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EXPLORATORY RESEARCH PROJECT

PN-II-ID-PCE-2011-3-0937

Contract nr. 302/05.10.2011

COMPLEX SYSTEMS BASED ON POLYMERS CONTAINING ALICYCLIC STRUCTURES FOR HIGH PERFORMANCE APPLICATIONS

- 2011 -

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BRIEF REPORT

concerning the results obtained by the project team in the period October ^{5th}, 2011 - December 15th, 2011

Objective 1. Synthesis and characterization of polyimides (PIs) containing the alicyclic dianhydrides (DOCDA and BOCA) for high performance alignment layers.

Associated activities:

- 1.1. Scientific Documentation;
- 1.2. Purification of monomers and solvents;
- 1.3. Synthesis of PIs based on DOCDA and BOCA;
- 1.4. PIs structure confirmation by IR and ¹H-NMR spectroscopy

Objective 1. Synthesis and characterization of polyimides (PIs) containing the alicyclic dianhydrides (DOCDA and BOCA) for high performance alignment layers.

1.1. Scientific Documentation

Complex polymer systems for applications in modern technology, require:

* development of new polymers with special characteristics by the proper selection of the components system so that to generate polymeric structure with performance properties for desired applications.

The literature data on polyimide (PI) show that:

- a) the incorporation of alicyclic units in a **PI** structure promotes the growth of solubility and thermal stability, negligible birefringence, low refractive index and loss of color (all associated with the absence or inhibition of intra- and/or inter-molecular interactions with charge transfer (CT), multiple link and the alicyclic structure rigidity);
- b) the aliphatic **PI** structures compared with the aromatic ones, present a lower dielectric constant and a greater transparency, as a result of their lower density and molecular polarity and a lower that reduce the probability of the intra- or inter molecular CT interactions.

1.2. Purification of monomers and solvents - Synthesis of **Pis** proposed for this step was carried out using a number of materials that have been purified by various methods which are shown in Table 1.

Table 1. Materials used in polymer synthesis and purification methods

Chemical name	Provider	Abbrev.	Purification method
N-methyl-2-pirolidone	Aldrich	NMP	Vacuum distillation at 10 mmHg, dried on CaH ₂ , stored on 4 Å molecular sieves
5-(2,5-dioxotetrahydrofuryl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride	Merck	DOCDA	Recrystallization from acetic anhydride, vacuum dried at 160°C, p.t. = 170°C
Bicyclo[2.2.2]-7-octene-2,3,5,6-tetracarboxylic dianhydride	Aldrich	BOCA	Recrystallization from acetic anhydride, vacuum dried at 160°C, p.t. = 248°C
4,4'-(Hexafluoroisopropylidene)-diphthalic anhydride	Aldrich	6FDA	Recrystallization from acetic anhydride, vacuum dried at 160°C, p.t. = 244°C
4,4'-oxydianiline	Aldrich	ODA	Recrystallization from ethanol; p.t. = 189°C
4-(4-{[4-(4-aminophenoxy)-phenyl]sulfonyl}phenoxy)aniline	Aldrich	p-BAPS	Recrystallization from ethanol; p.t. = 195°C
4,4'-(Hexafluoroisopropylidene)-bis(p-phenyleneoxy)dianiline	Aldrich	6FADE	Used without purification; p.t. = 160°C

1.3. Synthesis of PIs based on DOCDA and BOCA

Seven homopolyimide (**hPI**) were synthesized. The synthesis strategy involves the control of chain flexibility and segmental mobility by *incorporation of alicyclic groups and flexible links*, so that the strong intra- and inter-molecular interactions which exist in the classical PIs to diminish by the separation of

electronic chain segments and the destruction of the polymer chain co-planarity, conjugation and symmetry. At this stage it is proposed the PI chain chemical transformation to obtain soluble and transparent PIs by:

- * *incorporation in the polymer backbone of alicyclic dianhydride: DOCDA* (a large, nonsymmetrical and flexible molecule) and BOCA (rigid and symmetric molecule) to increase the solubility (by induction of weak polymer-polymer interactions) and to preserve the thermal stability (due to the multiple bond from the alicyclic structure);

- * *incorporation into the backbone of flexible links (-O-, -SO₂-, -C(CF₃)₂-)* which decreases the polymer chain rigidity, inhibit packing and reduces the intermolecular interactions, increasing the solubility and decreasing the color intensity.

Six partially aliphatic hPIs derived from the proposed alicyclic dianhydrides DOCDA and BOCA (PI1-PI6) and an other aromatic PI based on the 6FDA dianhydride (PI7) were synthesized. The chemical structure of the synthesized PIs and the used monomers and their corresponding abbreviations are shown in Figure 1.

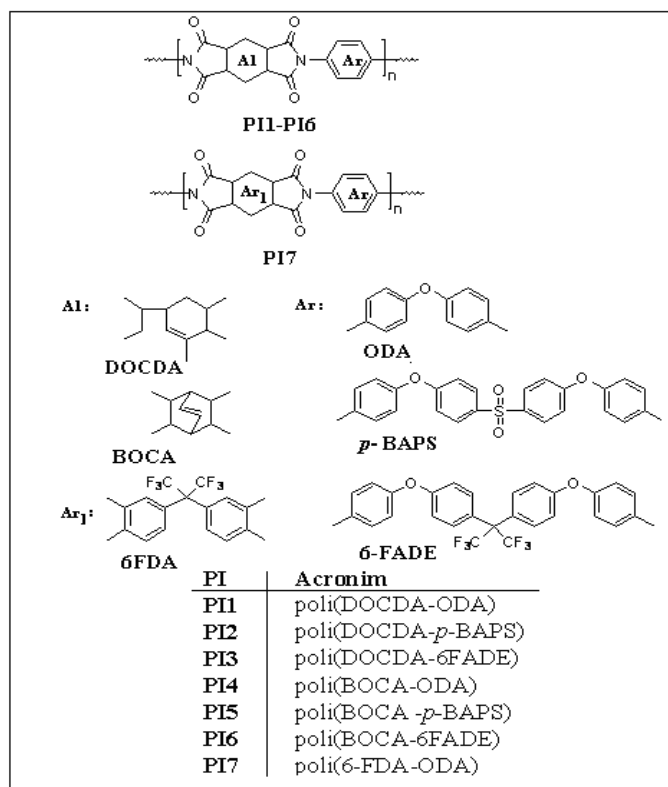


Figure 1. The chemical structures and the abbreviations for the PIs and the used monomers

Polymer films preparation

Pure PI films were obtained by thermal imidization of their corresponding PAA films cast on glass substrate. The PAA films were initially held for 10 hours at 80 ° C for slow solvent evaporation. Semi-dried PAA films were further thermally treated and converted to the PI form according to the following heating program: 120 ° C, 160 ° C, 180 ° C, 210 ° C and 250 ° C (one hour at each temperature). After removal from the glass, the resulting films were dried in vacuum for 24 hours at 65° C.

Blend PI films were obtained for the system PI1/PI7 by imidization of the corresponding PAA mixture films. The each polymer proportion in the blend ranged from 25% grav to 75%grav. The mixtures were shaken 10 h at rt, were degassed and molded on the glass substrate, followed by the same protocol as that shown for the pure PI films. The thickness of the resulting films was about 40 μm.

PIs have been prepared by a solution polycondensation reaction in two steps which involves: a) the polyamide acid (PAA) preparation and b) the thermal imidization of PAA to the PI form (6h at 180 ° C).

The polymers were obtained by the polycondensation reaction of equimolar quantities of diamine and dianhydride, under anhydrous conditions using NMP as the solvent.

1.4. PIs structure confirmation by IR and ¹H-NMR spectroscopy

IR spectra confirmed the synthesized polymer structures (PI1-PI7):

a) *by the presence of absorption characteristic peaks* for:

- the *imide structure*, to approx. 1770 cm⁻¹ and 1710 cm⁻¹ (associated with symmetric and asymmetric stretching vibration of C = O imide), approx. 1380 cm⁻¹ (associated with the C-N stretching vibration of the imide ring) and approx. 775-760 cm⁻¹ (associated with imide ring deformation vibration);
- the *aromatic structure* at approx. 1510 cm⁻¹ (pic attributable link = CH in the benzene ring);
- the *aliphatic structure* (PI1-PI6) at 2930-2920 cm⁻¹ (absorption aliphatic groups associated of DOCD A and BOCA sequences);
- the *ether bridges* (PI1-PI7) at about 1230 cm⁻¹ (associated with - O- aromatic);

b) *by the absence of peaks* at approx. 3350-3450 cm⁻¹ (broad band, associated with the NH group of the amide bond) and 1650-1660cm⁻¹ (associated with the C = O amide bond) which signify the completion of the thermal imidization reaction of PAA to the final structure of PI.

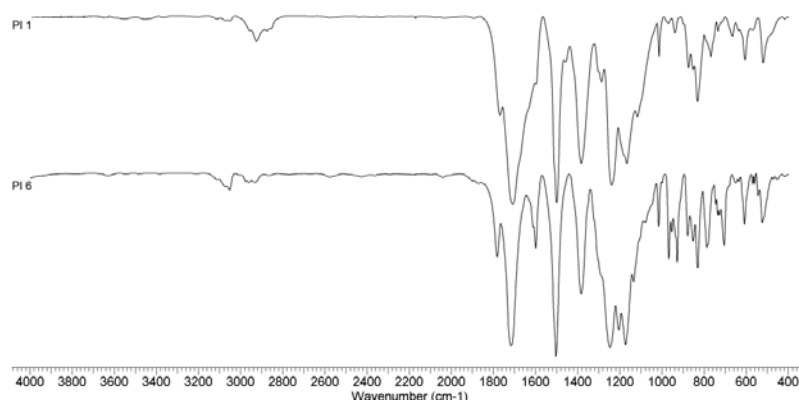


Figure 2. IR spectra of polyimides PI1 and PI6

¹H NMR characteristic spectral data for the synthesized PI1-PI7 are listed in Table 2.

Table 2. ¹H-NMR spectral data for the PI1-PI7

PI	^{a,b} ¹ H-NMR Spectral data / δ (ppm)
PI1	7,33 (m, 4H, orto -N<); 7,17 (m, 4H, orto -O-); 3,58-2,38 (m, 5H, CH, CH ₂ , IM, SIM, cAl); 2,17-1,73 (m, 5H, CH ₃ , CH ₂ , Al, cAl); 1,72- 1,04 (m, 2H, CH, CH ₂ , cAl)
PI2	7,72 -7,70 (d, 4H orto - SO ₂ -); 7,16 -7,14 (m, 12H orto - O - și orto -N<); 3,58-2,37 (m, 5H, CH, CH ₂ , IM, SIM, cAl); 2,17-1,87 (m, 4H, CH ₃ , CH ₂ , Al, cAl); 1,50- 1,02 (m, 3H, CH, CH ₂ , cAl)
PI3	7,38 -7,34 (m, 4H orto 6F); 7,22 -7,14 (m, 12H orto - O - și orto -N<); 3,55-2,37 (m, 5H, CH, CH ₂ , IM, SIM, cAl); 2,17-1,88 (m, 4H, CH ₃ , CH ₂ , Al, cAl); 1,51- 1,03 (m, 3H, CH, CH ₂ , cAl)
PI4	7,20 (m, 4H, orto -N<); 7,13 (m, 4H, orto -O-); 6,30 (s, 2H, HC=, cAl); 3,53 (s, 2H, CH, cAl); 3,42 (s, 4H, CH, cAl)
PI5	7,71 -7,68 (d, 4H orto- SO ₂ -); 7,20 -7,12 (m, 12H orto - O -și orto -N<); 6,31 (s, 2H, HC=, cAl); 3,53 (s, 2H, CH, cAl); 3,42 (s, 4H, CH, cAl)
PI6	7,40 -7,38 (d, 4H orto 6F); 7,22 -7,12 (m, 12H orto - O - și orto -N<); 6,31 (s, 2H, HC=, cAl); 3,55 (s, 2H, CH, cAl); 3,43 (s, 4H, CH, cAl)
PI7	8,17-8,15(d, 2H orto 6F); 7,96 -7,94 (d, 2H orto C=O); 7,74 (s, 2H orto 6F); 7,44 -7,22 (d, 4H orto -N<); 7,39 - 7,37(d, 4H orto - O -)

^a Multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet; Solvent DMSO-d₆; internal reference TMS ^b Abbreviations: IM = imide, SIM = succinimide, Al = aliphatic, cAl = cycloaliphatic

The results show that the proposed polyimides (PI1-PI7) were synthesized and the estimated structures were confirmed by IR and ¹H-NMR spectroscopy, according to the objective 1 and the associated activities at this stage of project.

The obtained polymers are soluble in aprotic dipolar solvents and are able to form transparent and flexible films.

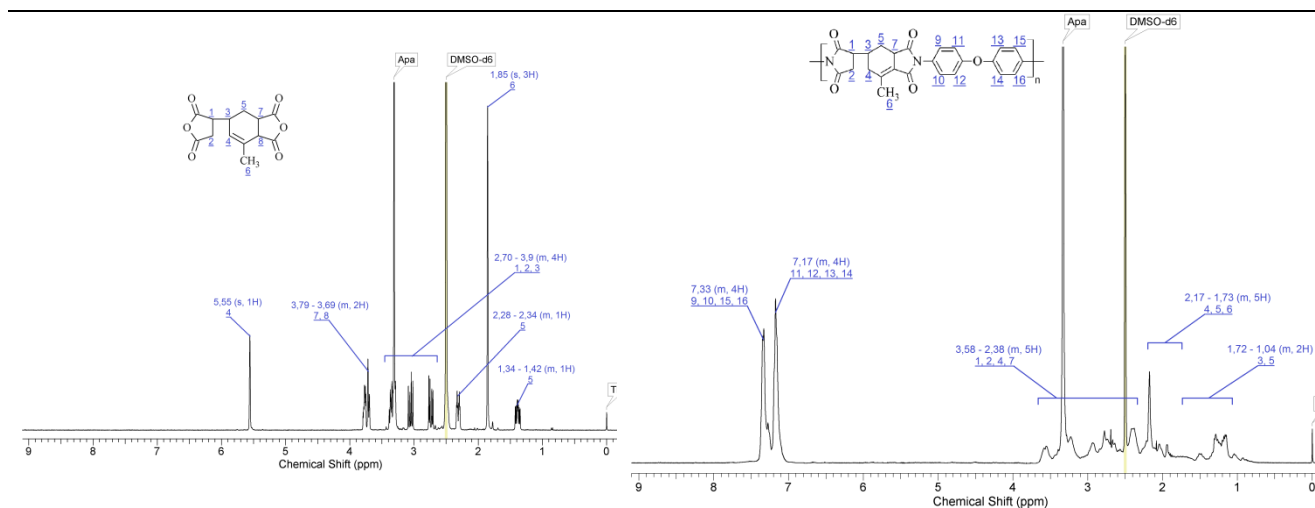


Figure 3. ¹H-NMR spectra: a) monomer DOCDA; b) polymer PI1

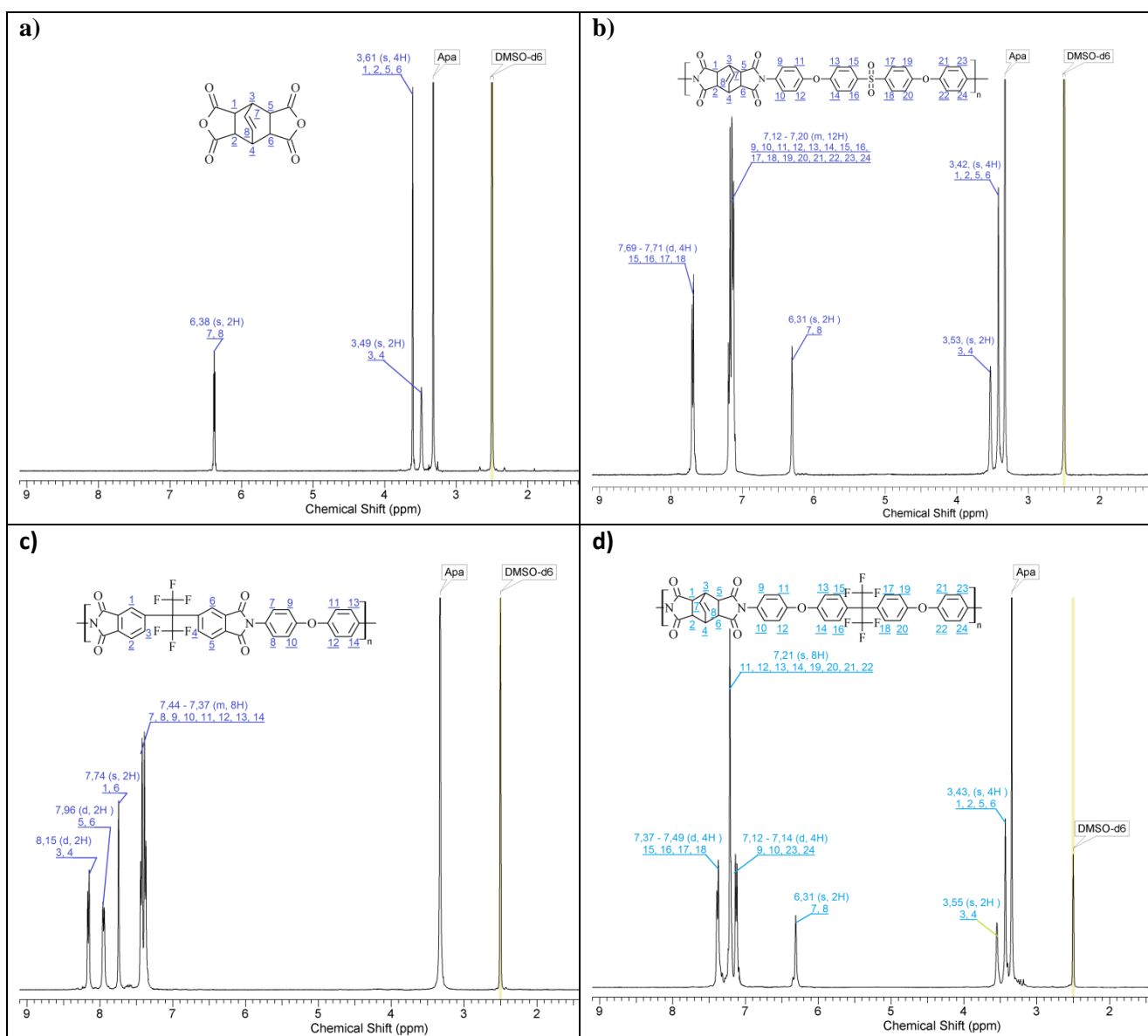


Figure 4. ¹H-NMR spectra: a) monomer BOCA; b) polymer PI5; c) polymer PI6; d) polymer PI7

Development of industries based on modern technologies has intensified the research into new polymeric systems with high thermal stability, and certain functional properties required for specific uses. In this context, a first complex binary polymer system consisting of polyimides PI1 (poly (DOCDA-ODA)) and

PI7 (poly (6FDA-ODA)) - Scheme 1 - was developed and studied in terms of thermodynamic optimization and morphological characteristics under the influence of external factors.

The results, with potential applications perspectives are summarized in section 1.5. of this material.

1.5. Effect of the aliphatic / aromatic structures on some properties of polyimide blends

The properties in solution and in solid state for a complex polymer system consisting of two pure PIs and their mixture in various compositions and were studied.

Figure 5 presents the FTIR ATR spectra for polymers selected (PI1 and PI7) and the mixture PI1 / PI7 50% grav/50%grav. It is noted: * absorptions typical for the imide structure at: 2930-2920 cm^{-1} (PI1) associated with the sequences aliphatic; at 1192-1209 cm^{-1} due to symmetrical and asymmetrical stretching vibration of -CF 3 (PI7); and the absence of peak at approx. 3400 cm^{-1} (NH amide) and approx. 1640 cm^{-1} (C = O amide), for all examined systems, indicating the complete imidization of PAA in the final PI structure.

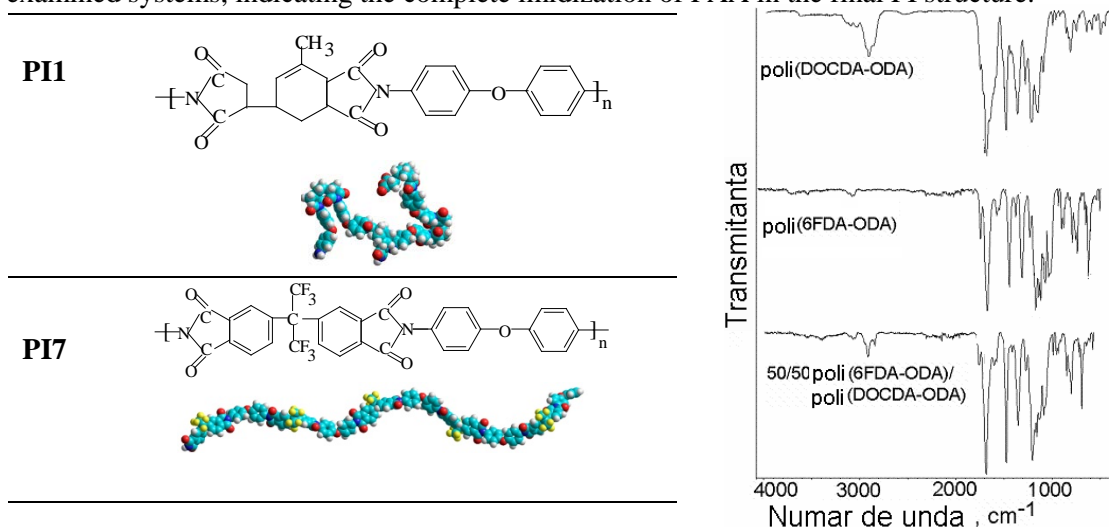


Figure 5. FTIR ATR spectra for polymers selected PI1 and PI7 and the mixture PI1 / PI7 50/50 grav/grav.

DSC analysis. One of the most important ways to assess polyimide blends miscibility is to determine the glass transition *temperature* (T_g) and its dependence on composition. The experimental data of differential scanning calorimetry (DSC) for the mixture of poly (6FDA-ODA) / poly (DOCDA-ODA) demonstrated through the T_g temperature variation with composition, the system miscibility over entire range of compositions. In this respect, theoretical studies have been conducted based on Gordon-Taylor and Couchman equations concerning these temperatures and the deviations from additivity law in order to evaluate an adjustable parameter, $k > 0$, which is a measure of miscibility and intermolecular interactions of the components of system. Positive deviations from additivity curve obtained from T_g temperatures are an indication of the inter-catenary interactions generating a good strong miscibility for all polyimide blends compositions considered.

1.5.1. Optical properties of polyimide system poly (6FDA-ODA / poly (DOCDA-ODA))

Since in practice the volume of material properties play an important role, the first evaluation was made on optical characteristics, namely the refractive index and transparency, considering also the determination of the corresponding dielectric constant in the visible frequency spectrum, through the Maxwell relationship.

Studies on transparency and optical energies. Optical transparency of poly(DOCDA-ODA), poly(6FDA-ODA) films and their mixtures for different compositions was evaluated in the range of 200-1100 nm wavelength. It is well known that relatively high permittivity, low transparency and the color of aromatic PI are generated by inter- and intra-molecular CT. The efforts for overcoming these types of interactions have included the incorporation of groups that minimizes the polarizability of atoms, from aliphatic and fluorinated compounds. In this case it was attempted to increase transparency by introducing alicyclic dianhydride DOCDA with flexible structure, which through the conformational influences induced to the polymer can reduce inter-chain interactions. Transparency obtained for the system poly(6FDA-ODA) /

poly(DOCDA-ODA) indicates homogeneity of the mixture. It is found that the transmittance of the film **poly(DOCDA-ODA)** is 90% in the 450-1100 nm, comparable to that of **poly(6FDA-ODA)** of 92%. The reason is the generated by the fact that alicyclic structure from DOCDA sequences may reduce the probability of $\pi-\pi^*$ transition, due to the low polarizability induced to the polymer chain, in a similar manner like-CF₃- group from the bridge hexafluoroisopropylidene (6F). In addition, it is observed that the presence of DOCDA dianhydride sequences from PI structure further increase transparency in the visible range to the UV region. An effect in improving the transparency it is given by -O- bridge from the diamine residues (ODA). The transmittance data it was analyzed the influence of chemical structure and the structural disorder on the optical properties and electronic transitions that probable affect PI transparency by applying the Tauc method for amorphous semiconductors. It is found that the values obtained for the optical energies (band gap, E_G , Urbach E_U energy – caused by electric fields produced by impurities or fluctuations in density and Tauc E_T energy - sensitive to structural defects) increase with increasing transparency, and are higher for **poly(6FDA-ODA)**, followed by the 50/50 mixture of **poly(6FDA-ODA)** / **poly(DOCDA-ODA)** and **poly(DOCDA-ODA)**.

Refractive index and relative permittivity. The refractive indices were evaluated experimentally for the studied PI (Abbé refractometer, 25 ° C), and theoretically - using the Lorenz-Lorentz equation. The obtained values for refractive indices are in the range of 1.56 to 1.69, and are specific to transparent materials. They reflect the effect of synergism induced by the presence of fluorinated structure (6FDA), aliphatic (DOCDA) and ether linkage (ODA) which ultimately reduces the relative permittivity values, in the range of 2.44 to 2.86 (compared with PI of high CT for which > 3).

1.5.2. Viscometric and viscoelastic properties of polyimide system poly (6FDA-ODA/poly (DOCDA-ODA)

Because most times the processing of the polymer starts from solution phase, we studied the rheological behavior of both PIs and their corresponding mixtures, under the influence of composition, temperature and concentration, in conjunction with their chemical structure. The study noted the influence of different flexibility of polymers and the interactions that occur in the system.

Polyimides dynamic viscosity. It was found that pure polyimides, such as **poly (DOCDA-ODA)** and **poly (6FDA-ODA)**, exhibit Newtonian flows with constant viscosity in the considered shear rates domain of 10^{-1} - 10^3 s⁻¹. Summed effects of flexible ether groups of ODA sequences and of 6F groups from 6FDA sequences (last inducing steric hindrance) - alter the chain packaging and determine maximum viscosity for **poly (6FDA-ODA)**, compared with **poly (DOCDA- ODA)**. The flow behavior of these PIs mixtures, for equal concentrations and different compositions revealed that the viscosity decrease with increasing content of **poly (DOCDA-ODA)**. At the same time, there are two Newtonian regions at low and high shear rates, between which there is also a domain of thinning. The latter decreases with increasing of the **poly (DOCDA-ODA)** content in the system. Thus, it appeared that for mixed PIs, the flow indices values are slightly lower than unity as compared to pure PIs and the consistency indices present higher values as induced by **poly (6FDA-ODA)** component from the system. Low activation energy of flow, which implies a low energy barrier for moving an element of the fluid, is obtained for the **poly (DOCDA-ODA)** - polymer with higher flexibility. Activation energy increases with increasing content of **poly (6FDA-ODA)** in the mixture. The energy barrier may be related to the phenomenon occurring among the chains ("entanglement"), and also to the interactions along the chain segments, depending on the flexibility of the considered PI that increase in the following order **poly (6FDA-ODA)** < **poly (DOCDA-ODA)**.

Viscoelastic properties The effect of chemical structure and composition on viscoelastic properties of the polyimide mixtures is reflected in the mobility of the segments shear field. Higher values of the elastic modulus, G' , lower values of viscous modulus, G'' , and higher values of frequencies for which $G' = G''$ were obtained for more flexible PIs and polyimide compositions of mixtures with more flexibility. The increase of partially aliphatic PI in the mixture **poly (DOCDA-ODA)** increases the frequency for which $G' = G''$; the relative amount of energy dissipated in the material during an oscillatory cycle is lower for the mixture of **poly (6FDA-ODA)** / **poly (DOCDA-ODA)** than for pure components, with the increasing trend with enhancing the content of **poly (DOCDA-ODA)**.

1.5.3. Surface properties of polyimide poly (6FDA-ODA)/poly (DOCDA-ODA) system.

Surface tension parameters. Literature shows that by increasing aliphatic character of the PI structure and by introducing ether bridges, the hydrophobicity of the polymer film surface increases. Evaluation of surface tension parameters by geometric mean method and acid / base, shows that the disperse component values of the aromatic PI **poly (6FDA-ODA)** film are smaller, and polar components are larger than the corresponding partially aliphatic **poly(DOCDA- ODA)**. On the other hand, the studied mixtures are characterized by a low hydrophilicity. The presence of the 6F group (6FDA sequences), alicyclic structure (DOCDA sequences) and ether linkage (ODA sequences) induces a cumulative effect on improving the hydrophobicity of mixtures PI and also the changes the electron donor and electron acceptor interactions. For the analyzed binary system, the electron-acceptor parameter of the polar component increases the upto a volume fraction of approximately 0.5 **poly (DOCDA-ODA)**, and then decreases, while the electron-donor parameter of the polar component decreases to the same composition, then increases. The results reflect the synergism influence of comonomers which, by their chemical structures containing specially selected 6F bridge, aliphatic and asymmetric cycles and ether groups, influence the hydrophobicity and electron donor and electron acceptor characteristics of binary mixture of PI.

Interfacial free energy and surface free energy. Values of surface free energy, ΔG_w - expressing the balance between hydrophilicity and hydrophobicity of the surface - shows a high hydrophobicity ($\Delta G_w > -113 \text{ mJ} / \text{m}^2$) for all **poly(6FDA-ODA) / poly(DOCDA- ODA)**blend compositions. Interfacial free energies, ΔG_{sws}^{GM} - evaluated from interfacial tension in solid-water γ_{sl} , confirmed hydrophobic characteristics of analyzed polymer mixtures. Due to the hydrophobicity of the investigated surface, the work of spreading of water $W_{s,w}$ presents negative values in agreement with negative values of interfacial free energy of mixed polyimides, the work of water adhesion to the surface is smaller than the work of water cohesion to surface.

Surface polyimide morphology. The PI surface roughness and morphology are dictated by the existence of nodular formations that are determining factors in regard to the adhesion of the PI to various inorganic components of the devices in which they are applied.

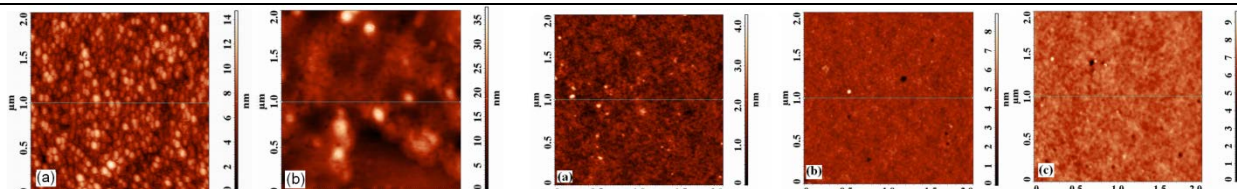


Figure 6. AFM images:
(a) **poly(DOCDA-ODA)**
(b) **poly(6FDA-ODA)**

Figure 7. AFM images:
poly(6FDA-ODA)/poly(DOCDA-ODA) blends
for different compositions: 25/75 (a), 50/50 (b) and 75/25 (c)

*Roughness parameters and nodules dimensions (AFM images) changes depending on the PI structural flexibilities: * decrease in the order of **poly (6FDA-ODA)** > **poly (DOCDA-ODA)** - surface morphology influence - and * decreases with increased hydrophobicity (the increasing of the PI partially aliphatic **poly (DOCDA-ODA)** in the system).*

1.5.4. Biocompatibility studies of poly(6FDA-ODA)/poly(DOCDA-ODA) polyimide system

Polyimide surfaces have considerable technological potential for various applications due to their hydrophobicity. In this context, we studied blood compatibility with polymer surfaces and how they interact with some of its components, such as red blood cells and platelets. Starting from the studied PI and the blood surface tension parameters we determined the work of spreading for the red cells, and, the platelet, respectively. Blood exposed to the surface of a biomaterial can generate adhesion of red blood cells and the degree of adhesion decide the life of the implanted biomaterial, or can activate blood clotting, printing an important role in the immunological cascade. The impact of cell adhesion on thrombogenicity and immunogenicity, that dictates the compatibility of considered polyimide mixtures with the blood, is summarized in Figure 7, together with the parameter which describes the hydrophobicity.

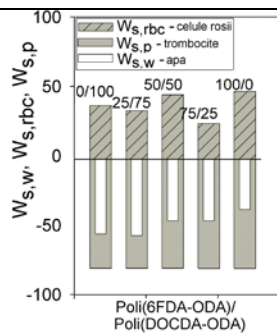


Figure 8. Spreading work of water, red blood cells and platelets from the blood to the surface of pure or mixed polyimide PI films

Were obtained:

- Negative values of $W_{s,w}$ denoting the surface hydrophobicity of PI, i.e. water cohesion > water work adhesion to the polymer surface;
- Positive values of $W_{s,rbc}$ denoting compatibility PI surface, that is RBS work of adhesion > RBC work of cohesion;
- Negative values of $W_{s,p}$ denoting platelet work of cohesion > platelet work of adhesion to the surface, helping to prevent blood clotting.

The conclusions of this study contribute to the optimization of the results for obtaining imposed parameters from the thermal, optical, dielectric, as well as surface properties and biocompatibility point of view, in the case of complex polyimide systems, for applications in microelectronics and/or biomedical fields.

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The objectives for this stage were fully realized and some results were included into a manuscript elaborated in 2011, finalized and published in 2012.

Dissemination of the results

Surface Properties and Blood Compatibility of Some Aliphatic/Aromatic Polyimide Blends, Simona-Luminita Nica, Camelia Hulubei, Iuliana Stoica, Ghiocel Emil Ioanid, Silvia Ioan, *Polym. Eng. Sci.*, [DOI 10.1002/pen.23260](https://doi.org/10.1002/pen.23260)

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