

Scientific report

Regarding the project implementation in the period October–December 2011

Project title: “Advanced researches related to the behavior of multicomponent polymer systems under simulated environmental factors action”

Objectives:

1. Comparative analysis of the current status on the behavior of polymers under environmental factors
2. Documentation in modern instrumental techniques and methods
3. The implementation of a management and administrative plan

Introduction

Establishment of resistance of aging polymeric materials under environmental factors now gained a new approach. This deals with tracking changes in the physico-chemical properties and/or in the polymers structure, generated by the exposure to the main degradative factors that act in the environment such as: light, heat and humidity. It is known that environmental factors induce adverse effects on polymer materials, which may vary from changing their surface properties (color, gloss, contact angle) with negative implications on the aesthetic aspects of the material, up to the overall deterioration of the mechanical properties and premature shortening of lifetime. Degradation of polymer materials represents all complex processes, reactions and changes that occur in chemical structure, morphology and their properties under the action of different degradative agents. As a result of the degradation process new products are formed that retain the macromolecular structure but whose physical and chemical properties are modified. Degradation effects occur after a period of time, called induction period, consisting of all changes in macroscopic properties and are usually followed by disintegration. Induction period coincides with the lifetime of the material, considered as the time elapsed until a 50% loss of initial properties. It was shown that the combined action of two or more stress agents leads to an increase in the rate of aging and a shortening of life. The chemical structure of polymers is important in evaluating of degradation degree in the artificial aging and in the biological degradation processes. Evaluation of effect of environmental factors on properties of polymeric materials can be achieved by laboratory tests of accelerated aging or by following the aging in natural conditions. Formation of degradation products depends on the type of polymer, the mechanism of disintegration and the type of additives present in polymer material. Mixtures of synthetic polymers / natural polymers represent a new class of materials, with applications as biomaterials. The important applications of these polymeric materials are due to the superior mechanical properties, ease of fabrication and of the low prices. The natural polymers for biotechnological and biomedical applications, have been extensively studied, due to their unique combination of properties including non-toxicity, biodegradability and biological compatibility.

1. The polymers behavior under environmental factors

Aging is a generic name used to define the slow degradation of various polymeric materials exposed to environmental factors. The mechanism of the degradation process depends on the type of material, but is usually caused by a synergistic combination of natural factors including moisture, sunlight, heating / cooling, chemical agents, biological agents and abrasion by wind exposure

Primary photochemical reactions occur as a result of the activation of macromolecules by direct absorption of light radiation. In an inert atmosphere of nitrogen or argon degradative reactions occur, including splitting of macromolecules and crosslinking, while in the presence of air, oxygen is able to initiate photo-oxidative processes. Photo-oxidative degradation processes of polymers take place by radical intermediates, carried every time by following the steps of a chained mechanism (Figure 1).

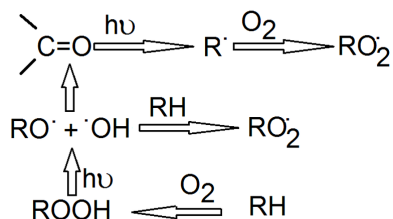


Figure 1. The photo-oxidative degradation mechanism of polymers

Polyvinyl alcohol (PVA) is a polymer with a number of exceptional features (film forming capacity, emulsifying and adhesive properties, resistance to oils, no smell, non-toxic, biodegradable, biocompatible). PVA polymer-based materials are often exposed to UV spectrum of sunlight or artificial sources.

UV irradiation is sometimes used as a cross-linking agent in order to obtain new materials from mixtures of polymers. The photochemical stability of PVA films in the presence of collagen was studied. UV radiation was used to obtain films of mixtures of starch/PVA. The thermal stability of films increased after incorporation of lignin in PVA because the lignin has a protective role against UV radiation. Photochemical stability of PVA can be modified by incorporating small concentrations of chromophores that absorb a large amount of UV radiation, protecting the polymer against photodegradation.

Cyclodextrins are cyclic oligosaccharides, natural and semi-synthetic, with a hydrophobic central cavity, able to incorporate various molecules of the same polarity with the formation of inclusion complexes. Their main applications are due to solubilizing properties and high dissolution rate. Generally, cyclodextrins are in the form of hydrates, containing various amounts of water, depending on the mode of obtaining and storage conditions. The thermogravimetric analysis and differential scanning calorimetry are the main techniques used for physico-chemical characterization of these oligosaccharides and of inclusion complexes. Lately, various methods such as TG-FTIR coupled, TG/DTA, FTIR, TG-MS, TG/DTA-MS, DTA or DSC, XRD (X-ray diffraction powder samples) are also used. All these methods allow simultaneous determination of changes of mass and energy, together with the structural/functional identification, and of the decomposition products. Generally, natural cyclodextrins have similar thermal behavior, the only difference being regarding water content, temperatures of thermal degradation and losses of mass at certain values of temperature. B-cyclodextrin thermal degradation is performed in three steps:

- water loss occurs by heating from room temperature up to 120°C, depending on experimental conditions (crucibles with or without lids, static or dynamic conditions);
- thermal degradation - accompanied by oxidation in air - a process that begins over 250°C in solid state and continues in the melt state until about 300°C;
- burning in air at temperatures above 300°C.

Wood is a composite material with multiple applications. Aging, in this case, is a surface degradation process, initiated mainly by solar radiation and by other factors. Wood aging is mainly determined by the fraction of ultraviolet (UV) with wavelengths greater than 300 nm from the whole solar spectrum. The process of photo-oxidation or photochemical degradation affects only the wood surface. Wood degradation starts immediately after exposure to solar radiation, accompanied by color changes and then the wood surface begins to slowly erode. UV radiation has enough energy for photochemical degradation of structural components of wood (lignin, cellulose and hemicellulose) - Figure 2. The polymers from the wood composition behave differently during the aging process -Figure 3. Variations in photo-stability depend mainly in the differences in chemical structure and specially of the functional chromophore groups. Metal ions and other impurities that are introduced during some wood treatments can initiate damage under the light action. Chemical modifications and various other treatments may significantly contribute to improving dimensional stability and to decreasing of stress factors that act on the wood properties.

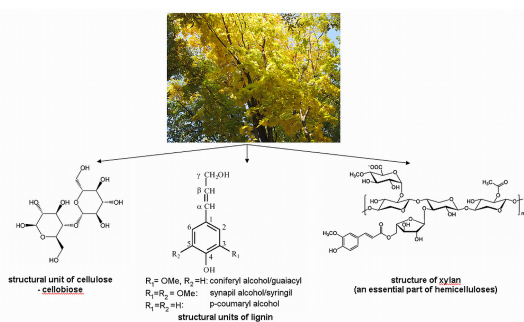


Figure 2. The chemical structure of the cell wall of plant biomass

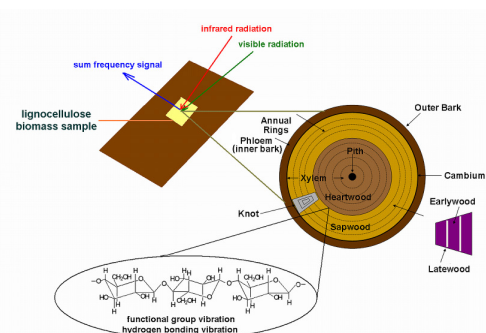


Figure 3. Schematic representation of the light action on woody biomass

The current trend of obtaining multicomponent systems has led to the synthesis and study of some semi-interpenetrated polymer networks based on natural polymer/synthetic polymer with collagen, sensitive to changes in environmental conditions. Such polymeric networks may be obtained by using polymers or monomers sensitive to changes in external parameters, such as temperature, pH, chemical composition of solvent, presence of electric field or of light, with reversible swelling modifications or changes in the chains conformation. In terms of applicability, the semi-interpenetrated networks may be used in various fields, such as pharmaceutical, regenerative medicine,

agriculture and wastewater purification or obtaining of sensors. Collagen may be modified by intra- and intermolecular crosslinking which contributes to the formation of fibrils and fibers, that may be used for obtaining of macroscopic tissues. Supplementary cross-linking of collagen by treatment with crosslinking agents (based on chromium salts or aluminum, with formaldehyde or glutaraldehyde, etc.), by physical treatment (UV radiation, freeze drying, heating) or by blending with other polymers (acid hyaluronic PLA, PGA, PLGA, chitosan) are designed to increase mechanical strength and resistance to enzymes action, to increase the biodegradation time and to limit swelling characteristics and solubility. All sterilization processes generate changes more or less in the collagen structure, making it more susceptible to enzymatic degradation in vivo, reducing its availability to support host tissue regeneration; the most accurate and efficient method of collagen sterilization is the exposure to γ rays or to UV radiation. Temperature variations cause changes in collagen structure, especially in the three polypeptide chains untwisted region. Some properties, such as high mechanical strength, temperature resistance and biodegradation of collagen fibers are industrially important. In vitro chemical cross-linking of collagen materials can be used to improve the thermal stability.

2. Investigation methods of degradability

In recent decades aging studies of polymeric materials have shifted the interest from simple monitoring of properties changes, occurred due to the influence of environmental factors, to structural investigations by using modern techniques such as: Fourier transform infrared spectroscopy (FTIR), mass spectrometry (MS), nuclear magnetic resonance ($^1\text{H-NMR}$), optical and electronical microscopy and atomic force microscopy (AFM) with which the mechanisms of the degradative reactions are identified. Sophisticated mathematical methods may also be applied in providing the possibility of predicting materials lifetime, the design of new materials, sustainable, and predetermined lifetime intended for specific operating conditions with reduced negative impact on the environment. Analysis of chemical modification of polymeric materials occurred during natural or accelerated aging is not standardized, as is the case of the physico-mechanical properties. FTIR method allows detailed spectral analysis, both qualitative and quantitative. FTIR spectra are frequently used for monitoring photo-chemical and photo-oxidative degradation processes that take place in polymeric materials. The use of FTIR spectroscopy shows major advantages over other methods of investigation. In this case, samples prepared in the form of films or pills may be used by other analysis and investigations (such as Raman spectroscopy etc.). FTIR technique can be extended to the study of photochemical processes occurring on the surface of samples by introducing a cell with attenuated total reflection. With this cell, IR radiation penetrates only 20 μm in depth and sample characterization is made with a high resolution. The IR spectra recorded with a FTIR device equipped with a cell of attenuated total reflection (ATR) have identified functional groups found in very small quantities localized on the samples surface. Photo-oxidative processes of the polymers are limited to surface layers due to the diffusion effect of oxygen and the low penetrability of UV radiation in the material. The specific regions of carbonyl or hydroxyl groups from FTIR or ATR-FTIR spectra provide important information on the photo-oxidative degradation of the studied materials. There exists the possibility to compare signal intensities from these regions with signal intensities specific to other groups (such as: vinyl groups, amide groups, aromatic structures) or other chemical functions which may be associated with products of oxidation reactions.

The elevated temperatures are commonly used to accelerate the aging processes in polymeric materials. Thermogravimetric analysis (TG) studies the mass changes of a polymer as a function of temperature. The following important data may be obtained: T_{onset} (defined as the lowest temperature at which mass loss is identified), T_{max} (the temperature at which decomposition reactions occur with maximum speed) or T_{final} (the temperature at which the thermal degradation process ends). On a thermogram there may be identified one or more T_{max} values, depending on the number of stages of thermal decomposition. T_{max} values are identified with the derivative curve (DTG). The final temperature of thermal decomposition (T_{end}) may be appreciated as the lowest temperature value at which a significant mass loss is not recorded during heating. By applying of simultaneous thermogravimetric analysis (TG) coupled with differential scanning calorimetry (DSC) high precision information may be obtained when compared with the situation in which the results derive from thermograms recorded with different devices. Differential thermal analysis (DTA) is a thermo-analytical technique somewhat similar to DSC. TG-DTA coupled technique allows

identification of processes accompanying thermal degradation, unlike the TG-DSC technique which is recommended to be used up to the start of thermal degradation. Assessments about fragmentations of chemical bonds and about secondary reactions, such as cyclizations and crosslinking processes, may be made. To identify the gaseous products resulted from thermal decomposition, thermogravimetric analysis devices may be coupled with other devices, such as FTIR and/or MS, able to characterize evolved volatiles. The X-ray photoelectron spectroscopy (XPS) may measure the ratio between oxygen and carbon atoms. Samples are analyzed to depths up to 100 Å. Although XPS is superior to FTIR-ATR in terms of resolution, the method does not penetrate deep enough to allow the identification of all oxidation products. An advantage of XPS to FTIR is that the method integrates all oxidation products. At the same time, XPS can not be used to establish the reaction mechanisms in absence of separation and identification possibilities of photo-degradation products.

It is well known that polymers change color under the action of UV radiation. The most popular tools that can analyze color variations are reflection spectrophotometers and colorimeters. To assess color changes, the CIEL*a*b* system may be used. In the CIEL*a*b* system, the colors which belong to the visible spectrum are expressed in three-dimensional space and on three perpendicular axes. Each color may be characterized by the combination of parameters L*, a* and b*. In this system the lightness is represented on the vertical axis (L). Lightness is a dimensionless parameter which varies between 100 and 0, values corresponding to white color (100) and black color (0). The color parameters a* and b* are represented on the two other horizontal perpendicular axes. The color factor a* describes the position on the color scale ranging from -a, value that corresponds to pure green, to +a, which corresponds to pure red. The b* color factor may also vary between the same limits, however value -b signifies pure blue, while +b pure yellow. A representation of the CIEL*a*b* system is shown in Figure 4.

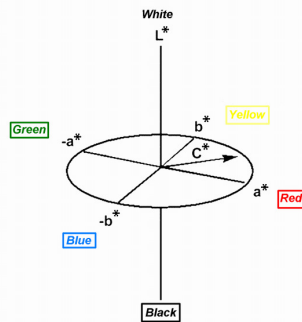


Figure 4. Schematic representation of the CIEL*a*b* system

The global color changes induced by aging may be calculated according with ASTM D 2244 with the formula:

$$\Delta E_{ab} = [(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2]^{1/2}$$

In the formula ΔE represents the color difference, L_2^* , a_2^* and b_2^* represent color parameters of aged samples and L_1^* , a_1^* si b_1^* are the color parameters of the initial sample. Yellowing of polymer surfaces that undergo photochemical treatment may be assessed using the yellowing index (YI). YI values are mainly used to quantify, by a single parameter, the color changes of polymer surfaces exposed to sunlight, artificial light or other physico-chemical factors which lead to contamination of polymeric materials surfaces with degradation products. Assessment of yellowing index value may be made with the equation:

$$YI = 142.86 \times \frac{b}{L}$$

The white index (WI) may be also calculated using the parameters which resulted from the color analyses, with the following formula:

$$WI = 100 - [(100 - L)^2 + a^2 + b^2]^{1/2}$$

Another characteristic of polymer surfaces that is changing under the influence of light is gloss. From a physical point of view the gloss of a material is a complex quantity that is associated with surface properties and how the spatial distribution of the reflected light is changed by the surface of sample. The tools used for monitoring of gloss changes are called "gloss meters". In principle, the devices measure the intensity of light that is reflected at an certain angle on the analyzed surface. The incident radiation angle may be 20°, 60° or 80°. The gloss observations are often made under an angle of 60°. Usually, the gloss of polymer surfaces decreases during photochemical aging. The decrease of

gloss is mainly related to and increase in surface roughness. The gloss changes may be evaluated by gloss retention values (G_r %), which represents the ratio between the gloss measured for the aged sample (G_f) and that for the initial sample (G_i):

$$G_r(\%) = \frac{G_f}{G_i} 100$$

The operating diagram of a gloss meter device is shown in Figure 5

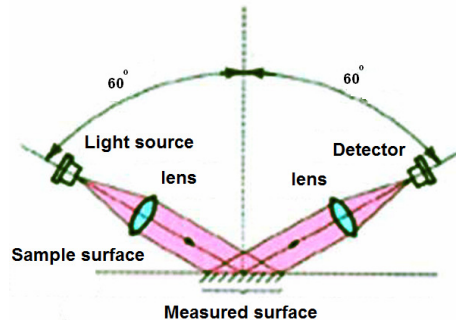


Figure 5. Schematic diagram of a Gloss-meter device. (from prospect of device Horiba Gloss Checker IG-320)

The data obtained using the methods of characterization are usually represented depending on the exposure time. Most often they are processed by the method of least squares to establish a mathematical relationship between a property and its change during aging. The mathematical relationship allows extrapolation of data resulted from measurements in order to predict from calculus the time evolution of polymer material properties. Such predictions are made on the exposure time needed to reach a certain degree of modification of the monitored properties. Investigations to establish new methods that ensure lifetime prediction of polymer materials with high confidence is underway.

3. The implementation of a management and administrative plan

The project team has performed the following activities:

- monthly work sessions with team members;
- counseling activities of PhD students by senior researchers;
- organization of panels of senior scientific team for problem solving;
- drawing an article and submitting for publication in an ISI journal;
- preliminary data presentation by participating in a scientific event (Days of "Al. I. Cuza" Iasi);
- establishing and purchasing the necessary materials to conduct research program;
- human, financial and material resource planning for the next stage
- planning of acquisition activities, preparing documentation for acquisitions;
- tracking the flow supply and the use of funds;
- preparing of the report stage.

Conclusions

The research team developed a database with recent information on the behavior of polymers under environmental factors. Documentations in modern instrumental techniques and methods for problem definition and elaboration of the experimental study also were made. For this purpose, new specialized articles were purchased and based on these, the techniques and methods for investigating degradability of polymer systems were selected. In order to develop and implement management structure, research team members met monthly and established detailed activity plans. An effective and efficient communication of administrative, technical and financial research problems, both within the team and with the contracting authority was followed. The entire research team was involved in drafting the report of stage. Young doctoral students from the team have developed and presented four scientific papers under the guidance of senior researchers in the scientific session organized by the University "Alexandru Ioan Cuza" Iasi, Faculty of Chemistry - October 28, 2011 and have sent an article for publication toward a journal with international recognition.

The research team has met its objectives with a total degree of achievement.

Project Manager,