shows typical absorbance curve of TiO_2 constituent at $\lambda \geq$ 300 nm. In far UV region the two bands centered at ~ 250 (with a shoulder at 246 nm) and ~285 nm have been detected. The first band is attributed to tetrahedral titanium units in surface layer of the composites, which position could be changed due to interaction if titanium atoms with ions [7]. Last band was identified as an absorbance of polymeric Ti-O-Ti chains with octahedral titanium units in the crystalline structure.

Thus prepared mixed TiO_2-SiO_2 composites could successfully applied for catalytic epoxidation of alkenes into epoxy monomers and oligomers using modern ecofriendly and economically attractive technology. Epoxies produced could be widely used as reagents in chemical industry, isolation compositions in electronics and as binders for special applications.

Acknowledgements

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STAR-SHAPE POLYLACTIDESTEREOCOMPLEXES AS POTENTIAL MATERIALS TO DRUG DELIVERY SYSTEMS

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Possiblebiomedicalapplicationsof polyester such as poly-(L)-lactide (PLLA) are ofgrowing interest. Biocompatibility and biodegradability together with their ability to form a PLLA/PDLA stereocomplexare highlydesirable. On the other hand, combination of PLA biocompatibility and ability to form second order interactions between each other, can lead to an interesting drug delivery systems. Star-shape polylactides build on cores with different number of reactive groups, opens an easy way, to obtain materials with various macromolecular architectures [1,2].

In the present work di(trimethylolpropane) (4-arms), dipentaerythritol (6-arms), tripentaerythritol (8-arms) and*β*-cyclodextrin(21-arms) have been used as initiators of the ring-opening polymerization of L,L-lactide and D,D-lactide. Controlled polymerization was mediated by two types of catalysts: $Sn(Oct)_2$ and metal free 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) strong base. Enantiomeric PLAs have beenfurther used for preparation of thestar-shaped stereocomplexes. These stereocomplexes and atropine have been used as a model, drug delivery system which exploits a secondary interactions between the components. The obtained materials were characterized by SEC, ^{1}H NMR, ^{13}C NMR, FT-IR, DSC and SEM techniques.

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ELECTRICAL AND THERMAL CONDUCTIVITY OF EPOXY COMPOSITES CONTAINING METALLIC FILLERS

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Polymer composites consisting of polymer matrix and filler (dispersed metal or carbon) can offer a combination of properties and a diversity of applications unobtainable with metal, carbon and polymer alone. The structure of these materials is composed of two discrete phases which have evolved to provide the proper balance of electrical and physical properties. Polymer composites filled with metal are of interest for many fields of engineering. This interest arises from the fact that the electrical and physical characteristics of such composites are close to the properties of metals, whereas the mechanical properties and processing methods are typical for plastics [1-3]. The achievement of metallic properties in such composites depends on many factors and it is just the possibility of controlling the electrical and physical characteristics, which determines the variety of ranges of their application.

Applications of polymer/metal composites embrace many engineering areas, for example:

- electrically conductive materials for electronic industries, including conductive adhesive pastes and elastic elements;
- electromagnetic shielding for any electrical and electronic devices;
- radiation shielding associated with nuclear power devices;
- polymer magnets for household devices and for electrical fractional motors;
- high performance parts that are lighter in weight than conventional metal in aerospace industry
- and many the others.

This study is devoted to investigation of electrical and thermal conductivity of polymer composites filled with dispersed copper and nickel depending on content of the metal particles in polymer matrix.

Polymer/metal composites were prepared on the base of epoxy resin (ER) ED-20 filled with dispersed metals. ER was hardened by polyethylenepolyamine (PEPA) taken in a ratio 100/10, respectively. We used such dispersed metals as carbonyl nickel with average particle size of 8-12 μm and spherical shape of particles (Ni) and electrolytic copper with average particle size of 90-120 microns with (Cu).

Polymer/metal composites (Ep-Ni and Ep-Cu) were prepared through mechanical mixing resin and metal filler, then the hardener was added followed by pumping to remove air inclusions. Liquid vacuumed mixture was placed in the Teflon mold and put in the heat chamber at 70 C for 4 hours with a special device, in which the mold was rotated with speed of 1 s^{-1} to prevent sedimentation of the metal particles.

Samples of the disk shape with the diameter of 30 mm and the thickness of about 1.5 mm were used for measurements both electrical and thermal conductivity. DC electrical conductivity was measured by teraohmmeter E6-13A using polished brass electrodes at 100 V of applied voltage. For measurements of thermal conductivity the device IT-4 was used in the regime of stationary heat flow.

The dependence of electrical conductivity on the filler concentration demonstrates percolation behavior. When a certain concentration φ_c (so called percolation threshold) is reached the conductivity undergoes a jump by several orders of magnitude. The percolation theory offers the following expression to describe the dependence of the electrical conductivity σ on filler volume content φ in the $\varphi > \varphi_c$ region:

$$\sigma = \sigma_0(\varphi - \varphi_c)^t . \qquad (1)$$

where t is a critical exponent equal to 1.7–2.0 [4] and σ_0 is the parameter of conductivity which is often considered as conductivity of filler. Experimental values of conductivity of the Ep-Cu and Ep-Ni composites are shown in Fig. 1.

The values of the percolation threshold concentration φ_c and the critical exponent t and conductivity σ_0 were determined by the least square fitting of experimental points using eq. (1) in a logarithmic form:

$$\log\sigma = \log\sigma_0 + t\cdot\log(\varphi - \varphi_c) \qquad (2)$$

Correctly chosen values of t, φ_c and σ_0 give linear form of junction $\log\sigma \sim \log(\varphi - \varphi_c)$ which is presented as the insertions in Fig. 1. It can be seen rather good correlation between the experimental data and theoretical prediction. The values of t, φ_c and σ_0 are presented in Table 1. With use of these parameters the theoretical conductivity curves were calculated for both of composites accordingly to eq. (1) and overlaid on the experimental points (Fig. 1).

For Ep-Cu composite the value of percolation threshold φ_c = 0.099 (9.9 vol.%) while for Ep-Ni composite φ_c = 0.04 (4 vol.%) that is also clearly visible in

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Fig1. Since the conductivity of filler $\sigma_0(Cu) < \sigma_0(Ni)$ and percolation threshold $\varphi_c(Cu) > \varphi_c(Cu)$ it can be concluded that the particles Cu are oxidized and conditions of charge transport in Ep-Cu composite are worse than in Ep-Ni composite.

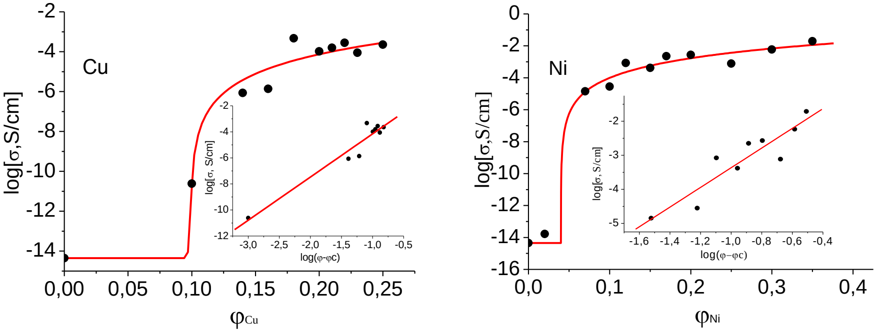

Figure 1. Experimental (points) and theoretical (solid line) percolation conductivity depending on the volume content of Cu and Ni filler in epoxy matrix.

To describe the properties of thermal conducting systems the equation of Lichtenecker was used [5]:

$$\lambda = \lambda_p^{(1-\varphi)} \lambda_f^{\varphi}. \qquad (3)$$

which is much more often applied in logarithmic form:

$$\log\lambda = (1-\varphi) \log\lambda_p + \varphi \log\lambda_f \qquad (4)$$

where λ_p is thermal conductivity of polymer and λ_f is thermal conductivity of metallic phase.

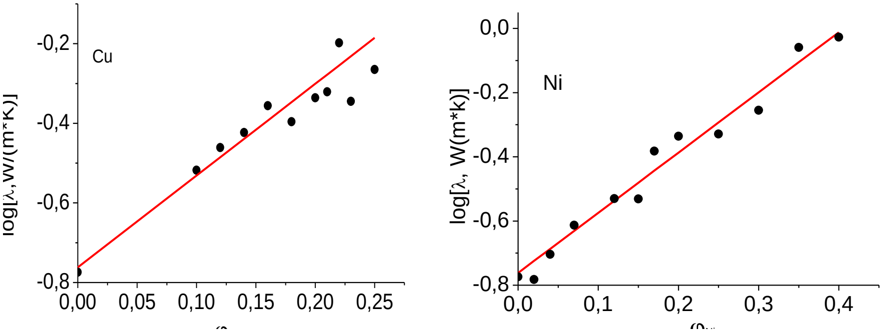

Figure 2. Experimental (points) and theoretical (solid line) concentration dependence of thermal conductivity on the content of Cu and Ni filler in epoxy matrix.

Calculated values of thermal conductivity with use of eq. (4) were overlaid on experimental points (Fig. 2). Lines correspond to the least square fitting of the experimental data and allow us to define the value of thermal conductivity of metallic powder λ_f. For polymer composites filled with Cu the value λ_f = 35 W/(m·K) and filled with Ni the value λ_f = 13 W/(m·K). Comparison of the powder thermal conductivity λ_f and the solid metal conductivity λ_m demonstrates that the thermal conductivity of metallic powders is significantly less than the solid metals, thus ratio of thermal conductivities λ_m/λ_f equals to 6.9 for Ni and 11.4 for Cu powders (Tab.1). In composites with dispersed filler heat transfer occurs through both the polymer phase and the filler phase, and transition of phonons between these phases and between metallic particles causes the scattering of phonons on these inhomogeneities that reduces thermal conductivity. Also the oxide layer covering powder particles gives its contribution in worsening of conductivity.

Table 1. Parameters of electrical and thermal conductivity.

Composite	t	σ_0, S/cm	φ_c, vol.%	λ_p, W/(m·K)	λ_f, W/(m·K)	λ_m, W/(m·K)	λ_m/λ_f
Ep-Ni	2.9	0.33	4.0	0.173	13	90	6.9
Ep-Cu	3.3	0.14	9.9	0.173	35	400	11.4

As a result of this study possible to conclude that the electrical conductivity of Ep-Ni and Ep-Cu composites has percolation character with values of percolation thresholds equal to 4.0 vol.% (Ep-Ni) and 9.9 vol.% (Ep-Cu). At the same time, the concentration dependence of the thermal conductivity of composites does not present the percolation effects. The appropriate models to analyze both types of conductivity were used. The Lichtenecker model makes it possible to determine the value of thermal conductivity of metallic powders: λ_f = 35 W/(m·K) for Cu and λ_f = 13 W/(m·K) for Ni that is much less than the thermal conductivity of solid metals. This effect can be explained by phonon scattering on the boundaries between polymer phase and filler phase, and between contacting metallic particles in the process of phonon transport through the heterogeneous structure of composites.

Acknowledgements

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PREPARATION AND OPTICAL PROPERTIES OF POLYACRYLATES WITH LEUCINE AND PYRIDINE MOIETIES

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The incorporation of amino-acid units into synthetic polymers [1] has deserved a significant research interest because they may lead to create of new non-biological macromolecules which offer new opportunities for various biological and medical applications, such as controlled release of drugs, conjugation of biomolecules, biocompatible and biologically active materials [2]. *L*-Leucine is one of the essential hydrophobic amino acids due to its aliphatic isobutyl group, for which reason it can be used as an attractive candidate in the stabilization of peptides and proteins [3]. Poly(meth)acrylates with leucine exhibit characteristic interactions of *D*- and *L*-isomers that allow stable micelles to be formed. [4]

Recently [5], copolyacrylates derived from *N*-acryloyl-(*D*/*L*),(+/-)-phenylalanine and (*D*/*L*)(-/+)*N*-methacryloyloxyethyl-*N′*-2-hydroxybutyl(urea) designed for tailored biomaterials with a large spectrum of applications were reported. In this contribution, we are studied copolymerization of acrylates monomers, *N*-acryloyl-*L*-leucine and (*N*-methacryloyloxyehtyl-*N′*-4-picolyl)-urea, that were subsequently quaternized at the pyridine nitrogen with (*R*/*S*)-(-/+)-10-camphorsulfonic acid or modified at carboxyl group with (*R*)-(+)-α-ethylbenzylamine to generate copolyacrylates with optical properties.

The structure and optical properties of the synthesized polymers were examined by FT-IR, ^{1}H-NMR, ^{13}C-NMR spectroscopy and optical measurements.

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GRAFT COPOLYMER BASED ON REACTIVE OLYGOMERS OF LINSEED OIL AND ETHYLENE-VINYL ACETATE COPOLYMER AS A COMPATIBILIZER OF COMPOSITE POLYMER MATERIALS

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Polymeric materials, due to their unique properties, are widely used in almost all spheres of human life. Volume of their production and use are increasing every year. However, this is accompanied by the rapid growth of problems, which are associated with disposal and recycling of plastic waste. One way to resolve an environmental problem is obtaining of the composite polymeric materials based on polymer waste. This will allow to save primary polymeric raw materials too. Polymer composite materials are characterized by low physical and mechanical properties. Addition of compatibilizers allows to improve characteristics of composites. Compatibilizers can be static, block, graft copolymers or polymers which contain functional groups that are similar in chemical nature with the polymer components of the mixture.

According to the results of the work graft copolymer based on a renewable, environmentally friendly natural resources - oil, was obtained. Application of vegetable oils for the synthesis of copolymers will allow to expand scope of their use in polymer chemistry and will help protect the environment and conserve resources of oil. The graft copolymer was prepared from the isocyanate-reactive oligomers of linseed oil and a hydroxyl-containing ethylene-vinyl acetate copolymer. The chemical structure of the copolymer was confirmed by IR-spectroscopy and gel permeation chromatography. Physico-chemical characteristics of the graft copolymer were studied by differential scanning calorimetry. It was found that the glass transition temperature of the copolymer shifted towards lower temperatures. The graft copolymer has a lower value of specific heat. This can be explained by grafting isocyanate reactive oligomers of linseed oil, which limit the mobility of the molecules of ethylene-vinyl acetate copolymer.

Efficiency of use of graft copolymer as a matrix for the creation of rubberplastics and as compatibilizer for polymer composite materials based on recycled thermoplastic (polypropylene or polyethylene) and crumb rubber was shown. It was established that the tensile strength of the composite polymer material increased by 41% and depended on the quantity of compatibilizer.

P50

LIGHT-RESPONSIVE CHIRAL PHOTOCHROMIC POLYMER SYSTEMS

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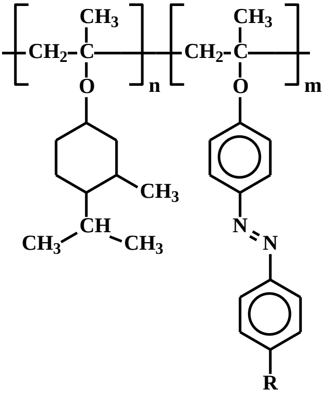
Rapid development of various modern systems for recording, transfer, processing, and display of data, visualization of images, as well as miniaturization of the optical devices requires, both solving numerous technological problems and creating new materials capable of providing rapid and reliable response to the control signals transmitted by electromagnetic fields, particularly by the light and laser actions.

Among various inorganic and organic photoresponsive materials usually referred to as “smart or intelligent materials”, the photochromic polymers systems are of indubitable interest [1,2]. All these polymers successfully combine the physico-chemical properties of macromolecular compounds (with their ability of forming films, fibers, elastomers), and photosensitivity of chromophores, covalently incorporated into the polymer chain as the side groups.

The simplest molecular structure of such polymers consists of photochromic fragments chemically linked to the main chain (backbone) (Fig. 1). Such macromolecular nature of photochromic polymers has great advantages over polymer–dye-mixtures.



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The number of photochromic copolymers containing photosensitive fragments such as double N=N bonds, and chiral menthyl groups were synthesized. Such copolymers were obtained, for instance, by radical polymerization of two monomers with the appropriate functionalities.

After the UV-irradiation *E*–*Z*-isomerization of photochromic units takes place and configuration and shape of the side group are drastically changed. In this case β_2 value becomes less than β_1 and region of selective reflection of light shifts to the red region. In other words, it means that the helical structure is untwisted. However, this process is completely reversible and heating of the sample leads to the twisting of the helix.

Examination of such multifunctional chiral photochromic copolymers is interesting not only from the viewpoint of optical data recording; investigation of, at least, two competing photochemical processes taking place in such system presents an independent interest.

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P51

NEW 4-SUBSTITUTED 1,3-BIS(4-((E)-(PHENYLIMINO)METHYL)PHENOXY)PROPAN-2-OLS WITH THE POTENTIAL NON-LINEAR OPTICAL PROPERTIES

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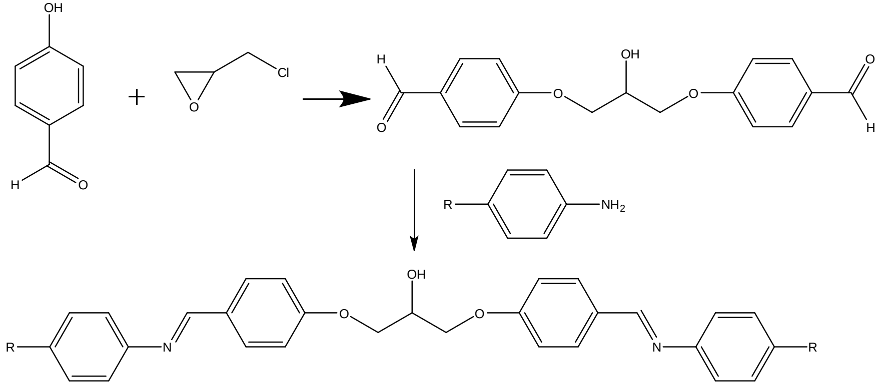
Perfection of devices for optical recording and reading of information requires constant search for new photochromic compounds. One of the most promising (between investigating presently photochromic molecules) are chromophores capable to reversible and well-controlled isomerization [1]. To improve operational characteristics is better to enter the chromophore into the polymer chain by covalent bonds.

Were investigated and optimized synthesis techniques of azomethines based on a bifunctional aromatic aldehyde and aromatic amines, wherein substituents at the para-position to the CH=N group capable to isomerization were varied. Substituents have a different donor-acceptor nature, which directly affects on the optical properties of molecules. Monomers were prepared by acrylation of alcohol groups in the starting compounds by methacrylic anhydride using standard procedure [2].



where R= -H, $-OCH_3$, $-NO_2$

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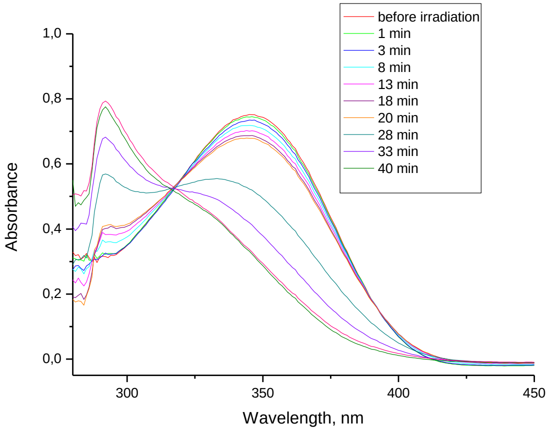
The structure of all compounds was determined by H-NMR, IR and UV-spectroscopy. The kinetics of trans-cis isomerization under the action of light with a wavelength of 360-400 nm has been studied.



R=-NO_2, in THF (C=1.25*10^{-5} mol/l)

Also, using the software package MOPAC2012 (quantum-chemical semiempirical PM-7 method) were calculated polarizability parameters for the cis- and trans-forms of the initial molecules and monomers.

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P52

IMPROVE THE ANTIMICROBIAL ACTIVITY OF PARTIALLY CYCLOALIPHATIC CO-POLYIMIDE FILMS BY PLASMA TREATMENT

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Aromatic polyimides, due to the fact that they are biologically inert and provides a good mechanical, chemical and hydrolytic strength, started to be successfully used in the manufacture of various biomedical devices, such as probes, biosensors or implants. However, these polyimides present a major drawback, namely the difficulty of processing in the completely imidized form.

To avoid this inconvenience, in the macromolecular chain structure may introduce aliphatic or cycloaliphatic sequences. These groups prevent the formation of charge-transfer complex (CTC), and significantly improve the solubility of these polyimides.

For this purpose, a series of partially cycloaliphatic co-polyimide structure, both derived from the dianhydride and diamine, which provides a good solubility in polar organic solvents such as NMP, DMF, DMAc, DMSO have been synthesized.

Surface modification co-polyimide films by cold plasma treatment, followed by stabilization of functional groups with $AgNO_3$, have been aimed to improving antimicrobial properties. We thus observed a significant increase in antimicrobial action against the control sample, both Gram-positive (*Staphylococcus aureus*) and the Gram negative (*Escherichia Coli*) bacteria. Furthermore, polyimide Kapton® taken as reference for this study has not changed antimicrobial properties after plasma treatment.

The hemocompatibility of partially cycloaliphatic co-polyimide films have been evaluated using the contact angle. After calculations using the van Oss, Good and Chaudhury equations have been obtained a good hemocompatibility of these materials.

Following these observations, it can be concluded that these polymers can be successfully used as biomaterials in sterile environments or devices that come into contact with blood.

Acknowledgements

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INFLUENCE OF THE MICROBIAL CULTURES ON THE POLYURETHANE ELASTOMERS

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Polyurethane elastomers, as well as other polyurethane materials are characterized by a unique set of properties (high firmness modulus and tear strength, resistance to swelling in various oils and solvents, exclusive wear resistance, ozone- and radiation resistance), and therefore are widely used in industry. At the same time, polyurethane products coming out of the operation, as well as most of synthetic polymers are able to maintain their inherent properties virtually unchanged for a long time, which results in environmental problems and environmental pollution. Recently, in order to minimize the environmental impact of waste polymer materials, there are carried out studies in the direction of detection of enzymes and bacteria capable to degrade some synthetic polymers (*e.g.*, polylactide [1, 2]). The aim of this paper is to investigate the influence of some microbial cultures on the structure of polyurethane elastomers (PUE), type the Tecoflex® (EG-80A, Lubrizol, U.S.A) and the Tecothane® (TT-1085A, Lubrizol, U.S.A

A flexible component of these PUE is polytetramethylene glycol (MW = 2000) of the general formula: $HO\text{-}[(CH_2)_4O\text{-}]_nH$, with using as a cross-linking agent for PUE of the type EG-80A methylenedicyclohexyl diisocyanate: $OCN\text{-}(C_6H_{10})\text{-}CH_2\text{-}(C_6H_{10})\text{-}NCO$ (MW = 262.35); and for the type TT-1085A - methylenediphenyl diisocyanate: $OCN\text{-}(C_6H_4)\text{-}CH_2\text{-}(C_6H_4)\text{-}NCO$ (MW = 250.25), the chain extender - 1,4-butanediol - $HOCH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2OH$ (MW = 90.12).

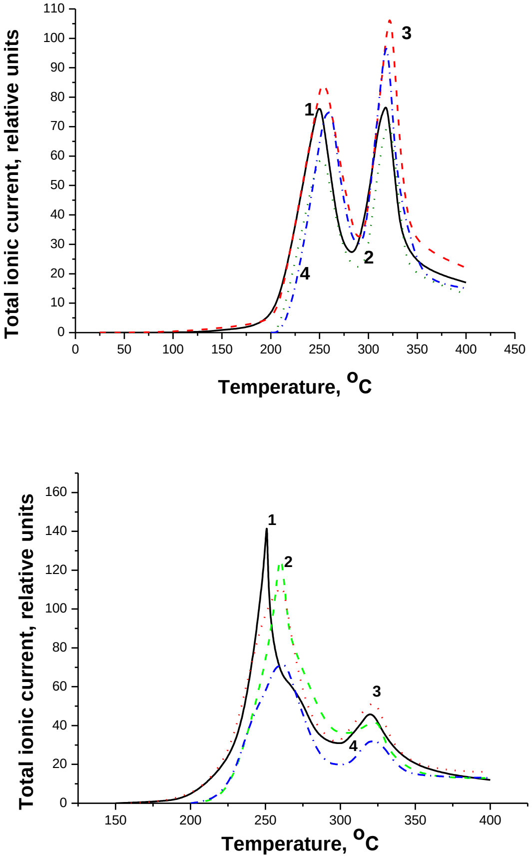
Samples of PUE EG-80A and TT-1085A were incubated for 1 month with microbial cultures of bacteria ***Pseudomonas denitrificans* (*Ps. den.*)** and

Pseudomonas fluorescens (***Ps. fl.***), as well as the yeast ***Yarrowia lipolytica*** (***Y. lip.***). The choice of these microorganisms was due to the fact that bacteria of the genus ***Pseudomonas*** belong to the group of Gram-negative chemoheterothrophs which use as a carbon and energy source organic compounds with more than one carbon atom. One of the most distinctive properties of aerobic chemoheterothrophs in general is their unpretentiousness with regard to nutrition. In many natural habitats, these bacteria are the main agents responsible for the aerobic mineralization of organic material [3, 4]. An important feature of the ascomycetous yeast species of ***Yarrrowia lipolytica*** is the ability to high-speed utilization of economically available substrates of diverse composition (paraffin oil, crude hydrolysates of biomass, industrial waste), while accumulating a large amount of biomass [5].

Structural changes in polyurethanes occurring under the influence of microorganisms were determined using the method of pyrolysis mass spectrometry (PMS) using the mass spectrometer MX-1321 according to the method described in [6].

Fig.1 shows the thermograms of the studied PUE samples before and after incubation with microbial cultures during 1 month. All thermograms are characterized by two maxima of releasing volatile products, due to the supramolecular structure of these polymers consisting of flexible oligoether and rigid diisocyanate blocks [7]. The analysis of mass spectra shows that on the first stage (200 – 275^{o}C), there occurs a thermal destruction of rigid segments, bound from diisocyanate units and 1,4-butanediol, and on the second (275 - 325 ^{o}C) – of the flexible oligoglycol links [8]. During pyrolysis of PUE samples, incubated with cultures of ***Ps. den.*** and ***Y. lip***., compared with the untreated elastomers, there is observed a decrease in the levels of total ion current, the amount of volatile components and their intensity, with a greater degree for ionic fragments, produced in the first stage of destruction of diisocyanate blocks. This is especially noticeable for volatile species with the nitrogen atom: with *m*/*z* 42 (NCO); 43 (HNCO) for EG-80A and with *m*/*z* 132 (CH_2-(C_6H_4)-NCO), 208 (C_6H_4-CH_2-C_6H_4-NCO), 221 (CH-C_6H_4-CH_2-C_6H_4-NCO), 250 (OCN-(C_6H_4)-CH_2-(C_6H_4)-NCO), 251 (OCN-(C_6H_4)-CH_2-(C_6H_4)-NCOH) for TT-1085A, the intensity of which is decreased by 40 - 70%. At the same time for PUE, which was under the influence of *Ps. fl*., contrary, these values are increasing, and in more extent for volatiles formed during the decomposition of flexible oligoglycolic component.

The obtained results indicate structural changes in the polyurethane matrix. Thus, the decrease in the number and specific intensity of ionic fragments of PUE under the influence of ***Ps. den.*** and ***Y. lip.*** can be clearly explained by the destruction of the polyurethane macromolecules. And the effect of *Ps. fl.* culture during 1 month results, likely, only in weakening the bond strength between PUE macromolecules. With respect to the action of microorganisms, TT-1085A polyurethane is less stable than the EG-80A that can be explained by the presence of conjugated double bonds in the benzene rings of diphenylmethane diisocyanate.



A **B**

Figure 1. Thermograms on total ion current of releasing volatile products of thermal destruction of EG-80A (**A**) and TT-1085A (**B**) before (1) and after incubation with ***Ps. denitrificans*** (2); ***Ps. fluorescens*** (3) and ***Y. lipolytica*** (4).

Thus, the results obtained by PMS method suggest that among the tested microorganisms, more preferred biodestructors of polyurethane elastomers are ***Pseudomonas denitrificans*** and ***Yarrowia lipolytica*.**

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P54

MODIFIED URETHANEUREASILSESQIUOXANES

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Hybrid organic-inorganic nanocomposites are widely used in optics, electronics and membrane technology due to the inherent peculiar properties: thermal and mechanical stability as well as optical transparency [1,2]. Using sol-gel method, nanocomposites can be obtained in terms of factors of spatial restriction, allowing to control their structure and level of porosity [3].

In order to study the influence of self-association of bissilane precursors on the hybrid organic-inorganic polymers' structure formation the organic- inorganic precursor based on macrodiisocyanate PEG 1000, 1,6- hexametylenediisocyanate, which has been subjected to interaction with benzidine followed by subsequent interaction with APTES - 3-(aminopropyl)trietoxysilane has been synthesized. Sol-gel hydrolytic polycondensation was carried out in the presence of zinc acetate at different molar ratios of precursor and Zn acetate: 1:1; 1:2; 1:3; 1:6. Non-modified hybrid was served as a reference sample. The resulting composites were subjected to extraction with water and acetone with following determination of their density. The changes in the structure were controlled by means of IR spectra. The contribution of individual types of associates to the total absorption of obtained zinc-containing polymers has been determined by computer processing of IR spectra with decomposition of the strips contour onto constituent - Lorentz functions (programs Fityk).

A comparative thermogravimetric analysis of obtained nanocomposites in terms of 5% mass losses has shown that the matrix loses the pointed amount at 289°C, while the composites at 235- 260°C, indicating the formation of a high porous structures. The dependence of glass transition temperature on Zn acetate content was studied by DSC method.

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P55

HEAT CONDUCTIVITY OF POLYMER COMPOSITE MATERIAL BASED ON PENTON AND SILVER IODIDE (AgI)

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Introduction

Disperse filling of polymers is effective method of polymer composite material (PCM) physical properties controlled regulation, that allow materially widen of derived products use limits and stipulated actuality of their properties especially heat conductivity systematic investigation.

For real description of heat conductivity processes in (PCM) is necessary to fixing their effective heat conductivity dependence from structure, interaction, heat physical parameters, system components content and dimensional disposition geometry peculiarities.

Formation of neighboring to the filler layer (wall layer state) with different from polymer in volume properties caused insertion of disperse particles into the polymer is special feature of PCM. Such fact may caused also by appearing of polymer molecules dimensional orientation on filler particles surface under the interior radial strains influence, whose values in penton - AgI system able to reach $4 \cdot 10^7$ *Pa*, by-turn caused by components linear expansion temperature coefficients difference, fissures appearance, other polymer structure changes etc.

Therefore upon estimation of PCM effective properties, in the absence of porous space, them regards as tricomponent system, where wall layer state take the part in the capacity of third component.

Experimental

In the capacity of polymer matrix were choose powdery penton industrial production. Original powder dispersed by mechanical method with following fractionating by using of laboratory sieves УКС-СЛ-200 mark with loops size *50* and *40* micron. Before pressing penton powder aged pending *24* hour at *323 K* for elimination of fugitive low-molecular impurities.

Disperse filler – silver iodide were prepared from ultrapure potassium iodide KI and silver nitrate $AgNO_3$. Solution of KI infused under continuous mixing in silver-bath. Mixing of solutions and washing of AgI precipitate carry out in the dark.

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Residual were carried over at filter-paper and oven dried at *383 K*. Dried AgI were dispersed using mechanical method. Particles dimension controlled using optical microscope. Outlet AgI purity control realized using X-ray analysis. X-ray diffraction patterns of investigated specimens registered using ДРОН-4-07 in CuK_α emission with nickel filter in reflected rays and Bragg-Brentano observation geometry.

Penton – disperse AgI system specimens were prepared at following thermo-baro-time (*T-p-t*) condition: heating rate *3,5 K/min*, aging at *483 K* pending *15 min* under pressure of *20 MPa*, cooling from melt with *0,5 K/min* rate, what correspond to better technological conditions of composite recycling with taking account of filler and polymer matrix properties.

Measuring of heat conductivity temperature dependence in *113 – 493 K* temperature rate were carried out at heater continuous temperature change in regime, closed to regular heating with dynamic λ – calorimeter using, which represents modernized “ИТ-λ-400” heat conductivity gauge.

Results and discussion

Let’s calculate effective heat conductivity of penton – AgI PCM composites according to this model, taking into account that discussed PCM represents the matrix of bind polymer – penton includes anisodiametrical particles of silver iodide. Such composite material structure changes can be described by following way. Filling of penton matrix by silver iodide caused appearing of isolated filler particles groups. At growing of filler volume concentration take place an isolated clusters – continuous cluster (IC - CC) transition. Following increase of concentration leads to CC volume growing, which by-turn at reaching of CV some value occupied whole composite volume. Thereby PCM effective heat conductivity estimation reduced to estimation of CC and whole composite properties.

Fig. 1 demonstrates graphical representation of averaged element (AE) of PCM penton – silver iodide system and equivalent scheme of AE heat resistances.

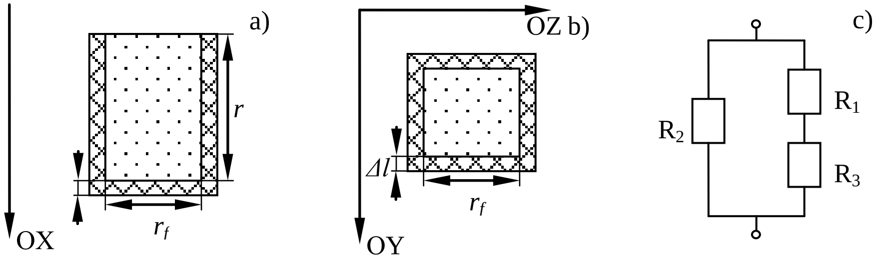

Figure 1. a) – averaged element; b) – cross-cut of averaged element in YOZ plane; c) – equivalent scheme of averaged element heat resistances.

For the determination of heat resistance, that offer averaged element to heat flow passing along OX axis, use the derived formula

$$R_a = \frac{(r+\Delta l)(r\lambda_l + \Delta l\lambda_f)}{\lambda_f \lambda_l r_f^2 (r+\Delta l) + 4\Delta l \lambda_l (r\lambda_l + \Delta l \lambda_f)(r_f + \Delta l)}, \qquad (1)$$

where the polymer wall layer whose altitude - $r_f + \Delta l$ and cross-cut area - $(r_f + 2\Delta l)^2 - r_f^2$, λ_l – heat conductivity of polymer in wall layer state.

On the other hand resistance of averaged element:

$$R_a = \frac{r+\Delta l}{\lambda_a (r_f + 2\Delta l)^2}, \qquad (2)$$

where λ_a – heat conductivity of averaged element.

$$\lambda_a = \frac{\lambda_f \lambda_l r_f^2 (r+\Delta l) + 4\Delta l \lambda_l (r\lambda_l + \Delta l \lambda_f)(r_f + \Delta l)}{(r\lambda_l + \Delta l \lambda_f)(r_f + 2\Delta l)^2}. \qquad (3)$$

Considering CC like quasihomogeneous area with heat conductivity coefficient equal to λ_a. In this case composite material can be represents like two-component with applicable heat conductivity coefficients λ_a and λ_m, where λ_m – heat conductivity coefficient of polymer matrix. Now using percolation model [2] one can define heat conductivity effective coefficient of penton – AgI composites by equation:

$$\lambda_{eff} = \lambda_m \left[\frac{\lambda_a}{\lambda_m} \bar{S}_{1a} + \frac{\bar{S}_{3a}}{\bar{l}_{1\kappa}\left(\frac{\lambda_m}{\lambda_a} - 1\right) + 1} + \frac{\bar{S}_{2a}}{\bar{l}_{2\kappa}\left(\frac{\lambda_m}{\lambda_a} - 1\right) + 1} + \bar{S}_{4a} \right] \qquad (4)$$

where at: 1) $0 \le C_{Vp_1} \le C_{Vc}$: $\bar{l}_{1a} = 0$; $\bar{l}_{2a} = C_{Vp_1}^{\frac{1}{3}}$; $\bar{S}_{1a}^{(M)} = 0$; $\bar{S}_{2a} = C_{Vp_1}^{\frac{2}{3}}$; $\bar{S}_{3a} = 0$; $\bar{S}_{4a} = 1 - C_{Vp_1}^{\frac{2}{3}}$;

2) $C_{Vc} < C_{Vp_1} \le 0{,}5$: $\bar{l}_{1a} = \bar{S}_1^{\frac{1}{2}}$; $\bar{l}_{2a} = C_{Vc}^{\frac{1}{3}}$; $\bar{S}_{1a}^{(M)} = \frac{1}{3}\left(\frac{C_{Vp_1} - C_{Vc}}{1 - C_{Vc}^{\frac{1}{3}}}\right)$; $\bar{S}_{2a} = C_{Vc}^{\frac{2}{3}} - \bar{S}_1$; $\bar{S}_{3a} = 2\bar{l}_1(1 - \bar{l}_2)$;

$\bar{S}_{4a} = 1 - C_{Vc}^{\frac{2}{3}} - \bar{S}_{3a}$ (here and then $\bar{S}_i = \left(\frac{C_{Vp_1} - C_{Vc}}{1 - C_{Vc}}\right)^{1,6} + u(z)\left(\bar{S}_{ia} - \left(\frac{C_{Vp_1} - C_{Vc}}{1 - C_{Vc}}\right)^{1,6}\right)$, $C_{Vp_2} = 1 - C_{Vp_1}$,

$u(z) = 5{,}53z - 8{,}3z^2 + 3{,}23z^3 + 0{,}54z^4$, $z = \frac{\lambda_m}{\lambda_a}$);

3) $0{,}5 < C_{Vp_1} \le 1 - C_{Vc}$: $\bar{l}_{1a} = 1 - \bar{S}_4^{\frac{1}{2}}$; $\bar{l}_{2a} = 1 - C_{Vc}^{\frac{1}{3}}$; $\bar{S}_{1a}^{(M)} = 1 - C_{Vc}^{\frac{2}{3}} - \bar{S}_3$; $\bar{S}_{2a} = C_{Vc}^{\frac{2}{3}} - \bar{S}_{4a}$;

$\bar{S}_{3a} = 2\bar{S}_4^{\frac{1}{2}}\left(1 - C_{Vc}^{\frac{2}{3}}\right)$; $\bar{S}_{4a} = \frac{1}{3}\left(\frac{C_{Vp_2} - C_{Vc}}{1 - C_{Vc}^{\frac{1}{3}}}\right)$;

4) $1 - C_{Vc} < C_{Vp_1} \le 1$: $\bar{l}_{1a} = 1$; $\bar{l}_{2a} = 1 - C_{Vp_2}^{\frac{1}{3}}$; $\bar{S}_{1a}^{(M)} = 1 - C_{Vp_2}^{\frac{2}{3}}$; $\bar{S}_{2a} = C_{Vp_2}^{\frac{2}{3}}$; $\bar{S}_{3a} = 0$; $\bar{S}_{4a} = 0$.

Whereas, that, proceeding from geometric considerations, thickness of penton wall layer by concentration $C_V = 50\ \%$ is $0,288\ nm$, values of penton - AgI PCM's effective heat conductivity can be calculated.

System penton - AgI composites effective heat conductivity calculation by using model of quasihomogeneous environment with polymer wall layer consideration allows with sufficient approximation describe concentration dependences of PCM heat conductivity, finding in papers [5, 6].

It should be notice, that using of quasihomogeneous environment model allows confirm hypothesis about high wall layer heat conductivity coefficient than the polymer in volume have, their dependence on temperature and allows estimate λ_l value at quantitative level. Thus, best approximation of calculated by experimental method at temperature of $113\ K$ reached to $\lambda_l = 0{,}348\ W/(m\cdot K)$ of penton wall layer heat conductivity value, at $T = 193\ K$ corresponding value of heat conductivity coefficient is $\lambda_l = 0{,}296\ W/(m\cdot K)$, at $T = 273\ K$ – $\lambda_l = 0{,}249\ W/(m\cdot K)$ and at $T = 353\ K$ – $\lambda_l = 0{,}212\ W/(m\cdot K)$.

Conclusions

Values of penton wall layer heat conductivity coefficients at temperatures of *113*, *193*, *273* and *353 K* exceeds corresponding values for polymer in volume up to *94,3; 55,4; 31,9* and *14,2 %*. High values of penton wall layer heat conductivity at PCM penton – AgI, caused more ordered in regard to polymer in volume structure, what certifies by researches of ultrasound dissemination velocity and absorption [3], linear expansion, heat capacity[4], electrical conduction and dielectric relaxation in SHF region [5-7]. Decreasing of λ_l values with increasing of temperature can be caused by gradual destruction of wall layer ordered structure, occur in the issue increasing of polymer chains and separate kinetic units vibrations amplitudes.

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P56

FERROMAGNETIC COMPOSITE CELLULOSE-MAGNETITE

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The study represents the experimental results on obtaining a compound cellulose-magnetite There are presented the steps of obtaining of this composite and the characterization made with infrared spectrometry, electronic microscopy and magnetic measurements.

P57

SUNLIGHT INDUCED PHOTOPOLYMERIZATION OF EPOXY-ACRYLATE INTERPENETRATING POLYMER NETWORKS

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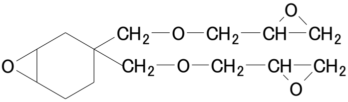
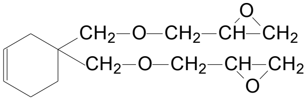
Photopolymerization due to such advantages as high polymerization speed and efficiency, easy handling, low energy consuming, and the absence of organic solvents, is the fruitful method to synthesize different macromolecular materials [1, 2]. One of the latest, most economical and ecologically friendly techniques within polymer photochemistry is a sunlight induced photopolymerization. The use of the sun as a source of ultraviolet (UV) radiation not only significantly lessens the production costs but also provides technological convenience in producing large objects for a building sphere and protective coatings for the outdoor application [3]. There are already some reports about sunlight polymerization of different macromolecular compounds [3, 4], but as well it would be interesting to polymerize the mixture of polyfunctional monomers, for example, acrylates, polymerizing via free radical mechanism, and epoxides, polymerizing via cationic mechanism, with the formation of simultaneous epoxy-acrylate interpenetrating polymer networks (IPNs) – an interesting class of polymer materials with the best properties of each component [1, 5]. Using of epoxy and acrylate resins allows one to combine high polymerization rate and UV-resistance from acrylates with low volume shrinkage and good adhesion properties from epoxides [1, 2].

Given this, the aim of the research was to study the formation process of epoxy-acrylate IPNs on the base of acrylate oligomer and epoxy oligomers of a similar structure under the natural sunlight irradiation and to compare it with the polymerization in a laboratory under the irradiation of UV-lamp.

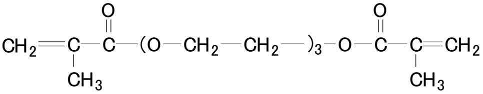
An epoxy component – a cycloaliphatic triepoxide 1,1-di-(2',3'-epoxy-propoxymethyl)-3,4-epoxy-cyclohexane (Epoxide 1) or an aliphatic diepoxide 1-(2',3'-epoxy-propoxymethyl)-1-(2",3"-epoxy-propoxy-methyl)-cyclohex-3-ene (Epoxide 2) was mixed with a difunctional triethyleneglycol dimethacrylate (TEGDM) in a weight ratio of 1:1. A cationic photoinitiator triphenylsulfonium hexafluorophosphate (TSHFP) (50 wt. % solution in propylene carbonate), which can induce not only cationic but also free radical polymerization processes because of its ability to produce both cationic and free radical reactive species, was added to a mixture in an amount of 4,0 wt % [1, 6]. The chemical structures of the compounds are presented below.



Epoxide 1

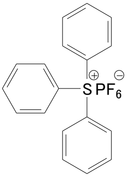


Epoxide 2



$CH_2{=}C(CH_3){-}C({=}O){-}(O{-}CH_2{-}CH_2{-})_3{-}O{-}C({=}O){-}C(CH_3){=}CH_2$

TEGDM



TSHFP

The kinetic specificities of the IPN formation processes were studied by means of infrared (IR) spectroscopy. For this purpose the prepared formulations were sandwiched between two NaCl plates and then – irradiated with the sunlight at July midday (50°27′00″ N.30°31′25″ E.). The average temperature was about 35°C. The sky was almost clear, and when the sun shined brightly the UV-light intensity reached its maximum – 1.48 mW/cm^2, when some clouds prevented the passage of the sun rays the intensity fell down to 0.52 mW/cm^2. Considering the duration of a cloudy and a sunny weather the average UV-light intensity at the sample position was defined as 0.95 mW/cm^2. To compare the polymerization under natural conditions with the polymerization under artificial laboratory conditions the parallel samples were irradiated with the high pressure mercury-quartz UV-lamp with the radiation maximum (4.0 mW cm^{-2}) at the wavelength of 365 nm at room temperature. The IR spectra of the UV-cured samples were recorded on Tenzor 37 Brucker spectrophotometer in the range 4000-600 cm^{-1}.

Firstly, the IR spectra of the Epoxide 1 – TEGDM photopolymerization system were analyzed. The acrylate conversion was followed by monitoring the decrease of the band at 1637 cm^{-1} attributed to the double bond stretching vibrations. The characteristic absorbance bands for epoxides are two types of epoxy groups bending vibrations: at 910-912 cm^{-1} for aliphatic epoxy groups and at 803 cm^{-1} for cycloaliphatic epoxy groups [7].

The dependences of a conversion degree (α, %) upon irradiation time (τ, min) of the different types of functional groups in a formulation Epoxide 1 – TEGDM polymerized under the sun radiation are demonstrated on a figure 1*a*, while the results of polymerization of the same system by means of UV-lamp are depicted on a figure 1*b*.

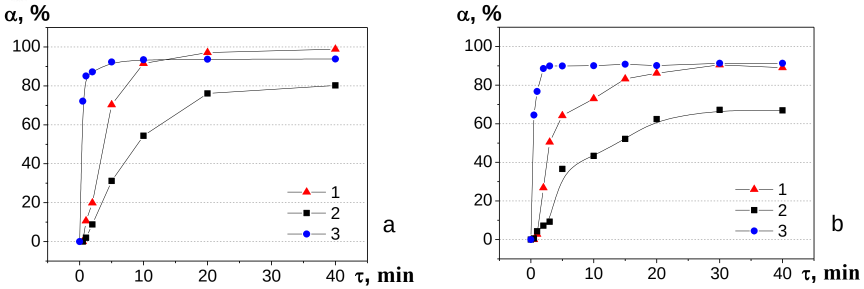


Figure 1. Kinetic curves of 1 – cycloaliphatic epoxy groups conversion, 2 – aliphatic epoxy groups conversion, and 3 – double bonds conversion under the sunlight (*a*) and under the UV lamp (*b*) in a system Epoxide 1 – TEGDM.

After 40 min of irradiation with the sunlight cycloaliphatic epoxy groups were found to reach 98.87 % of its conversion, aliphatic epoxy groups – 80.22 %, and double bonds – 93.79 %; while for the illuminated with the radiation of UV-lamp sample the conversion is 89.01 % for cycloaliphatic epoxy groups, 66.93 % – for aliphatic epoxy groups, and 91.33 % – for double bonds.

The results of the similar experiment with aliphatic epoxy resin Epoxide 2, which differs from Epoxide 1 with an absence of a cycloaliphtic group and with a lower viscosity, are presented on the figures below (fig. 2*a* for a formulation irradiated with the sun and fig. 2*b* for a formulation irradiated with the UV-lamp).

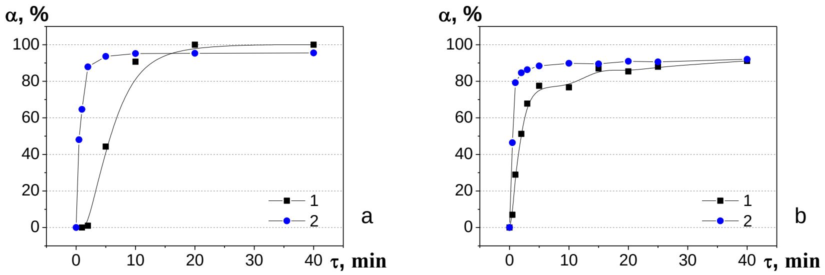


Figure 2. Kinetic curves of 1 – aliphatic epoxy groups conversion, 2 – double bonds conversion under the sunlight (*a*) and under the UV lamp (*b*) in a system Epoxide 2 – TEGDM.

In this case in 40 min 100 % of aliphatic epoxy groups and 95.47 % of double bonds react under the radiation of the sun, whereas 91.14 % of aliphatic epoxy groups and 92.06 % of double bonds react under the UV-lamp. In other words, two sets of the experiment have shown that despite a less intensity of the sunlight the polymerization under natural conditions at summer is more effective than under laboratory conditions. One of the reasons of this fact may be associated with a broad emission spectrum of the sun, which leads to a more effective light absorption of the photoinitiator in a range of its absorption maximum (300 nm) [3]. Another reason of the sunlight facilitating influence may be attributed to a high environment temperature, and, as a result, an intensive sample heating during photopolymerization. It also can be noticed that a positive effect of the sunlight is more significant towards epoxy groups, which is accounted for by a higher thermal sensitivity of a cationic polymerization compared to a free radical one [8].

Moreover, obtained kinetic dependences reveal a notable difference in reactivity of various functional groups. Thus, double bonds react so fast that their conversion levels off in 3-5 min but, nevertheless, does not reach 100 %. It is interesting to observe a unique glycidyl epoxy groups behavior in different epoxy resins. Hence, in trifunctional Epoxide 1 aliphatic epoxy groups are characterized by a much worse reactivity than in difunctional Epoxide 2. It may be accounted for by a rapid formation of a tight tridimentional network of Epoxide 1 – TEGDM IPN that prevents the further system mobility.

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P58

ANTICORROSIVE EPOXY COATING WITH POLYMER-SILICATE ADDITIVES

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The influence of polymer-modified fine silica fillers of different nature on the electrochemical properties of epoxy and polyester compositions has been investigated. For accelerated studies of developed anticorrosive coatings an electrochemical impedance spectroscopy method has been used. This method allows investigating coatings with inhibitory fillers in the first layer and with through defects. For these measurements a frequency response analyzer FRA connected with potentiostate IPC-Pro, a calomel reference electrode and an additional platinum electrode were used. Measurements were performed at the corrosion potential in the frequency range from 10 kHz to 5 MHz with signal amplitude of 20 mV.

It has been established that the coating based on alcohol modified polyvinyl silica fillers has the highest charge transfer resistance in this corrosive environment. The resistance of uninhibited coverage is about $9{,}0 \cdot 10^6$ to $1{,}1 \cdot 10^6$ Ohm, while for inhibited coatings its value is 6 - 9 times larger. Charge transfer resistance of the surface-modified coating with the inert filler is growing throughout the test, while without such a coating it passes through a maximum after two days of exposure. The increase in the resistance during the investigation for the covering with the surface-modified filler may be caused by the formation of a complex mixture of corrosion products and silica compounds on metal under the cover in the place of the through-defect. Visual observations revealed that the distribution area of steel corrosion products under the paint layer in the vicinity of the notch is much smaller than under other coverings.

Increase in the protective properties of primers with surface modified fillers in their composition has been revealed. It is shown that the mechanism of the protective effect of the modified filler in epoxy coatings on steel is similar to the effect of pure zinc phosphate, and its performance is on par with the well-known inhibiting pigment.

P59

EFFECT OF PERMANENT MAGNETIC FIELD ON PATTERNS OF SYNTHESIS AND STRUCTURE OF CROSS-LINKED COPOLYMER OF POLYVINYLPYRROLIDONE

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The cross-linked copolymers of polyvinylpyrrolidone (PVP)/2-hydroxyethyl methacrylate (HEMA) are applied with success in biomedical practice, including the manufacture of endoprostheses, medicated and correcting contact lenses, implants, dental compositions and so on. They are obtained, basically, thermo-, photo- and radiation polymerization in the presence of initiators or without them. The basic laws of such syntheses are established owing to the researches executed at the Department of chemical technology and plastic's processing of the Lviv Polytechnic National University; topological schemes of reactions' behaviour are offered; possibility of activation of polymerization process is revealed both for homogeneous conditions, and on the phase boundary as a result of the charge-transfer complex formation into the system of monomer – polymeric matrix – protophobic solvent.

It is provided, that reactivity of polymeric matrix in the conditions of a complex-radical polymerization can be strengthened by orientational, diffusive and solvation effects generated by external energy fields, including a permanent magnetic (MF) one.

It is determined, that homopolymerization of HEMA both in a magnetic field, and without it proceeds with identical rate (FIG. 1, curves *5* and *5′*), i.e. it is possible to ascertain that MF doesn't exercise influence over homopolymerization of HEMA. At the same time, MF accelerates process in case of polymerization of PVP-containing compositions with peroxide and also without it. At that, as well as in case of the thermo initiated polymerization, the rate increases proportionally to the accretion of polymeric matrix quantity in composition (FIG. 1).

For the phenomena which are observed, it is possible to give the most probable explanation, proceeding from previously determined the mechanism of matrix polymerization of (meth)acrylates in the presence of PVP. The process evidently is accompanied by monomer molecules' salvation on the PVP-matrix with the charge-transfer complex formation [1].

P59

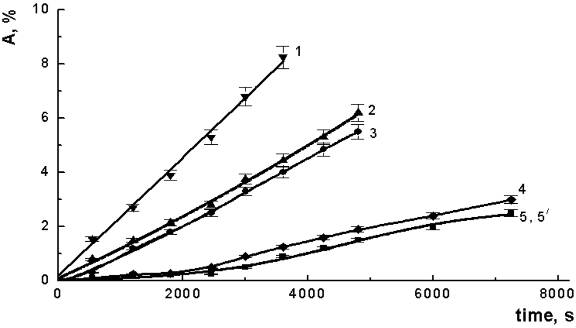

Figure 1. Initial polymer dependence on the composition content: Composition content HEMA:PVP, w. p.: *1* – 7:3; *2* – 8:2; *3, 4* – 9:1; *5, 5′* – 10:0; [PB] = 0,3 mass. % ; MW_{PVP} = 28000; MF voltage H, кА/м: *1-3, 5* – 310; *4, 5′* – 0; T = 313 К

The dissociation of double bond in molecules of monomer is facilitated by means of complexation and the polymerization rate increases. On the other hand, probably [2], orientation in the magnetic field is caused, mainly, anisotropy of a diamagnetic susceptibility of molecules. The single bond has the greatest diamagnetic susceptibility when the field is directed along a bond axis therefore the molecule is orientated perpendicularly to a field, and double bond – inversely, when the field is directed perpendicularly to a bond axis, the molecule is orientated in parallel to the magnetic field. Considering the aforesaid and similarity the peptide bond with the bond into the PVP macromolecule, it is possible to foretell, that the plane of the single bond into the PVP macromolecule aspires to be orientated perpendicularly to MF, and bond which connects a cycle to the main chain – in parallel (as well as a plane of double bond into monomer).

Therefore it is possible to foretell that aggregation of monomer molecules near the polymeric matrix weakens owing to such orientation at MF influence. It, in turn, facilitates access of monomer molecules fragments to active groups of the PVP macromolecules that strengthens complexation which is the factor of polymerization acceleration [3]. As a result of the oriented placing of macromolecules the mobility formed associates decreases, the best kinetic conditions of chain growth are created, and also prerequisites for the structure formation of (co)polymers with the arranged distribution of macro chains are pawned.

At the same time, it is ascertained, that the MF perceptibly influences the structuring during HEMA homopolymerization – in the MF cross-link density decreases considerably increasingly, than at polymerization of PVP which is a part of compositions (TABLE), though, as shown above, the MF practically doesn’t influence on the homopolymerization kinetics of HEMA.

Table. Structure features of the net and synthesized in magnetic field copolymers properties (T = 313 К, [PB] = 0,3 mass. %)

HEMA:PVP, w. p.	MF voltage, кА·m^{-1}	Mn, kg·mol^{-1}	$\nu = 10^2/Mn$, mol·kg^{-1}	$D_{NaCl} \cdot 10^{12}$, m^2·s^{-1}	F^*, MPa	T_V^*, К
10 : 0	0	6,2±1,0	16,1	0,83	200±5	357±1
	310	17,3±2,0	5,8	0,94	278±5	378±2
9 : 1	0	7,0±1,0	14,3	0,89	219±5	365±1
	310	9,5±1,0	10,5	1,00	258±5	377±1
8 : 2	0	11,3±1,0	8,9	2,11	288±5	369±1
	310	11,9±1,5	8,4	2,61	333±8	383±2
7 : 3	0	11,7±1,5	8,6	3,49	296±7	372±1
	310	14,6±1,5	6,9	4,17	340±8	385±2

Mn – molecular weight of the net fragment; ν – cross-linked density; D_{NaCl} – NaCl diffusion coefficient; F – surface hardness; Tv – heat resistance by the Vicat,
* – properties in the solid state, others – in the equilibrium swelling state

The received dependences good are conformed to the offered above orientation scheme of components of monomer-polymeric composition in the magnetic field and are caused by its influence on aggregation of monomer molecules as a result of the polarising and orientational phenomena. So long as planes of double bonds both HEMA, and ethylene glycol dimethacrylate (DMEG) which is responsible for formation of the structural network at polymerization of HEMA, are orientated in parallel to an external magnetic field, the best kinetic conditions of chain growth in reaction of binary copolymerization of HEMA with DMEG are created. Therefore the part of the last in cross-linking reaction decreases and copolymer is formed with smaller cross-link density (with bigger value of Mn) and the best operational properties (TABLE).

Interrelation between the conditions' obtaining, the structure and the basic operational properties synthesised copolymers in MF is ascertained for the purpose of engineering development of copolymer synthesis and from them of products medical function, including contact lenses.

The researches results of the MF influence on structure formation of copolymers have been used for technological implementation of hydrophilic polymers obtaining in the form of cylindrical blocks for production from them of ultra-thin contact lenses "Glipox" and the accommodative crystalline lenses by mechanical treatment method.

P59

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P60

CROSS-LINKED HYDROGEL COPOLYMERS OF POLYVINYLPYRROLIDONE AS THE MATRICES FOR THE DIRECTED AND CONTROLLED DRUGS RELEASE SYSTEMS

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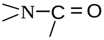
Polymer hydrogel matrices for the systems of directed and controlled drugs release are of great importance among a wide range of medical polymers. Using such systems provides drugs transportation to the diseased area of patient body, their prolonged and even release, as well as significant reduction of a single therapeutic dose. Moreover, hydrogels eliminate the danger of secondary harmful effect of polymer decomposition products on the organism compared with that caused by water-soluble polymer shells. Such polymer prolongators function by the principle of drug sorption and its release with a certain rate in the necessary place for definite time. The concentration of the drug in the body is within the range of effective therapeutic dose.

The spherical crosslinked copolymers of polyvinylpyrrolidone (PVP) with the grafted hydrophilic chains of poly-2-hydroxyethylmethacrylate (polyHEMA) were used as polymer hydrogels. They were synthesized via specially developed technology. Such polymers have limited swelling in water and physiological solution, high permeability for water and various dissolved substances. Their characteristics are determined by structural parameters of polymer net, which can be directionally controlled during synthesis.

Sorption and desorption properties of above-mentioned copolymers relative to gentamicin sulfate antibiotic have been investigated. As the mentioned drugs are dangerous in a great amount, it would be actually to prolong their action in the human organism.

The effect of synthesis conditions, initiation systems nature (metal ions with changeable oxidation degree and benzoyl peroxide) and structure of polymer carrier on sorption and desorption properties of granular copolymers have been determined. It has been established that HEMA-PVP copolymers have higher sorption ability compared with polyHEMA in the case of gentamicin sulfate. The introduction of PVP chains into the copolymer essentially increases both the sorption rate and maximum amount of sorbed drugs. Obviously, there are several reasons to explain mentioned phenomenon. The main one is the appearance of additional functional groups ( $>N{-}C{=}O$) in copolymer and the increasing of granules porosity.

Relative to gentamicin sulfate, hydrogel particles synthesized with the use of ferrum sulfate, have sorption ability almost by 25 % higher than that of hydrogels synthesized in the presence of benzoyl peroxide. According to the experimental data the reason is more developed surface of above mentioned copolymers. Drugs release from such copolymers proceeds with permanent rate up to the high degrees of desorption (75...80 %). Desorption degree and rate significantly depend on the environment pH.

Carried out investigations of sorption and desorption of drugs and model substances of different chemical structure determine the correlation between functional groups nature and dispersion characteristics of copolymers with their sorption ability. PVP copolymers have the increased immobilizing ability relative to anionic substances which further release in the alkali medium. This effect was used for the production of drugs with prolonged action for predicted choice of copolymers composition necessary for immobilization of particular preparation.

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ONE-POT SYNTHESIS AND CHARACTERIZATION OF DOUBLE-NETWORK POLYACRYLAMIDE/POLYSILOXANE HYDROGELS

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Hydrogels based on cross-linked highly hydrophilic polymers have attracted a great attention in biomedicine, organ engineering, agriculture, etc. In general the hydrogels are very fragile that limits their using as modern functional materials. Recently, a novel, double-network (DN) hydrogel was developed by combining highly cross-linked rigid polymers (the first network) with flexible polymers (the second network) [1]. Introduction of inorganic constituent into organic polymer network allow regulate a structure as well as some functional characteristics of hydrogels, like tensile strength, flexibility, swelling degree, thermal stability.

In this work, a novel DN nanostructurized composite was prepared by facile one-pot polymerization of organic and inorganic precursors. An organic polymer network was prepared by free radical polymerization of acrylamide (AAm) in a presence of N,N'-methylene-(bisacrylamide) (BAAm) as a cross-linker, while inorganic polysiloxane network forms during catalytically-induced polycondensation of sodium silicate (SS) precursor. A series of PAAm/SS based nanoscaled hydrogels with different SS content (up to 35 wt.%) have been successfully prepared *in situ* by aforementioned procedure.

FTIR spectral analysis indicates a formation of DN network structure of obtained hydrogels. Complete conversion of AAm and a formation of organic PAAm network has been satisfied by disappearance of stretching vibration bands of C=C and C-H bonds of AAm with maxima at 1610 and 3080/2975 cm^{-1} (Fig. 1), respectively. Additionally, an appearance of new bands at 1682 and 1406-1410 cm^{-1} attributed to C=O and C-N stretching vibrations of organic polymer constituent was also identified.

Presence of inorganic silicate network was identified by an appearance of intensive broad band at about 1100 cm^{-1} ascribed to the symmetric stretching vibrations of Si-O-Si bonds and a band at 789-794 cm^{-1} attributed to the stretching vibrations of Si-O-Si bonds in three-dimensional polysiloxane structure [2].

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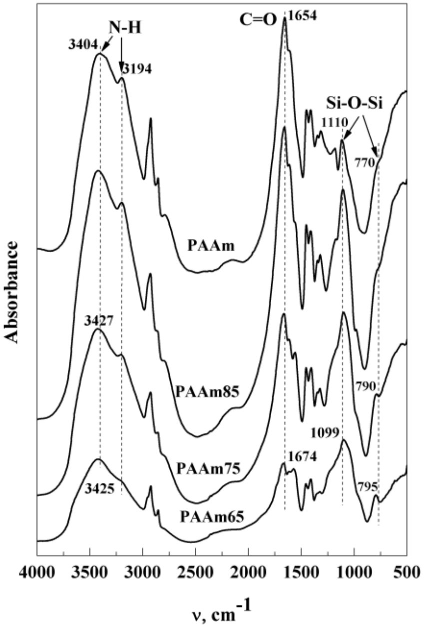

Figure 1. FTIR spectra of PAAm and double-network nanocomposite hydrogel with different PAAm content.

The effects of SS content on thermal stability were estimated from TGA. The PAAm/SS hybrid hydrogels decomposed in a three or four-step pattern depends on content of SS component. First stage in the temperature range of 208-234 °C was attributed to the evaporation of water absorbed by hydrogel samples. The second stage since 270 to 309 °C was interpreted as a destruction of amide bonds of organic polymer network [3]. Third stage in temperature interval of 317–410 °C belonged mainly to the degradation of the PAAm macrochains with breaking of interchain crosslinking bridges. Both 2-nd and 3-rd stages are characterized by partial weight loss with elimination of low-molecular gaseous products of degradation of PAAm constituent. Finally, a fourth degradation step in the temperature range of 418–445 °C, which is typical for the samples with increased SS content (25 and 35 wt.%), is related to high temperature deep degradation of organic constituent (PAAm) stabilized by thermostable inorganic component in mixed organic-inorganic phase. Consequently the thermograms of PAAm/SS DN nanostructured material have shown enhanced thermal stability of composite samples in comparison with individual PAAm hydrogel, due to formation of thermally stable hybrid hydrogen bonding network between amide groups of PAAm and siloxane inorganic network.

It was estimated that equilibrium swelling ratio of PAAm/SS composite hydrogels was much larger than that of the neat PAAm hydrogel. This fact could be explained by loosening of a structure in hybrid systems. Such behavior is a result of combining follow factors: (i) a formation of both organic and inorganic networks that leads to an appearance of considerable part of mixed organic-inorganic phase and (ii) high hydrophilicity of both networks, which allow to take up increased quantities of water molecules and form $(H_2O)_m$ bridges of different length within organic, inorganic and mixed PAAm/SS phases as well as at the interface [4].

Thus, the novel DN nanostructured hydrogels consisting of organic PAAm network and inorganic polysiloxane network were successfully synthesized by one-pot *in situ* polymerization approach. Spectral studies indicate a formation of double-network structure of obtained composite hydrogels. Detailed study of the composites showed defined structurizing of hybrid hydrogels on molecular and nanolevel as well as intra- and intercomponent interactions via H-bonds. Nanostructurizing have a great impact on final properties of the composite hydrogels. Prepared materials characterized by improved thermal stability and swelling ratio. Swelling degree of hybrid composite hydrogels depends on components ratio and reaches 2700 %.

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PRECISION SYNTHESIS OF TRIMETHYLENE CARBONATE AND LACTIDE COPOLYMERS VIA POLYMERIZATION WITH SUPPRESION OF TRANSESTERIFICATION

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Aliphatic polyesters, such as poly(lactide) (PLA), poly(glycolide) (PGA), poly(ε-caprolactone) (PCL) and poly(trimethylene carbonate) (PTMC), as well as copolymers of the corresponding monomers, are well-known bioresorbable materials with proven biocompatibility and visibly increasing importance in biomedicine [1].

Compared to the rigid poly(lactide)s, materials with a lower modulus are advantageous when applied in soft tissue. Therefore, poly(trimethylene carbonate) (PTMC), a highly elastic polymer, seems to be an interesting candidate to introduce modifications to rigid PLA [2].

The incorporation of carbonate units to the main copolymer chain allows not only to obtained greater flexibility, but also simultaneously reduces the acidity of degradation products [3].

Nowadays block copolymers containing polycarbonates segments became promising bioresorbable materials due to a possibility of the biodegradation rate, hydrophilic-hydrophobic balance as well as temperature sensitivity varying via changing of the blocks length and the chains composition.

The presentation employs the investigations of the trimethylene carbonate (TMC) and lactide (D,D- and L,L-LA) copolymerizations, using sterically extended (S)-(+)- and (*R*)-(−)-2,2’-[1,1’-binaphtyl-2,2’-diylbis(nitrylomethilidyne)]-diphenolate aluminium isopropoxide (SBO_2Al-O*i*Pr).

Recently, it has been shown that a prerequisite necessary for the controlled synthesis of multiblock CL/LA copolymers employing the “polylactide block first” route, could be based on a decoration of >AlO*i*Pr moiety with a bulky, sterically hindranced ligand, Schiff’s base derivative: (*S*)-(+)- and (*R*)-(−)-2,2’-[1,1’-binaphtyl-2,2’-diylbis(nitrylomethilidyne)]-diphenolate. That approach results in a suppression of the segmental exchange and leads to the well-defined di- and triblock copolymers formation [4].

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The similar prerequisites have been applied in the synthesis of block TMC/LA copolymers, employing the ‘polylactide block first’ route [5].
For comparison, the results of TMC/LA copolymerization initiated with a bare trimeric $\{Al(O\textit{i}Pr)_3\}_3$ [6] are also presented, confirming that selective active centers, giving rise to segmental exchange side reaction, results in partially random copolymers formation.

The present contribution reports the syntheses and the characterizations of the chains microstructure as well as the properties of the block and the random copolymers. The results of the preliminary cytotoxicity studies of obtained copolymers, which are expected to serve as the biomaterials in various applications, are also presented.

Acknowledgements

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STRUCTURE-PROPERTY RELATIONSHIPS FOR POROUS POLYAMIDOIMIDE-POLYURETHANE FILMS

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Polyimides (PIs) possess desirable characteristics, such as high thermal and thermal-oxidative stability and good mechanical properties [1]. PI-based film materials are widely used as thermostable membranes for separation of gases and liquids working at high temperatures. Polyurethanes having excellent physical-chemical and mechanical characteristics are used [2,3] for modification of polyimide membranes. Thus, obtaining film materials from PI / PU blends allows increasing elasticity and permeability which are important in their application for the separation of liquids or gases.

In this work, the polyamidoimide/polyurethane porous and precursor non-porous films were studied. The chemical structure and properties of the materials were investigated by means of Fourier-transform infra-red spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM).

Poly(trimellitic anhydride chloride-co-4,4′-methylenedianiline) (PTACM) supplied by Sigma Aldrich, USA was used as received. Polyurethane (PU, under the trade name “Vitur T-261”, Mw ≈ 40 000) was purchased from SPC "Vitur" Ltd. (Vladimir, Russia), and was used as received. N-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure. *In situ* synthesis of PAI/PU films was carried out as follows. PTACM solution (20 % in NMP) and PU solution (20 % in NMP) were mixed in various weight ratios and stirred vigorously during 10 min at ambient temperature. Than the blend solution was cast on treated glass plate and thermally treated using step-by-step heating from 25 to 250 ºC for 7.5 h for *in situ* imidization of PATCM. The PAI/PU films with PU content c = 10, 20 and 30 wt. % were synthesized. Porous structure was formed by extraction in methyl ethyl ketone (MEK) (for ~32 h) of PU from the corresponding PAI/PU films.

FTIR spectra were recorded on a Bruker Tensor 27 DTGS spectrometer using the Attenuated Total Reflection (ATR) mode between 4000 and 450 cm^{-1}. The thermal stability of the PAI/PU films obtained was evaluated with a TA Instruments TGA Q-50, using ca 3 mg of sample at a heating rate of 20 ºC min^{-1} from ambient temperature to 700 ºC under nitrogen atmosphere. Differential Scanning Calorimetry (DSC) measurements were performed with a TA Instruments Q100 calorimeter under nitrogen atmosphere. The morphology of the samples was examined by a Jeol JSM-6490 Scanning Electron Microscope (SEM). Prior to analyses, the samples were coated with a Pt.

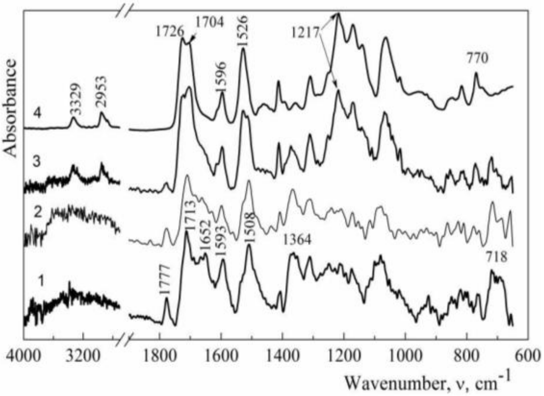

Figure 1. FTIR-spectra of individual PAI (1), porous PAI/PU film(2), non-porous (precursor) PAI/PU= (70/30) wt.% film (3) and individual PU (4).

FTIR spectra of individual PAI and PU and PAI/PU=70/30 porous and non-porous films are presented in Fig.1. In the FTIR spectrum of the individual PAI the absorbance bands at ν ~ 1364 cm^{-1} (C-N-C, imide), ν ~ 1652 cm^{-1} (C=O, amide-I), ν ~ 1713 cm^{-1} (C=O, imide), ν ~ 1777 cm^{-1} (C=O, amide) and ν ~ 719 cm^{-1} (imide cycle) evidence that the structure of individual PAI consist of both amide (in small amounts) and imide fragments [4, 5].

From comparison of FTIR spectra of porous PAI/PU film and precursor non-porous one (cf. Fig. 1, curves 2 and 3, respectively), we can conclude that PU-component was totally removed from PAI/PU composition by extraction in MEK (gel-fraction content was ~ 68.1 %), since the absorption bands of individual PU (in particular, band at 1217 cm^{-1} (C-O-C urethane)) are not observed in the spectrum of the porous PAI/PU sample.

The thermal stability of individual PAI and PU as well as PAI/PU films were studied by TGA; typical TGA curves for non-porous samples are shown in Fig.2 and the corresponding numerical data are listed

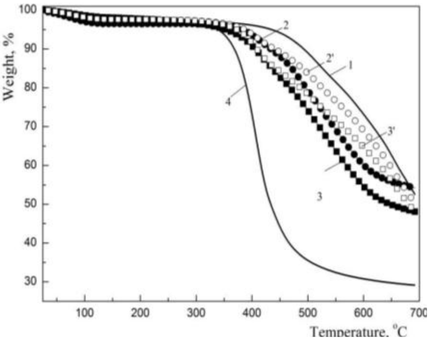

Figure 2. TGA curves obtained for non-porous PAI/PU films with PU content, wt.%: 0 (1), 10 (2), 20 (3) and 100 (4) (2′ and 3′ corresponding additive curves.).

in Table 1. For individual PAI sample, two stages of the intense mass loss, in the regions of ca. 395 to 543°C (1st stage) and 548 to 689°C (2nd stage), are observed in the TG curves, which are associated with degradation of polyimide backbone. For individual PU, we could observe one basic degradation stage in a temperature range of T ~ 357-520 °C with mass loss value Δm ~ 65 %.

Table 1. TGA data obtained for the individual PAI, PU and PAI/PU precursors

Characteristics (by stages)	PAI	PU	PU content in PAI/PU, wt.%		
			10	20	30
$T_{d1\ onset}$, °C	-	356.9	356.0	348.4	348.8
$T_{d2\ onset}$, °C	417.7	-	446.7	462.0	456.7
$T_{d3\ onset}$, °C	631.0	-	544.8	545.0	550.1
$T_{d1\ max}$, °C	-	408.9	414.2	415.8	414.7
$T_{d2\ max}$, °C	517.7	-	493.1	519.6	516.7
$T_{d3\ max}$, °C	658.0	-	560.0	552.5	578.7
dm_1/dT, %/ °C	-	0.83	0.09	0.17	0.14
dm_2/dT, %/ °C	0.16	-	0.17	0.21	0.21
dm_3/dT, %/ °C	0.26	-	0.20	0.21	0.18
Δm_1, %	-	65.7	6.3	13.3	9.6
Δm_2, %	14.7	-	16.3	17.4	18.1
Δm_3, %	28.3	-	18.5	16.9	14.5
Δm_{ash}, %	52.6	29.2	54.2	48.1	54.3

Three steps of thermal decomposition for non-porous PAI/PU blends are observed. The thermal stability of the blends is between the values for the individual components (cf. Fig. 2, Table 1). First step in a temperature range of 350-440 °C corresponds to degradation of PU-component, whereas the second and third steps correspond to decomposition of PAI-component.

Introduction of PU into PAI leads to logic reduction of thermal stability since PU is less thermostable. However, the afore-mentioned decrease in thermal stability has non-additive behavior so far as experimental and calculated TGA curves for all PAI/PU compositions do not coincide (cf. Fig. 2, curves 2,3 and 2',3'). This fact can indicate the effect of the components on each other due to *in situ* formation of the PAI/PU blends. From the numerical data presented in Table 1 one can see a convergence temperatures of maximum degradation rate ($T_{d\ max}$) for all compositions studied. Thus, $T_{d1\ max}$ corresponding to PU-component shifts by ~ 5-7 °C to higher temperatures whereas $T_{d2\ max}$ and $T_{d3\ max}$ corresponding to PAI-component shift to lower temperatures by ~ 25 °C (at 10 wt.% of PU) and ~ 79-105 °C, respectively. Note that char residue in all PAI/PU samples is quite high (Table 1).

TGA curves for precursor and porous PAI/PU films are shown in Fig.3. It was found that PAI/PU precursors had distinguished degradation stage at ~ 410 °C corresponding to PU-component but for porous samples, the abovementioned stage is very weak. This fact confirms the elimination of PU from PAI/PU blends. After removal of PU component through extraction the thermal stability of the residual polymer matrix was logically higher than that of the precursory polymer blends. The higher the PU has been removed from the PAI/PU precursor the higher difference in thermal stability of porous and non-porous samples.

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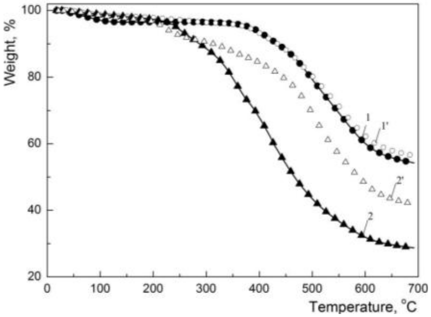

Figure 3. TGA curves obtained for precursors PAI/PU containing 10 (1) and 30 (2) wt.% of PU and corresponding porous films (1′) and (2′), respectively.

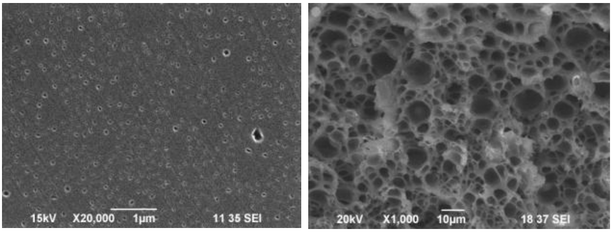

Figure 4. SEM micrographs of surfaces of the porous PAI/PU samples with initial PU content, wt.%: a) 10; b) 30.

The SEM results for porous PAI/PU films produced are shown in Fig.4. One can see the formation of porous structure after extracting of PU-component from PAI/PU blends. It can be seen from Fig. 4 that pores are well distributed in the PAI matrix, and the dimension of the pores increases with increasing the PU content. Increasing PU content in PAI/PU blends from 10 to 30 wt.% provides pore size increase from ~ 40-70 nm to ~ 2-4 μm accompanied by increasing amount and density of the pores in the PAI matrix. Thus, polyamideimide / polyurethane film materials were synthesized by the *in situ* method (non-porous films) followed by extraction of PU in MEK (porous films) and characterized. It was found that porous PAI/PU films had higher thermal stability compared to the precursor non-porous samples. The higher the PU has been removed from the PAI/PU precursor the higher porosity of resulted films.

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POLYURETHANE NANOCOMPOSITES CONTAINING REDUCED GRAPHENE OXIDE

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The authors developed a new polyurethane nanocomposites by using a derivative of graphene (thermal reduced graphene oxide - TRG) to modify the polyurethane matrix of polyurethane nanocomposite elastomers, and polyurethane nanocomposite foams, containing the TRG. Developed polyurethane nanocomposites possess unique properties, show higher mechanical strength, higher thermal stability and better resistance to aging than the corresponding polyurethane elastomers, allowing to use them as innovative construction materials.

Department of Polymer Technology, Faculty of Chemistry, Gdańsk University of Technology together with the Leather Industry Institute in Łódź and the company MB Market Ltd. Baniocha are working on the industrial implementation of the project.

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PROTIC OLIGOMERIC IONIC LIQUIDS

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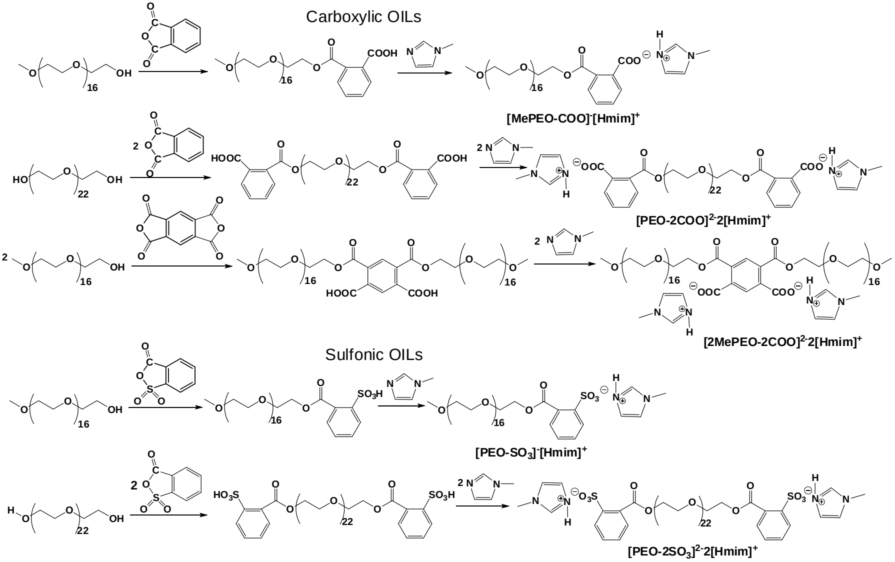
Organic ionic liquids (IL) represent a new class of electrolytes and are attractive both as a fundamental research field and for practical applications [1-4]. The practical interest to these compounds is due to their inherently high chemical and electrochemical stability, low flammability, low saturated vapor pressure, and high ionic conductivity [1-4]. Recent developments of the ionic liquids with polymerizable groups have enabled synthesis of polymer ionic liquids, which combine the unique properties of low molecular mass ionic liquids with the macromolecular properties of traditional polymers [2-4]. This has already led to creation of a new class of polymer electrolytes with a number of prospective applications [2-4]. Such compounds are losing their low melting transition point property and ability to exist in a liquid state over a broad temperature range when polymerized [2,3]. Therefore, they rather should be considered as polymeric analogs of traditional ILs [4].

Polymer chemistry distinguishes oligomer materials as a special state of macromolecular compounds [5]. Thus, combining properties of ionic liquids with those of oligomers would be interesting for both applied and basic science. So far, the oligomeric state (i.e., an intermediate state between low molecular weight and macromolecular state) of the ionic liquids was barely considered in literature; and the term oligomer ionic liquid (OIL) is not generally accepted yet. The OILs can be broadly defined as ion-containing oligomers that exist in a liquid state below 100 °C (in analogy with ordinary ILs), as well as those that can be viewed as oligomeric analogs of ILs regardless of their aggregate state (following classification suggested in Ref. [4]).

The most important characteristic feature for OILs (besides the intermediate "oligomeric-type" molecular weight and a specific aggregate state) is an existence of distinctive for ordinary ILs, so-called "ionic liquid groups", "ionic-liquid functionalities", or "imidazolium-type ionic compounds" [6,7]. Similarly to traditional ILs [1], OILs can be classified as protic or aprotic; while in analogy to the polymer ILs [2,3] they can be also divided into anionic or cationic ones.

To the best of our knowledge the protic OILs have not been systematically studied yet. So the aim of this work was to develop the methods for the synthesis of linear protic OILs of anionic type and to investigate their properties.

Synthesis of anionic protic OILs was based on introduction of carboxyl or sulfonic end groups into oligomer chains of various structures followed by their neutralization with N-methylamidozole (mim). Introduction of carboxylic or sulfonic groups was accomplished through reaction of hydroxyl-modified oligomers of different functionality with various acid anhydrides (particularly, phthalic, 2-sulfobenzoic acids and pyromellitic ones). Linear chain oligomers oligo(ethylene oxide)diol with MW 1000 (PEO-1000) and its monomethyl ether with MW 750 (MePEO-750) were used as the initial hydroxylated oligomers for the OILs synthesis. Described synthetic routes for OILs are based on well known reactions of acylation and neutralization with application of commercially available initial compounds; they use relatively simple protocols and characterized as a rule by high yield of the final products.



All synthesized protic OILs behave as sticky viscous liquids at room temperature. They show good solubility in polar solvents such as water, ethanol, DMF, DMSO, and acetonitrile, poor or good solubility in weakly polar or nonpolar solvents such as acetone, ethylacetate, tetrahydrofuran, chloroform, and insolubility in nonpolar solvents such as diethyl ether, hexane, benzene, and toluene. The chemical structure of the synthesized compounds proved by the methods of IR- and ^{1}H NMR spectroscopy. The structure, thermal stability and ionic conductivity of the synthsized compounds in the range of 20-120 ^{o}C in anhydrous conditions is governed by the molecular architecture of the OILs and the type of the anion moieties. OILs under study are amorphous at room temperature but prone to form a low melting temperature crystalline phase. The obtained compounds are thermally stable up to 170-240°C. The ionic conductivity of the synthesized OILs can be varied in broad range reaching 10^{-3} S/cm value at temperatures over 100 °C under anhydrous conditions.

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PROTONCONDUCTING ORGANIC-INORGANIC MEMBRANES FOR FUEL CELLS SYNTHESIZED BY SOL-GEL METHOD

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Fuel cells in which proton-exchange membranes (PEMs) serve as electrolytes have found wide use as electric-power sources for various stationary and portable devices [1,2]. As PEMs, which are key elements of the membrane–electrode blocks of such polymer–electrolyte fuel cells, either ionomers containing predominantly sulfo-acid groups as proton donors [1-5] or composite PEMs composed of a polymer matrix containing proton-donor agents [1,2] are used. At present, fuel cells prepared with the use of PEMs based on sulfur-containing perfluorinated ionomers of the Nafion type feature the highest performance characteristics under conditions of moisturization of PEMs [1–3]. At the same time, further improvement of the functional characteristics of the fuel cell is associated with an increase in its operating temperatures above 100 °C under anhydrous conditions [1-5].

The sol-gel technology is a promising method for producing the nanostructured organic-inorganic polymeric PEMs with improved mechanical properties, chemical and thermal stability, enhanced conductivity under low humidity conditions at temperatures above 100 °C, and low permeability to methanol [1-5].

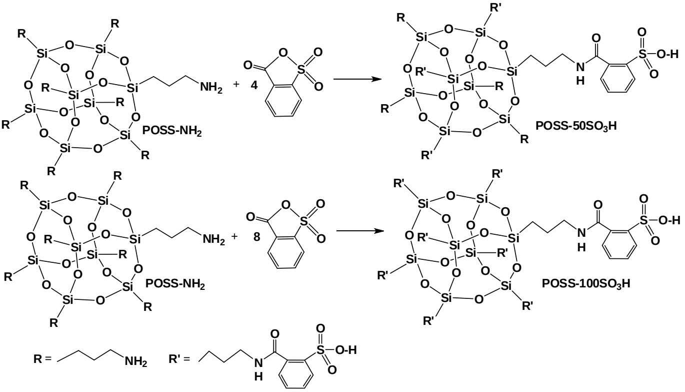
Another way to improve membranes properties is usage of oligomeric nanoscale fillers, including derivatives of polyhedral oligomeric silsesquioxanes (POSS) [6,7]. Nanosized POSS containing proton-donor groups in the organic frame of the silsesquioxane nucleus have attracted researchers’ attention owing to their potential for use as proton donors [6,7]. Above all, this circumstance is associated with the opportunity to attain a high concentration of proton-donor groups in a nanoparticle; to preserve the single-ion mechanism of conduction; to improve the thermal stability and mechanical strength of PEMs [6,7]; and to increase the amount of bound water [6], the dimensional stability, and the resistance of such compounds to segregation [6,7].

We develop the approach to the synthesis of nanostructured hybrid organic–

inorganic PEMs via the sol–gel method in an oligoether proton-conducting medium; these PEMs can function under anhydrous or low humidity conditions at increased temperatures [2,4,5]. This approach consists in the combination of oligoether-containing alkoxysilyl precursors forming the oligoether proton conducting phase with proton-donor dopants of various chemical structures, including those that can covalently bond to the polymer matrix, during the sol–gel synthesis of PEMs [2,4,5].

In this study, another type of nanostructured organic–inorganic PEM is synthesized within the framework of this approach. The used method includes the synthesis of new sulfo-acid POSSs of acidic and ampholytic types followed by their incorporation into the proton-conducting oligo(ethyleneoxide) component of the organic–inorganic matrix formed via the sol–gel method.

The synthesis of sulfo-acid POSSs was based on the reaction of POSS-NH_2 with the cyclic anhydride of 2-sulfobenzoic acid. The product obtained at an NH_2 to anhydride ratio of 1,0 : 0,5 contained both statistically distributed basic NH_2 groups and sulfo-acid groups (ampholytic dopant POSS-50SO_3H). At an NH_2 to anhydride ratio of 1 : 1, the POSS derivative being formed contained only sulfo-acid groups in the organic frame (dopant POSS-100SO_3H).



As an oligomeric alkoxysilyl precursor in the synthesis of the polymer matrix intended for incorporation into the sulfo-derivatives of POSS, the α,ω-di(triethoxysilyl) oligo(ether urethane urea) block precursor OEG-Si was used. This compound was prepared through the interaction of oligo(oxyethylene) glycol (OEG) M = 1000 with a 2-fold molar excess of toluene diisocyanate followed by blocking of the end isocyanate groups of the prepolymer with 3-aminopropyltriethoxysilane as described in [4,5]. Owing to the presence of ethoxysilyl groups, this precursor is capable of sol–gel transformations. The OEG component provides film-forming properties, the ability to solvate dopants, and the capability to dissociate to the precursor and ensures the transport of protons under anhydrous conditions [8].

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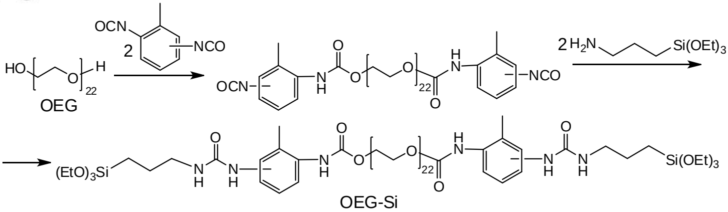

The combination of obtained sulfo-acid POSSs taken at concentrations of 20 and 50 wt % with OEG-Si and phenyltriethoxysilane via the sol–gel method using acidic catalyst (0,1N HCl) gives rise to hybrid organic–inorganic PEMs. The synthesized dopants are distributed in the oligoether component, but the nature of dopant distribution depends on their structure and concentration and has a significant impact on the structure of the resulting amorphous membranes (according to DSC, SAXS, and AFM data). The synthesized membranes are thermally stable up to 219 °C. Their conductivity is provided by the segmental mobility of oligooxyethylene fragments (the Grotthuss mechanism) and, regardless of the dopant structure, is primarily determined by the number of charge carriers and the membrane structure. The temperature dependence of the conductivity is described by the Vogel–Fulcher–Tammann equation. The maximum values of the ionic conductivity are attained at 120°C under anhydrous conditions and dopant concentration of 50%: $1{,}03 \cdot 10^{-4}$ for ampholytic oligosilsesquioxane and $7{,}43 \cdot 10^{-5}$ S/cm for fully sulfonated oligosilsesquioxane as a dopant.

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P67

THE INFLUENCE OF EXTERNAL FACTORS AND STRUCTURAL PROPERTIES OF IONIC LIQUIDS BASED ON POLYMERIC QUATERNARY SALT OF AMMONIUM - DERIVATIVES OF MORPHOLINE ON THEIR IONIC CONDUCTIVITY

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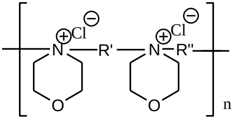
Introduction in manufacture new of science and technology, the emergence of new technologies, energy and materials led to revolutionary changes in society. Mankind has entered the era of technological revolution that increased anthropogenic impact on nature. Therefore, there is an actual solution to the problems of environmental protection. One of the solutions to many environmental problems associated with emissions of chemical plants is the use of low-temperature, thermally stable ionic liquid (IL). Today is the use of IL as new mersina environments in the field of optical measurements; electrolytes in various electrochemical processes; component in batteries, batteries, power sources, fuel cells, etc. IL have a high cost for a wide range of applications, therefore reducing the cost of these compounds is important.

There are a large number of works on IL with a variety of organic anion and organic or noorganic cationic parts. The particular interest are promising thermostable low-temperature IL based on mono- and bisfunctional quaternary salt of ammonium (derivatives of morpholine) with high ionic conductivity.

Therefore, the directed synthesis of a polymeric quaternary salt of ammonium (derivatives of morpholine) – ionic liquids (ILPQSAM) new type has a scientific and practical interested.

First synthesized new perspective low-temperature ILPQSAM general formula . It is shown that the new PQSAM find classic polyelectrolites behavior in solutions at different temperatures. The anomalous behavior of the synthesized PQSAM in aqueous-alcoholic solution has been detected – the viscosity of the polymer solution below the viscosity of the solvent. The influence of charge density of macromolecules polycations on the nature of the dependence of solution viscosity PQSAM in an alcohol solution from the composition of the solvent has been established.

The resistance to thermo-oxidative destruction, physical and chemical properties of PQSAM – IL new type has been studied. It is established that the synthesized PQSAM thermally stable up to 100–150^{0}C.

The ionic conductivity of new ILPQSAM has been studied (figure). Analysis of the results of the study of ionic conductivity at a temperature of 15^{0}C new IL showed that ILPQSAM with cation based on 1,3-dichloropropanol-2 and ED-20 have high ionic conductivity, the maximum value of which is 11,55 mSm·sm^{-1} (C-1-7).

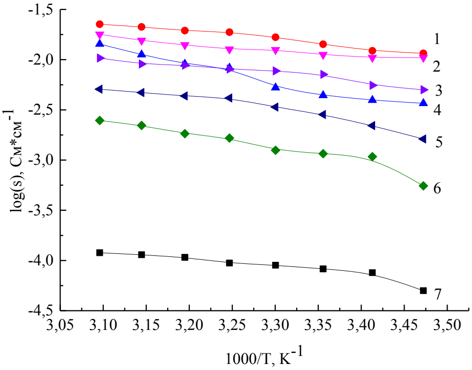


Figure. Temperature (1000/T) dependence of ionic conductivity (logσ) ILPQSAM: 1 – C-1-7, 2 – C-8-1, 3 – C-1-3, 4 – C-1-9, 5 – C-1-2, 6 – C-1-1, 7 – C-1-8

The systematical study of the influence of changes in external factors (temperature) and the analysis of the influence of structural properties of IL (the presence of functional groups in the radical cation, distances between atoms of the quaternary nitrogen in macromolecule, the length of the macromolecular chain) on the ionic conductivity of new ILPQSAM has been investigated.

The influence of external factors (temperature) on the ionic conductivity ILPQSAM. Temperature dependence of the ionic conductivity ILPQSAM shown in the figure. Data analysis showed that for all new ILPQSAM conductivity increases with temperature. The analysis of *influence* of temperature on the ionic conductivity and the viscosity ILPQSAM showed the correlation of these properties of polymers: for example, when reducing temperature ionic conductivity PQSAM decreases and the viscosity increases. A similar relationship between conductivity and viscosity in a wide temperature range recorded in *[1]*.

Ionic conductivity IL largely depends on organic cationic part *[2]*. Therefore, the influence of the nature of cations in ionic conductivity ILPQSAM has been investigated.

The influence of functional groups in the radical cation PQSAM on their ionic conductivity. It should be noted that the ionic conductivity of the investigated PQSAM with radical of alkilaromatic sructure is higher than PQSAM with radical of aliphatic sructure. So conductivity (at a temperature of 15^{0}C) C-1-7 is 11,55 mSm·sm^{-1} and C-1-8 – 1,62 mSm·sm^{-1}. Probably through a less viscous state IL in the first case.

For ILPQSAM with the cation radical containing aliphatic structure ion, conductivity varies in a wide range from 50,06 is 10^{-6} to 10,47 is 10^{-3} mSm·sm^{-1}.

Ionic conductivity ILPQSAM with cation based on 1,3-dichloropropanol-2 (C-1-2) less than ILPQSAM with cation based on DEG-1 (C-8-1). This is due to the substitution of one electronegative group $-CH_2-CH(OH)-CH_2-$ on a group of the $-CH_2-O-CH_2-CH_2-$ in the radical cation of the last ILPQSAM.

The influence of the distance between the atoms of the quaternary nitrogen in macromolecule PQSAM on ionic conductivity ILPQSAM. The distance between the atoms of the quaternary nitrogen in macromolecule PQSAM is also important when determining the ionic conductivity ILPQSAM. Comparison of ionic conductivity ILPQSAM with radical that is in the structure of the electronegative group $-CH_2-O-CH_2-CH_2-$ (C-1-9 and C-1-8). It is established that for electrolytes with increasing distance between the atoms of the quaternary nitrogen in macromolecule ILPQSAM ionic conductivity increases. This dependence may be explained also by the increase in the number electronegative group $-CH_2-O-CH_2-CH_2-$ in the radical cation part of the investigated polymer.

The influence of the length of the macromolecular chain of the polymer, the ionic conductivity ILPQSAM. An analysis of several ILPQSAM (C-1-1 C-1-2 C-1-3 C-1-8, C-8-1) with the same structure, but with different degree of polymerization showed that the ionic conductivity of the investigated ILPQSAM decreases with increasing chain length of the macromolecule polymer.

In *[2]* the influence of the cationic part of the IL on their ionic conductivity explain divergent diffusion coefficients of the components of the ions. In *[3]* this phenomenon is explained by the higher mobility of the cation due to the delocalization of the negative charge on anion that causes weakening of the ion-ion interactions constituent ions.

It is established that the low-temperature thermally stable ILPQSAM have high ionic conductivity ~10^{-3}–10^{-6} Sm·sm^{-1}. The investigational new ILPQSAM can be recommended for use as a component of liquid and polymer electrolytes for electrochemical devices of a new type.

Relevant is the use of hydrophobic IL when receiving processing of biofuels, for removal of sulfur-containing products of oil and gas fuels, for the implementation of electrochemical methods of analysis. It is known that to create electrochemical sensors are also important hydrophobicity, the insolubility in water of the IL, the possibility of polarization in their environment electrodes of different nature, extraction and plastification properties.

The relevance is the study of hydrophobic, low-temperature, thermally stable ILPQSAM capable of operating in the temperature range from –65^0C до 65^0C, with high ionic conductivity

The comparison of hydrophilic and hydrophobic ILPQSAM the influence of the hydrophilic part of the polymer structure on the electrochemical properties of these compounds, due to the influence of water on the viscosity of the IL has been showed. The calculation of the diffusion coefficient by the authors of *[4]* confirmed the dependence of the viscosity of the IL depends on the water content in these compounds. This effect is also noted in *[5]*.

Has been founded that The ionic conductivity of hydrophobic ILPQSAM C-1-7 – is 11,55 mSm·sm$^{–1}$.

That is hydrophobic ILPQSAM can effectively be used in electrochemical analysis methods, while creating sensors, as electrolytes in chemical current sources.

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POLYPROPYLENE *VERSUS* COPOLYAMIDE: A COMPARATIVE STUDY OF COMPATIBILITY TOWARDS LAYERED SILICATES IN VARIOUS FORMULATIONS

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The increasing use of polymers as composites in engineering is due to their specific properties, accessibility of manufacturing, and their wide range of applications. Therefore, a better understanding of materials behavior under operating conditions in real time is required not only to design optimum matrix-filler pairs, but also to assign the particular field of application.

Significant improvements in polymers mechanic properties have been achieved by their reinforcing with fillers of micrometer or nanometer dimensions (microfibers, nanoparticles of various types, etc.). However, different factors (the fillers aspect ratio, the matrix-filler interfacial strength defining their compatibility, and filler particles wettability in the matrix) strongly influence the properties improvement.

Layered silicates filled composites have received much attention in recent decades [1,2] on account of the associated improvement in certain properties, such as tensile strength and modulus, heat-distortion temperature, as well as a loss in others, as liquid and gas permeability and flammability, compared with pure polymers.

Our study aims to comparatively evaluate the compatibility of polypropylene (PP) and a ternary aliphatic copolyamide (coPA) towards some selected clays in terms of mechanical properties and morphology.

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POLY(VINYLPYRROLIDONE) – A VERSATILE BIOMATERIAL FOR MEDICAL AND NON-MEDICAL APPLICATIONS

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The high versatility of poly(vinylpyrrolidone) (PVP) can be explained by its diverse properties including its solubility in water and in a broad range of liquid media, high chemical and thermal resistance, and unique wetting, binding, and film-forming properties. Thanks to biocompatibility, absence of toxicity and high capacity to form interpolymer complexes, PVP is widely used for designing materials with a wide range of applications, such as biomaterials for medical and non-medical uses. This paper summarizes a vast diversity of applicative examples showing the tremendous opportunities for future research and developments of PVP based biomaterials.

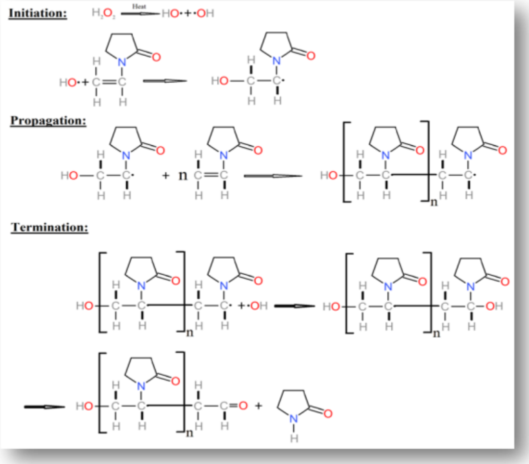

Figure 1. Polymerization of VP in aqueous solution.

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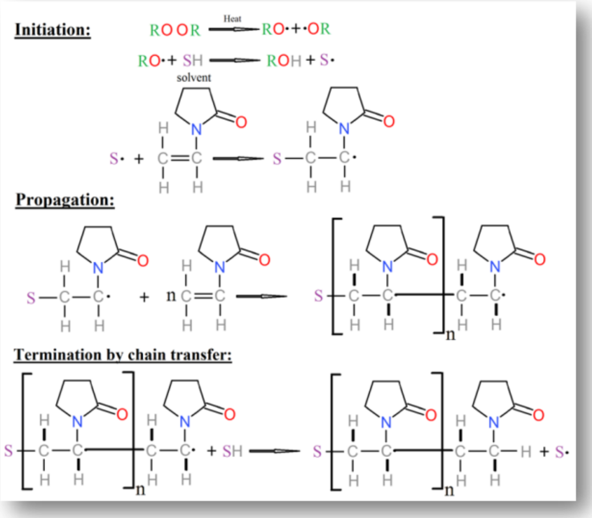

Figure 2. Polymerization of VP in organic solution.

From the literature review, it is concluded that PVP has an important role in meeting the demands of various fields of biomaterial applications, both medical and non-medical, which have been discussed with plenty examples. Since its synthesis in 1938 by Walter Reppe, a chemist form BASF, PVP have attracted much attention due to its impressive properties, such as biocompatibility, non-toxicity, solubility in water and many organic solvents, pH stability, affinity to complex both hydrophobic and hydrophilic substances, chemically inert in physiological reaction, etc. Among the various fields that have benefited from its discovery, some have been mentioned: pharmaceutical industry and medicine, optical and electrical applications, membranes, adhesives, ceramics, paper, coatings and inks, household, industrial and institutional, lithography and photography, fibers and textiles, environmental applications (water and waste treatment, and hygiene), etc. Therefore, PVP covers a broad range of biomedical applications as well as in everyday life and it is believed that further research can still bring great benefits to humanity.

The literature describing the multitude of PVP applications is very diverse and this work offers a useful review of research conducted in various fields. In this regard, there has also been prepared a visual representation in the form of a word cloud that can provide a fast understanding of the directions followed, without the need of reading large amount of information.

With respect to the aforementioned discussions, it can be said that although

PVP has been studied intensively in the last decades, it still presents tremendous opportunities for future research and developments of biomaterials.

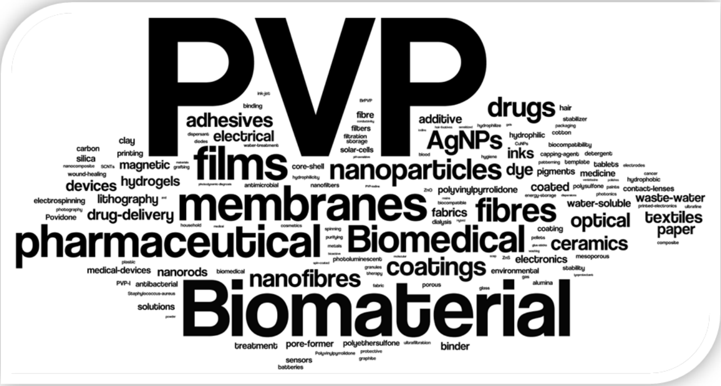

Figure 3. Word cloud showing the most popular terms encountered in papers on PVP research. The word size is proportional to the frequency of the terms in the papers.

Acknowledgments

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SYNTHESIS AND CHARACTERIZATION OF CORE-FLUORINATED AROMATIC POLYMERS

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Fluorinated aromatic polycondensation polymers represent a prospective recent trend in development of thermally stable organic compounds [1-3]. Introduction of perfluorinated aromatic fragments to a polymer backbone allows reduction of the polymer's dielectric constant, the refractive index, optical and dielectric losses making such materials attractive for modern hi-tech applications in microelectronics, aerospace industry, and, especially, in optical telecommunications [1, 2].

Synthesis of such compounds is typically accomplished with an application of monomers containing tetrafluorobenzene (TFB) or octafluorobiphenyl (OFB) fragments [1]. Usage of the TFB and OFB units as individual monomers presents a certain limitation, since only nucleus-fluorinated aromatic polyethers can be synthesized within such chemical route [1].

A broader application of perfluorinated aromatic polymers depends on diversification of their chemical functionalization through polymer analogous transformations**,** or by means of monomer units containing functional groups or fragments [1]. The latter strategy typically employs a combination of two monomer units: one being fluorinated and another one with appropriate functional groups. An alternative approach, in which the same monomer is fluorinated and simultaneously contains functional groups is less developed.

Thus, synthesis of new monomers based on TFB and OFB units and containing functional groups is crucial for further development in the field.

We have studied and developed synthetic routes for several new nucleus-fluorinated aromatic monomers containing allyl or acetyl fragments and bromine atoms. Optimal conditions for Claisen and Fries rearrangements were found and described [3].

We have developed synthetic routes for several core-fluorinated aromatic polyethers using TFB-containing monomers with isomeric fragments (CFAPE-1 (*para*-)), allyl or acetyl groups. Optimal conditions for the polymers preparation were found and described. Physical and chemical properties of the synthesized fluorinated polyethers appeared to be dependent on the isomeric nature of the polyether backbone and the type of functional groups. Thus, CFAPE-1 containing the rigid nonfunctionalized *para*-phenoxy units shows both high T_g value and good thermal stability. This compound is characterized with a limited solubility and forms brittle films. On contrary, the other synthesized polyethers exhibit excellent solubility in organic solvents and film-forming properties. This can be attributed to presence of the isomeric meta-phenoxy units and functional groups in their chemical structure [4, 5].

The synthesis methods of new fluoro-containing aminomethylated bisphenols on the base of 1,4-bis(4-hydroxyphenoxy)tetrafluorobenzene have been developed. The synthesized compounds were used for introduce of the tertiary atoms of nitrogen in aromatic polyethers by polycondensation of those with decafluorobiphenyl. The polymeric ammonium salts were obtained by interaction of such polymers with iodic methyl. All polymers were isolated with high yield and characterized by good film-forming ability [6, 7].

The method of synthesis of the aromatic polyether based on decafluorobiphenyl and 1,4-bis(3-hydroxyphenoxy)tetrafluorobenzene was developed with using NaH to generate phenoxide ions. Sulfogroups were incorporate by polymeranalogical transformations into the synthesized polymers using chlorosulfonic acid. The mechanical properties and the thermal oxidation stability of the synthesized sulfonated polymers were investigated [8].

A method for the synthesis of fluorinated allyll-containing bisphenol based on 4,4"-[(2,3,5,6-tetrafluoro-1,4-phenylene)bis(oxy)]diphenol has been elaborated. Curable aromatic polyethers have been prepared via polycondensation of the synthesized bisphenol with decafluorobiphenyl. The influence of bases, namely K_2CO_3 and NaH, on the molecular weights of polymers has been studied, and the conditions of their curing at allyl moieties have been found. Mechanical, physicochemical, and dielectric properties of allyll-containing polymers are dependent on the method of their preparation and curing [5].

The methods of synthesis of new bifunctional aromatic core-fluorinated monomers containing tetrafluoro-1,4-diphenoxybenzene fragment and acetyl, fluorophenylmethanone, hydroxyl, epoxide, brommethyl and azide groups were developed. The structure of the synthesized compounds was determined by IR, ^{1}H NMR and ^{19}F NMR spectrometry techniques [9].

Series of nucleus-fluorinated azomethine-containing bisphenols was obtained by interaction of aromatic diamines containing fragments of tetrafluorobenzene and oktafluorobiphenyl with salicylic aldehyde. Received diamines can be used as monomers to synthesize macromolecular compounds. Optical properties of the synthesized monomers were studied by UV spectroscopy, and acidity of their hydroxyl groups was evaluated by ^{1}H NMR spectroscopy [10].

By interaction of terephthalaldehyde and nucleus-fluorinated aromatic diamines, comprising amino groups in ortho-, meta- and para-position, was obtained series polyazomethines, containing perfluorinated mono- and biphenylene fragments along with 1,4-bisazomethinephenylens units, separated by nonfluorinated phenylenoxyde groups. The polymers obtained are characterized by high thermal stability, decomposition temperature which is in the range 325–452 ^oC. The glass transition temperature of polymers obtained by using diamines, comprising amino groups in ortho- and meta-position is in the range 144-166 ° C, whereas for polyazomethines based on diamines, comprising amino groups in para-position glass transition temperature do not appear in the flesh to 300 ^oC. By methods small-and wide-angle X-ray scattering show that synthesized polyazomethines have different structural organization (from crystalline to amorphous) induced by isomerism of azomethine groups and variation nucleus-fluorinated component [11].

We have synthesized two sets of new core-fluorinated isomeric azo-containing bis-diols of V-type with TFB or OFB electron-accepting fragments. Based on these azo-chromophores, polyurethanes were synthesized, incorporating the nonlinear-optical chromophores in the polymer backbone. Our study of physical, chemical, optical and nonlinear optical properties of the synthesized polymers shows that their nonlinear-optical properties are mainly dependent on the isomeric nature of the polyurethane backbone rather than on the electron-accepting properties of the azo-chromophore fragments. We demonstrate also high thermal stability of the synthesized polymers and possible variation of their second harmonic generation coefficients in the range of 1.0 to 10.0 pm/V by modifications of the chemical structure and isomeric form of their fluorinated fragments [12].

Due to presence of the nonfluorinated aromatic units in the structure of the synthesized polyethers the latter are capable for electrophilic substitution reactions (sulfonation, halogenation, acylation and so on), that further extend the range of their possible applications. Moreover, the polymer chain design of alyl- and acetyl-containing polymers enables further chemical modifications through so-called thiol-ene chemistry, hydrosilylation, epoxydation, cross-linking reactions using allyl fragments, or specific reactions by Mannich, Claisen-Schmidt condensation (using acetyl groups), etc. Additionally, due to existence of perfluorinated aromatic units in their structure these monomers are capable for nucleophilic substitution reactions, that further extends the range of their possible applications.

The obtained polymers are promising systems for a wide range of applications, e.g., as low-dielectric materials, in optical devices, membranes for gas and solvent separation, membranes for fuel cells, as well as polymer nonlinear optical media with enhanced time and temperature stability and polymer with liquid crystalline properties.

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THE INFLUENCE OF THE BONDLINE THICKNESS ON THE EPOXY POLYMER PROPERTIES

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An understanding of the effect of bondline thickness on the fracture and fatigue of adhesive joints can guide to the selection of an optimal bondline thickness and indicate the sensitivity to variations in thickness that may arise during curing [1, 2]. Therefore, the investigation of a scale factor effect on adhesion and viscoelastic properties of adhesive based on epoxy resin cured with triethanolamine was carried out. By using dynamic mechanical analysis method the viscoelastic behavior of both free epoxy films and adhesive joints (on copper and steel substrates) was studied. The thickness of adhesive layer and free films was varied in interval of 50-900 mkm.

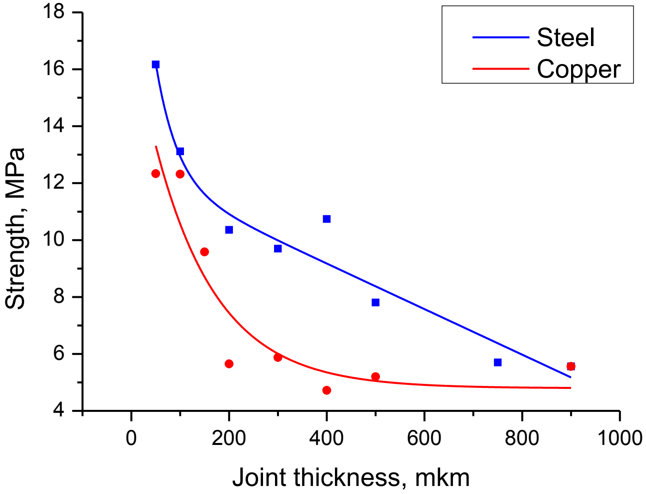

Figure 1. Influence of the joint thickness on overall strength for different substrates.

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The increase of epoxy adhesive layer thickness was shown to result in the nonmonotonic decrease in an adhesive strength value (Fig. 1). The dramatic drop of adhesion strength was observed for adhesive layers having thickness less than 200 mkm and more slowly decrease occurred in case of thicker ones. The overall strength was investigated on single-lap joint by shear stress mode.

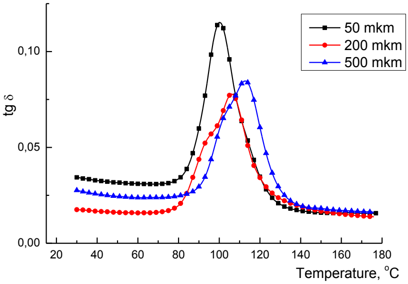

Figure 2. Temperature dependence of the tg δ for steel adhesive joint.

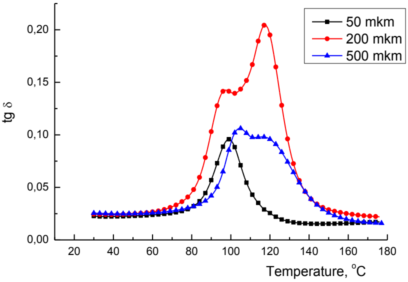

Figure 3. Temperature dependence of the tg δ for copper adhesive joint.

It was also shown that layer thickness influenced not only adhesion and viscoelastic behavior of adhesive but coupled with the effect of substrates (steel (Fig. 2) and copper (Fig. 3)) surface caused the changes in topology and morphology of epoxy networks. Particularly the appearance of shoulder associated with additional relaxation transition on the rising wing of the maximum at loss module temperature dependence for most thicknesses was assumed to indicate the fluctuation of cross-linking density of epoxy network.

Experimental tests and numerical analyses were carried out to investigate the influence of the adhesive layer thickness and the viscoelastic properties on the behavior of single-lap joints made of different substrates (steel and copper) and epoxy adhesive layers. It was established that the increase of thicknesses is followed by decrease of overall strength of adhesion joints.

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P72

THE NANOSTRUCTURE OF POLYMER LAYERS FORMED ON A SOLID SURFACE BY ADSORPTION FROM BINARY AND TERNARY SOLUTIONS

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The selfassembly of polymer nanolayers by adsorption from solution has been studied. A combination of sorption experiments and atomic force microscopy (AFM), including force modulation mode (FMM), have been applied to study the process of macromolecular adsorption from polystyrene (PS) and poly (butyl methacrylate) (PBMA) polymer solutions of various concentrations as well as the morphology of the adsorbed polymer films on solid substrates. The processes of self-assembly in polymer blends on the solid surface of silica leading to the formation of nanolayers are discussed. These processes proceed during adsorption of polymers from a binary (polymer-solvent) or ternary (polymer-polymer-solvent) solutions. As measured from sorption experiments on colloidal silica particles the adsorption layers have thickness of the order of 50 to 300 nm. The thickness of the adsorption nanolayer depends strongly on the applied adsorption regime. Single macromolecular transfer to the solid surface with a formation of the layers with the thickness of 20-50 nm is observed in case of the adsorption from dilute polymer solutions. The adsorption layer thickness increases for a semi-dilute solution adsorption regime. This effect is due a parallel process of changes in the conformational state of the polymer chains in the solution and their self-assembly into fluctuation molecular clusters of a nano-scale dimensions. Such clusters can be transferred late on to the solid surface during the adsorption process forming surface nanolayers of a different structure. The saturation of the surface by adsorption is reached usually at a very low concentration of the solution. Further increase in the concentration leads to the growth of adsorption, which is accompanied by diminishing of the fraction of the surface-bound segments. Simultaneously, the thickness of the adsorption layer increases due to changes in the conditions of the multiplayer assembly on the surface, and so due to reorganization of the adsorption layer structure.

The thickness of the adsorption layer, surface roughness and fractal dimensionality have been independently measured from AFM experiments and are

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used for quantitative characterization of the process of the self-assembly of nanolayers. The thickness of the adsorbed films is ~ 20-25 nm in case of low polymer solution concentration, and 35-50 nm for polymer films adsorbed from concentrated solutions. Much thicker films in the latter case are ascribed to the formation of clusters of highly entangled polymer chains in the polymer solution. A mosaic structure with alternation of PBMA and PS islands (200 nm average sizes) is revealed for polymer films adsorbed from binary solutions.

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ENVIRONMENTALLY FRIENDLY (BIO)DEGRADABLE XANTHAN BASED POLYURETHANES

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Introduction

The increased interest to the materials based on natural polymers has led to the development of new direction in polymer chemistry: creation of polymers based on polysaccharides and known synthetic polymers. Previously, we synthesized and studied polymers based on ionic polyurethanes and natural (poly)saccharides (starch, lactose, glucose, etc.) that degrade under the environment [1,2]. It has been proved that in particular the chemical bond between synthetic and natural components plays a crucial role in giving (bio)degradability to the synthesized polymer as a whole, opposite to the mechanical mixtures (decomposes only a natural component). Thanks to the success of biotechnology in the creation of biodegradable polymer materials, the microbial polysaccharides (exopolysaccharides), in particular, xanthan (Xn) – the extracellular polysaccharide of bacterium *Xanthomonas Campestris* are of increasing use in modern chemistry due to their climate and seasonal independence and simplicity of obtaining. This work describes the synthesis and study of the complex relationship: "composition - properties - ability to (bio) degradation" of structurally modified polymer materials based on polyurethane ionomer and microbial exopolysaccharide Xn.

Experimental

Xn-containig anionic polyurethanes (IPU/Xn) in the form of aqueous dispersions were synthesized by reaction of isocyanate precursor on the basis of oligooxytetramethylene glycol (MW=1030) and hexamethylenediisocyanate in the molar ratio of 1:2, respectively (reaction time-2h, $T=80^{o}C$) with dimethylolpropionic acid DMPA), followed by the chain extension with different Xn content (0.2%, 0.4% , 0.6%, 1.0%, 2.0%, 5.0%). Xn was administered in the form of a dry powder. Neutralization of DMPA was carried out using triethylamine. Then IPU/Xn was dispersed in water with following acetone removal. The polymer films were formed on Teflon substrates at room temperature, followed by drying in an oven at 65°C and in a vacuum oven at 55°C until constant weight. Reference dispersion IPU (matrix) obtained in a similar way, but without Xn. It should be noted that mechanical mixing of IPU and Xn did not result in film forming dispersion. The mixture was layered within 24 hours.

Results and discussion

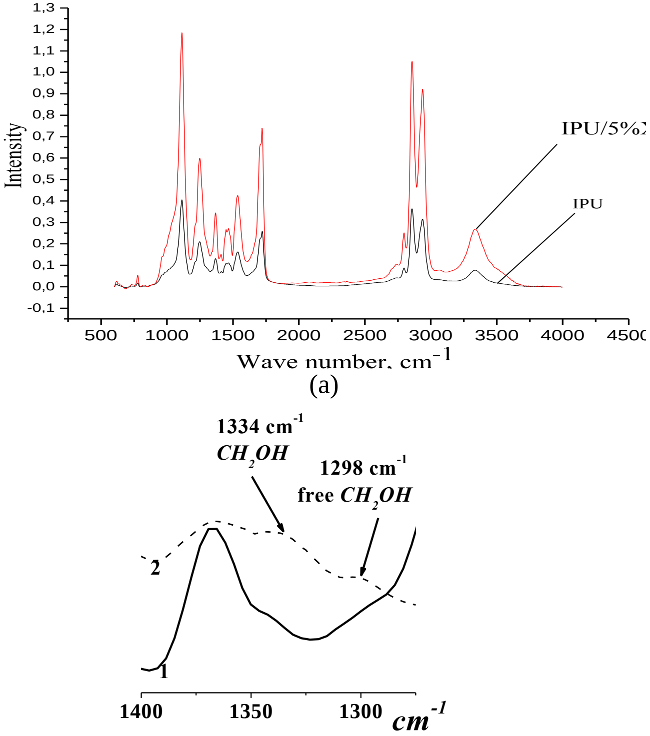
Composition, colloid-chemical, physic-mechanical properties of IPU/Xn dispersions and films are presented in Table 1.

Table 1**.** Properties of IPU/Xn dispersions and based films.

Xn, %	Dispersions		Films			
	r_{av}, nm	pH	Water absorption, % (24 h).	Contact angle	σ, MPa	ε, %
0	71	7,84	2,6	68	7,3	1470
0,2	114	8,13	8,4	64	6,8	1307
0,4	120	8,05	9,0	61	5,9	1142
0,6	161	7,79	9,7	58	5,3	1100
1,0	157	7,83	9,8	55	3,8	1055
2,0	166	7,37	11,4	52	3,3	940
5,0	176	7,17	22,9	50	2,3	742

The increase of Xn content in the composition has little effect on the particle size (r_{av}) and the pH of the dispersion. The r_{av} of IPU/Xn remains within the interval of stability. Water absorption of the films increases with the increase of Xn content, reaching maximum value at 5%. It is known that diffusion of water is determined by the material microstructure and affinity of the polymer components to water. Part of the Xn hydrophilic hydroxyl groups is involved in the formation of intermolecular bonds with IPU, however, with the increasing of Xn content the larger part of these groups is vacant, whereby Xn is allocated to a separate phase, contributing to the films' hydrophilicity increase, which results in contact angle reduction. The tensile strength (σ) and elasticity (ε) of the IPU/Xn films is generally lower in comparison with IPU matrix. Moreover, with Xn increase, the values of σ and ε are gradually reduced. σ reduction is observed due to a violation of the existing system of IPU hydrogen bonds as a result of the Xn introduction. This violation may affect the conformational mobility of the IPUs. In this case, the decrease in ε is due to the limitations of conformational changes of polyurethane molecules under the influence of external forces; and the amount of the Xn is sufficient to suppress the conformational mobility of the IPU. The most groups of the urethane oligomer capable to hydrogen bonding with the OH groups of Xn are bonded, and the part of Xn is allocated to a separate phase leading to reduced strength properties of the system due to the very low strength properties of Xn.

There are all characteristic bands of polyurethanes presented in IR-spectrum, (Figure 1a). The high-frequency shoulder at 3375 cm^{-1} in IPU spectrum indicates the presence of free NH- groups. In the IPU/Xn spectrum the shoulder disappears, and the intensity of hydrogen-bonded NH- groups (3325 cm^{-1}) is increased. The new broad weak band at 3540 cm^{-1} is appeared, indicating the presence of free OH groups of Xn. Appearance in the IPU/Xn spectrum of low-frequency shoulder 1013 cm^{-1} – the stretching vibrations of C-O and the reduction of this band's intensity indicates the hydrogen bonding of ether oxygen with the OH groups of Xn. However, the observed decrease of the intensity of the absorption C-H band of the CH_2O group of Xn 1334 cm^{-1}, indicates their participation in the formation of chemical bonds with the NCO-groups of oligouretane (Fig. 1b) and the disappearance of the band 1298 cm^{-1} – is the result of their involvement in hydrogen bonding with polar groups of oligouretane component.



(a)

(b)

Figure 1. IR-spectra: IPU and IPU/5%Xn - (a); IPU/5%Xn (1) and Xn (2) – (b)

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Influence of Xn on IPU degradation was studied by the method which allows to simulate the processes occurring in nature. Samples were exposed to the containers with a soil of medium biological activity (pH=6.82, relative humidity 60%; t = 14-25ºC) for 1-4 months. The determination of the soil microflora has showed the fungi presence of the following genera: *Rhizopus, Aspergillus,*

Penicillium. The rate of degradation was monitored by weight loss at certain time intervals (Table 2).

Table 2. Properties of IPU/Xn films after incubation into the soil.

Xn, %	Weight loss,% month			pH of the soil after test			Loss of (σ/ε), % after test,		
	1	2	4	1	2	4	1 mon	2 mon	4 mon
0,0	0,3	1,0	1,3	7,3	7,2	7,1	0,1/0,6	1,3/1,3	2,8/1,4
0,2	1,3	1,1	3.3	7,6	7, 5	7, 4	2,9/0,8	7,3/1,4	8,8/2,6
0,6	1,9	2,2	4,7	7,5	7, 4	7. 3	8,6/2,7	12,4/1,7	18,1/3,1
1,0	2,5	2,6	6,6	7,3	7, 3	7,2	14,2/3,6	20,7/2,6	22,6/5,2
2,0	2,7	2,8	7,3	7,4	7, 2	7, 2	20,2/5,0	23,3/7,7	27,4/9,0
5,0	6,2	6,3	9,9	7,3	6,8	6, 5	28,3/6,1	37,2/8,0	50,1/18

Weight loss increases with the increase of Xn content, regardless the test duration. For 4 months it is 3,3-10,2%, which is higher than the actual Xn content in 2-16 times and excides the corresponding characteristic of the matrix in 2.5 – 7.9 times. The results suggest that Xn promotes the degradation processes of IPU. The lowering of pH values indicates the presence of organic acids which are the products of vital function of microorganisms, using the sample as a power source. The action of microorganisms (MO) entails the lowering of physic-mechanical indicies. The σ and ε of IPU after 4 months in the soil reduces on 2,8 and 1,4%, respectively, whereas the same losses for the sample IPU/5%Xn amount to 50,1 and 18,0%, respectively. These data suggest the ability of polymeric materials to biodegradation due to the presence in their structure of Xn.

Conclusions

New environmentally friendly polyurethanes with different content of natural exopolysaccharide - xanthan have been obtained. It was shown that exactly the chemical interaction between Xn and polymer matrix confirmed by IR spectroscopy has determined the degradation ability of based materials. Xn - containing samples were shown to be more susceptible to alkaline and acid hydrolysis as well as to degradation under the influence of the soil microflora. Thus, it has been shown the ability to create degradable materials based on chemically bonded polyurethane ionomer and exopolysaccharide xanthan the rate of degradation and properties of which can be controlled by the component composition.

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CHARACTERIZATION OF PEI-BASED GENE DELIVERY SYSTEMS

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Gene therapy represents a revolutionary cure option that could provide solutions against certain maladies considered incurable, such as: genetic disorders, cancer, AIDS and other acquired or inherited diseases. This process consists in the delivery of an effective gene in certain cells or tissues replacing the defective ones and often is performed with the help of a viral or non-viral carrier.

Among non-viral carriers, polyethylenimine (PEI) is one of the most widely studied cationic polymers for DNA delivery. The PEI molecules of 25÷30 kDa molecular weight (Mw) proved to have a great potential in transfection efficiency, but with the drawback of an increase cytotoxicity [1,2]. By conjugation of low molecular weight hyperbranched PEI (about 2 kDa) with polyfunctional, symmetric molecules as compact cores, dendrimer-like structures were obtained. The core molecules used in present work are: fullerene C60, β-cyclodextrine (β-CD) and a cyclic siloxane (D4H). In order to prevent the immune system response, PEG chains were also considered regarding the carrier design [3]. This work deals with the characterization of the following PEI-based conjugated: C60-PEI, C60-PEG-PEI, D4-PEI and β-CD-PEG-PEI. The synthesis of these compounds was illustrated in scheme 1.

The confirmation of suggested structures was achieved by performing a number of complementary analysis methods: ^{1}H and ^{13}C NMR, FT-IR, XPS, TG, DSC and zeta potential. Morphological tests were performed when possible: AFM for fullerene-based compounds and TEM for β-CD-PEG-PEI. Because of the big amount of primary, secondary and tertiary amino groups in PEI, NMR or FT-IR techniques are not edifying concerning the newly formed C-N covalent bonds between core and PEI. XPS may detect and quantify all types of bonds and provide the mass percent of nitrogen that allows the determination of nitrogen (from PEI) to phosphorus (from DNA) ratio required in polymer-DNA preparation. The average number of PEI molecules linked to the core is determined by TG analysis and confirmed by XPS [4].

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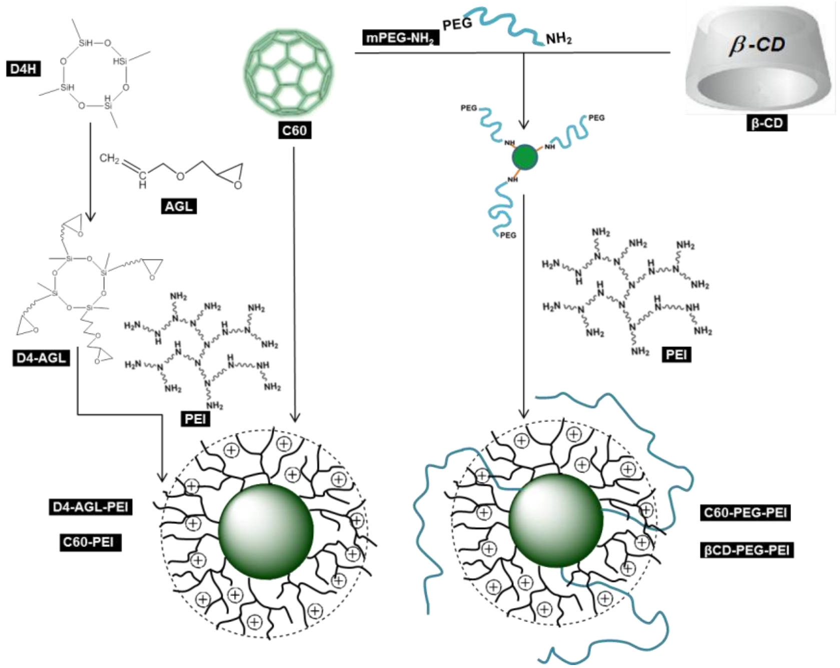

Legend

D4H	- 2,4,6,8-Tetramethyl-2,4,6,8-tetrakis cyclotetrasiloxane
C60	- Fullerene C60
β-CD	- β-cyclodextrine
AGL	- Allyl glycidyl ether
D4-AGL	- 2,4,6,8-Tetramethyl-2,4,6,8-tetrakis(propyl glycidyl ether)cyclotetrasiloxane
PEI	- polyethylenimine, Mw ≈ 2000 g/mol
D4-AGL-PEI	- the conjugate product between D4-AGL and PEI
mPEG-NH$_2$	- α-(2-aminoethyl)-ω-methylpolyethylene glycol, Mw ≈ 2000 g/mol
C60-PEI	- the conjugate product between C60 and PEI
C60-PEG-PEI	- the conjugate product between C60, PEG and PEI
βCD-PEG-PEI	- the conjugate product between β-CD, PEG and PEI

Scheme 1. Synthesis of D4-AGL-PEI, C60-PEI, C60-PEG-PEI and β-CD-PEG-PEI.

Acknowledgements

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Post-modification of poly(triphenylamine-vinylene)s: a way to tune their optical and electronic properties

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New polyarylenevinylenes based on triphenylamine units substituted in free *para* position with phenylethynyl- and 3-pyridylethynyl substituents were synthesized by Stille polycondensation of *trans*-1,2-*bis*(tributylstannyl)ethene with two new ethynyl substituted triphenylamine monomers, *i.e.*, N,N-bis(4-iodophenyl)-4'-(phenylethynyl)phenylamine and N,N-bis(4-iodophenyl)-4'-(3-pyridylethynyl)phenylamine. All polymers were characterized by usual methods such as ^{13}C and ^{1}H-NMR, FT-IR, UV-Vis and photoluminescence, and cyclic voltammetry. The electron-rich triple bond was then post-modified by [2+2] cycloaddition of tetracyanoethylene or pyridine ring was protonated with HCl or quaternized with methyl iodide forming thus new intermolecular charge-transfer (ICT) complexes between acceptor pendant groups and triphenylamine from the conjugated polymeric chain. A comparative analysis of the optical and electronic properties of the parent and chemical modified polymers was performed and the results were correlated using time-dependent density functional theory (TD-DFT) calculations. The absorption and emission spectra, HOMO and LUMO energy levels and gap energies were fine-tuned after the chemical post-modification of polymers, and density functional theory calculations (TD-DFT) provide a reliable interpretation of the observed spectra and electrochemical data.

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PHOTOPHYSICAL PROPERTIES OF A SERIES OF OLIGOMERS WITH VINYLENE, IMINE, AZINE AND ETHYNYLENE SPACERS BEARING TRIPHENYLAMINE MOIETY

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Five symmetrical oligomers containing triphenylamine moieties linked by vinylene, imine, azine and ethynylene spacers have been studied experimentally and theoretically, from point of view of UV-Vis absorption and photophysical properties. The comparative analysis of the optical and electronic properties was carried out by the density functional theory (DFT) with time-dependent (TD) approximation and solvent account by PCM (Chloroform), and the results reflect a good agreement between the observed spectra and TD DFT calculations which provide the orbital nature assignment of all absorption bands.

It had been predicted the positions of the lowest triplet states and their photophysical properties. The emission rate constants and radiative lifetime are estimated for fluorescence of all oligomers.

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THERMAL BEHAVIOR OF SEMIAROMATIC POLYIMIDES

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The thermal behavior of six semiaromatic polyimides was investigated. Thermal degradation processes had been conducted by dynamic thermogravimetry in nitrogen atmosphere, up to 700°C. Comparative thermal stability studies of the samples were undertaken. A coupling to a quadrupole mass spectrometer and a Fourier transform infrared spectrophotometer equipped with external modulus for gas analysis was used for the evolved gases analyses. Kinetic study was conducted by applying the Ozawa–Flynn and Wall [1,2] and non–linear regression methods. A decrease in kinetic parameters values with conversion degree was observed, suggesting the occurrence of a change in rate determining step.

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POLY(ETHYLENE GLYCOL) AND POLY(PROPYLENE GLYCOL)-CONTAINING AMINOFUNCTIONAL COPOLYESTERS FOR BIOMEDICAL APPLICATION

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Polyesters have been widely studied for the last years as materials for different medical applications. A number of synthetic approaches to the development of aminofunctional copolyesters (APE) were reported. The majority of such approaches are based on the use of tri-functional amino acids. The technique usually includes protection of amine fragments and the use of the other two functional groups (carboxylic, hydroxy, etc.) in polymerization process. Copolyester synthesis usually occurs in severe conditions, i.e. in the presence of strong acids and at high temperatures.

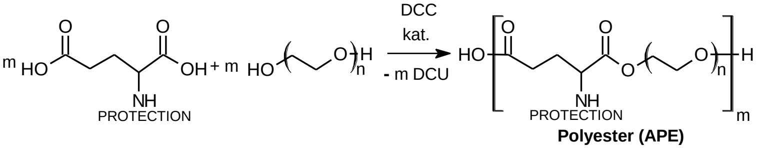

Figure 1. Polyester formation by Steglich.

One of the ways to overcome these experimental limitations is the use of coupling agents such as dicyclohexylcarbodiimide (DCC) that allows the polyester chain to grow under mild conditions (Steglich esterification) Fig. 1. Synthesized polyesters and copolyesters contain hydrophilic and lipophilic fragments in the structure and possess surface-active properties. Glutamic acid with different hydrophilic and hydrophobic protecting groups were used in the polycondensation reaction with a range of diols (polyethylene and polypropylene glycols, as well as diethylene glycol), to obtain the final aminofunctional copolymers [1].

In polyesters a polyoxyethylene chain plays the role of a hydrophilic polyester chain. The structure of the lipophilic part of polyesters is formed by N-substituted glutamic acid. Hydrophilic-lipophilic balance (HLB) of these amphiphilic polyesters can be controlled via changing of molecular weight of polyoxyethylene fragments, as well as changing of the length of the alkyl chain in the N-substituted glutamic acid. As macromolecules of synthesized copolyesters are formed of lipophilic and hydrophilic fragments, they possess surface active properties – 1÷2% water dispersions decrease surface tension to 34÷42 mN/m. Characteristic surface tension isotherms of aminofunctional copolymers have two inflection points: the first one refers to the critical micelle concentration (CMC1), the second – to the concentration at which structural rearrangement of the dispersed phase takes place (CMC2). Particle size of the dispersed phase makes 80÷300 nm according to the dynamic light scattering data depending on the polymer concentration. Dispersed phase particles have complex architecture consisting of lipophilic core and hydrophilic shell. The morphology of particles was studied using methods of small-angle neutron scattering and transmission electron microscopy. Such particle structure determines their ability to solubilize low-soluble in water organic compounds. In particular, solubilization Sudan (III) dyes was studied. Its shown that dispersed phase solubilize 0,5 ÷ 3,0 g of low-soluble compounds per 1 g of polymer in the dispersion depending on the polymer concentration and its composition. Maximal solubilization (up to 1-3,0 grams of dye Sudan III per 1 g of polymer dispersed phase) is observed at concentrations between CMC_1 and CMC_2.

The peculiarities of the release of organic compounds solubilized in aqueous dispersions into model lipophilic phase (octanol-1) have been investigated. Since the obtained polymers are biocompatible, the products of their biodegradation are non-toxic and due to a number of colloidal properties described above, synthesized polyesters are promising materials for dispersed drug delivery systems.

A number of APE were designed to be deprotected after the synthesis in order to fabricate polycationic macromolecules with primary amino groups for further DNA-binding studies. Novel amphiphilic polyesterethers based on natural occurring dibasic amino acids and their N-derivatives with controllable colloidal properties and ionogenic groups of cationic type (amino groups) were synthesized using developed technique. The complex of properties (amphiphilicity, biodegradability and non-toxic degradation products) and the ability to form self-assembled structures in aqueous medium allow using such polymers to form in vivo delivery systems. Thus there is prerequisite for polyionic interactions with genetic material (DNA) and development of new generation of polyplexes.

A combination of glutamic acid protected with cleavable protective groups (Boc-) and lipophilic N-lauroyl or N-stearoyl glutamic acids was used to fabricate amphiphilic cationic APE.

Cationic micelles were prepared using aminofunctional copolyesters containing randomly distributed fragments of glutamic acid and N-lauroyl glutamic acid coupled with PEG-300. These APE micelles are able to change their charge from positive to negative (in aqueous medium in response to pH change pH < 7 and pH >7 respectively. Cationic aminofunctional copolyester were used for plasmid DNA binding studies. The most effective binding of copolyester macromolecules and plasmid DNA occurs at pH 5.5. 60-70 mg of copolyester can bind 1 mg of nucleic acid. Gel electrophoresis of co-GluNH2/GluL [0,28/ 0,72]-co-PEG-600-DNA nanocomplex in 1% agarose gels shows that the amphiphilic aminofunctional copolyesters with free amino groups effectively bind DNA and macromolecules can be used as gene delivery carriers.

These studies show that cationic APE are promising materials for DNA binding and gene delivery technologies.

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CHEMICAL MODIFICATION OF POLYIMIDE MEMBRANES FOR CO_2 SEPARATION

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This work deals with the chemical modification of polyimides (PIs) designed to provide a combination of good gas permeability and selectivity in the removal of CO_2 from flue gases, easy processability, and high thermal, chemical and mechanical properties to meet the demands for high performance gas separation membranes. Two hydroxyl-functionalized polymers were synthesized using 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and 3,3'-dihydroxybenzidine. These polymers were chemically modified via Mitsunobu reaction [1] to introduce new functional groups into the PI chains. The influence of a substituent kind and the degree of substitution on PIs physical properties and gas separation characteristics was studied. The molecular structure of the obtained PIs was confirmed by ^1H NMR and FT-IR ATR spectroscopies. Their physical properties were characterized by DSC and TGA techniques and morphology was examined using WAXD. All polymers exhibited good solubility in common organic solvents, and high thermal stability. The gas transport properties were measured for all the obtained membranes. It was found that the substituted PIs show higher gas permeation rate and slightly higher selectivity for CO_2/N_2 then unmodified PIs. The two-fold increase of CO_2 permeability was observed for PIs with 4-pyridinemethanol based substituents at the substitution degree lower than 10%. The effect of the substituents on chain packing was related to the gas permeation properties. Fractional free volume (FFV), calculated using Bondi's group contribution method, and *d* spacing values determined from X-ray diffraction were used to judge chain packing.

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COPOLYIMIDES BASED ON HEXAFLUOROISOPROPYLIDENE AND ALICYCLIC DIANHYDRIDES FOR GAS SEPARATION APPLICATION

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A series of copolyimides (PIs) based on dianhydrides containing hexafluoroisopropylidene and alicyclic units were obtained and studied as membranes for gas separation applications. The polycondensation reactions of a mixture of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA), taken in equimolar ratio, with diamines containing different functional groups were carried out in N-methylpyrolidone. The resulting PIs were easily soluble in many organic solvents. Molecular structures of PIs were examined by ^{1}H-NMR and ATR-FTIR spectroscopies. Thermal characteristics of the membranes were studied by using DSC technique. The amorphous character of the polymers was confirmed by wide angle X-ray diffraction (WAXD) technique. Permeability coefficients and ideal selectivity values were determined for pure gases: N_2, O_2, He and CO_2. The correlations between polyimide structures and permeability coefficients were discussed. It was found that the presence of the most bulky diamine, 4-[(3-{4-[7-(4-aminophenoxy)-3-phenyl-2-quinoxalinyl]phenyl}-2-phenyl-6-quinoxalinyl)oxy]phenylamine, caused 3-fold increase in permeability for all the studied gases while maintaining high selectivity for O_2/N_2 and CO_2/N_2 gas pairs.

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COORDINATION POLYMERS AND NETWORKS BUILD ON THE BASIS OF FLEXIBLE DICARBOXYLATE LIGANDS AND DIFFERENT METALLIC IONS

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Metal–organic frameworks (MOFs) as well as coordination polymers (CPs) are an important class of solid-state materials with interesting properties and potential applications for gas storage, catalysis, magnetism and luminescence. In order to obtain desired CPs and MOFs, the ligands, metal ions and reaction conditions have to be judicious chosen.

In this approach two dicarboxylic acids, 1,3-bis(p-carboxyphenylene-ester-methylene)tetramethyldisiloxane and bis(carboxypropyl)tetramethyldisiloxane, containing flexible siloxane sequences were chosen as ligands for *3d* transition metals: Cu(II), Mn(II), Zn(II) and Co(II) in the presence of different co-ligands (imidazole, 4,4'-azopyridine and salicylaldoxime) [1]. The structures of the resulted compounds were elucidated by elemental and spectral analysis as well as by single crystal X-ray diffraction proving to be 1D, 2D or 3D coordination polymers or networks of the metals connected by flexible ligands and rigid co-ligands as well as by non-covalent interactions (H-bonding and π-π stacking) (Figure 1).

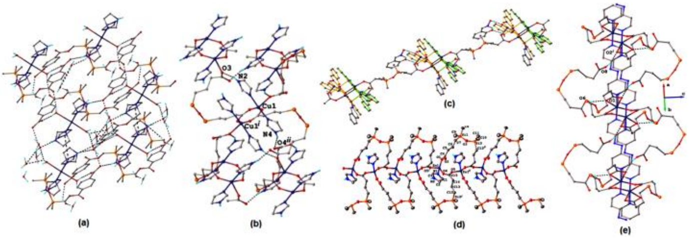

Figure 1. Views of crystal structures of coordination polymers or networks containing: (a), (b)-Cu(II), (c)-Mn(II), (d)-Zn(II) and (e)-Co(II).

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