

Synthetic scientific report

regarding the project implementation in the period 2011 – 2016

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

The aging of polymer systems involves different factors: natural (light, heat, humidity), structural and accidental (impurities, oxidation processes occurred during processing), all these being capable to significantly reduce the lifetime of materials. The mechanisms of polymers degradation are highly complex. Thus, there can be initiated photo-cross-linking or photo-oxidative reactions of polymers accompanied by decrease in average degree polymerization, increase of polydispersity and formation of chemical structures capable to modify the properties of polymers. The present project envisages increasing knowledge in the investigation upon effect of external factors on stability of multi-component polymer systems. It is aimed to create a research team comprising 4 experienced researchers and 3 doctoral students focused to acquire experimental data and to elaborate original theories in order to explain the performance loss of polymer systems during exposure to controlled environmental factors, and to evaluate their life-time prediction. It is considered that valuable scientific results will be provided, being comparable with those already existing at global level, and will contribute to increasing international visibility of Romanian research activity. The envisaged results will contribute to the finalization of doctoral theses to be realized by the young doctoral students included in the research team. The present research project is focused on the transformations of polymers with different structures under weathering conditions and especially solar light.

The following objectives were taken into consideration:

- Immobilization of dyes of different structures and concentrations onto natural and/or synthetic polymers
- Obtainment of multi-component systems containing polysaccharides
- Obtainment of semi-interpenetrating networks based on collagen or polyaspartic acid
- Study of the influence of controlled environmental factors upon polymer systems colored with dyes (solar light, heat, humidity)
- Study of the stability of the multi-component systems to weathering conditions

Stage 2011

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

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.

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.

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 (FT-IR), mass spectrometry (MS), nuclear magnetic resonance ($^1\text{H-NMR}$), optical and electronic microscopy and atomic force microscopy (AFM) with which the mechanisms of the degradation 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. FT-IR method allows detailed spectral analysis, both qualitative and quantitative. FT-IR spectra are frequently used for monitoring photochemical and photo-oxidative degradation processes that take place in polymeric materials. The use of FT-IR 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 FT-IR 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 FT-IR or ATR FT-IR 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 FT-IR 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 FT-IR-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 FT-IR 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 CIE L*a*b* system may be used. In the CIE L*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. The global color changes induced by aging may be calculated according with ASTM D 2244 with the formula:

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

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^* and b_1^* are the color parameters of the initial sample.

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 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 an increase in surface roughness. 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 are underway.

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.

Stage 2012

Objectives:

1. Obtainment of multicomponent polymer systems
2. Characterization of resulted polymer systems and investigation upon structure-properties relationships
3. Dissemination of results
4. Re-actualization and consolidation of managerial and administrative plan

1. Obtainment of multicomponent polymer systems

1.1. Semi-interpenetrated polymer networks (SIPN) based on polyurethane (PU) and epoxy resin (ER) were synthesized. PU elastomer was obtained by using 4,4'-diphenyl-methane diisocyanate and poly(ethylene adipate)diol. Epoxy resin (namely Ropoxid 501) was resulted by reaction between 4,4'-isopropylidenediphenol with epichlorhidrin. There were synthesized 6 types of SIPNs through variation of the above-mentioned two polymer components ratio.

1.2. It was performed a study related to the optimal methods in order to achieve a good fixation of some reactive dyes upon polymer substrates based on cellulosic fibres (100% cotton fabric). Thus, were investigated 5 types of reactive dyes, which were applied on polymer substrates by fleet depletion technique. The fixation capacity of reactive dyes decreased following the order: Yellow 143 reactive dye > Red 2 reactive dye > Red 183 reactive dye > Blue 204 reactive dye > Orange 13 reactive dye. The fixation degree (% covalent attached dye on substrate) increased with increasing initial dye concentration, reported to weight of painted fabric samples.

1.3. Multicomponent polymer systems under membrane form were obtained by using poly (vinyl alcohol) (PVA) and β -cyclodextrins (β -CD), in the presence of glutaraldehyde as cross-linking agent. There were resulted 4 types of polymer membranes through variation of PVA/ β -CD ratio.

1.4. A new type of hydrogel based on poly(N-isopropyl acrylamide-co-diethylene glycol diacrylate) inserted into a porous membrane of collagen. Polymer networks were obtained through radical copolymerization reaction between poly(N-isopropyl acrylamide) (pNIPAM) and three different cross-linking agents in the presence of a protein based matrix. The cross-linking agents used in reaction are as follows: diethylene glycol diacrylate (DEGDA), tetraethylene glycol diacrylate (TEGDA) and N,N'-methylene-bis-acrylamide (BisAam), respectively. The resulted polymer networks were coded as ND, NT, and NB, respectively, as a function of the cross-linking agent used in reaction.

1.5. Softwood samples were chemically pre-treated with succinic anhydride (SA). The modified wood samples were further treated with epoxy functionalized soybean oil (ESO) (obtained in the laboratory by peracid process)

in the presence of triethylamine (TEA) as catalyst. Studies regarding wood behavior under polychromatic light action (UV radiation with $\lambda > 300$ nm) after chemical pre-treatment of wood with SA and further treatment with ESO under controlled accelerated ageing processes are under progress.

2. Characterization of resulted polymer systems and investigation upon structure-properties relationships

2.1. There were synthesized 6 types of S-IPNs with composition presented in **Table 1**, the schematic representation being showed in **Fig. 1**. Structural characterization was performed by means of FT-IR spectroscopy (**Fig. 2**). The absorption band at 3324 cm^{-1} (**Fig. 2c**) is specific to O-H group vibration in ER and to N-H group vibration from PU.

Table 1. Composition of synthesized S-IPN

Sample	PU (%)	Epoxy resin (ER) (%)
S-IPN-1	95	5
S-IPN-2	90	10
S-IPN-3	85	15
S-IPN-4	80	20
S-IPN-5	70	30
S-IPN-6	60	40

Fig. 1 Structure of S-IPN: (a) PU; (b) ER

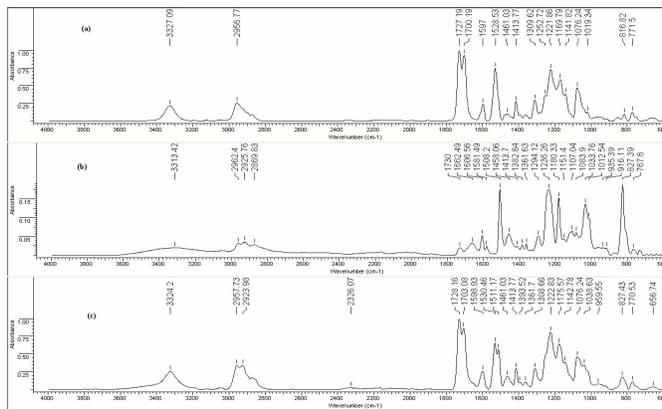


Fig. 2. FT-IR spectra for: PU (a); ER (b) and S-IPN-3 (c)

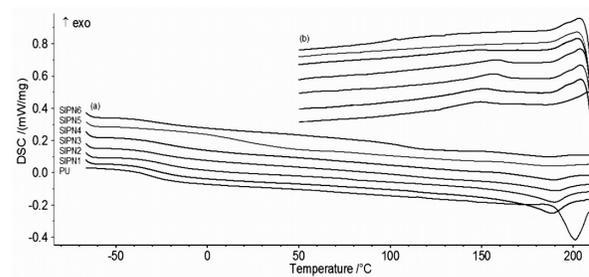


Fig. 3. DSC curves for S-IPNs and initial polymers: heating (a) and cooling (b)

The glass transition temperature values (T_g) for the synthesized S-IPNs based on PU and ER were determined by dynamic differential calorimetry method (DSC) – **Fig. 3**. It was investigated the influence of ER content upon T_g values. There were initiated miscibility studies by applying Fox and Gordon-Taylor equations. Morphology studies were performed by using electron microscopy (SEM) and optical microscopy (OM) methods.

2.2. An evaluation study and quantitative analysis for 5 reactive dyes were performed by using UV-Vis spectrophotometry method, following the maxima absorption values for validation of analytical methods to be further applied for characterization (**Fig. 4**).

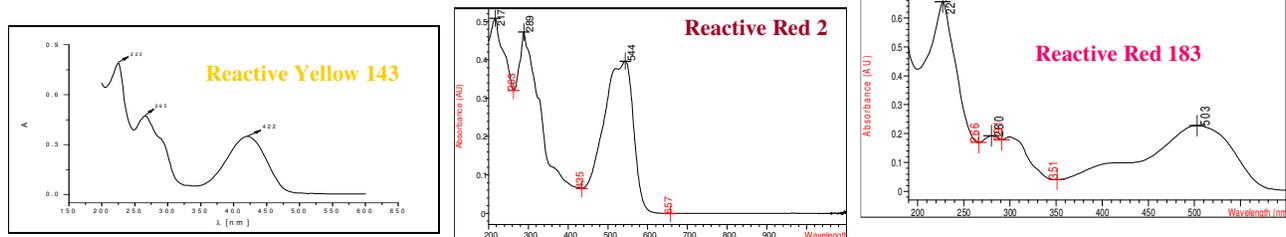
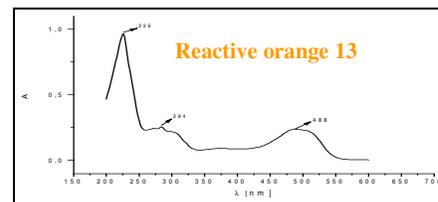


Fig. 4. UV-Vis absorption spectra for reactive dyes

The maximum absorption (λ_{max}) in visible domain for reactive dyes are as follows: 422 nm (Yellow 143 reactive dye); 544nm (Red 2 reactive dye); 503 nm (Red 183 reactive dye); 636 nm (Blue 204 reactive dye); 488 nm (Orange 13 reactive dye).



The resulted preliminary data are important for evaluation of biological impact exerted by dyes upon human organism under action of UV radiation from solar light spectrum with occurrence of photo-chemical transformations.

2.3. The effect of β -CD on the thermal stability of PVA based membranes, previously chemically cross-linked in the presence of glutaraldehyde used as cross-linking agent, was investigated. The DSC thermograms recorded for chemically cross-linked PVA/ β -CD membranes are presented in **Fig. 5**.

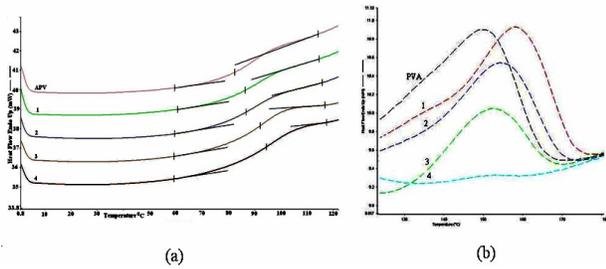


Fig. 5. DSC thermograms for PVA and PVA/ β -CD chemically cross-linked membranes: (a) 0-120 °C, (b) 125-180 °C

It can be noticed an increase of glass transition temperature T_g with increasing β -CD amount in samples. The melting temperature value exhibits the same tendency as T_g . This evolution is due to interactions occurred between the two components of the blend.

The swelling behavior investigation was performed at two different temperature values using bidistilled water, the curves being presented in **Fig. 6**.

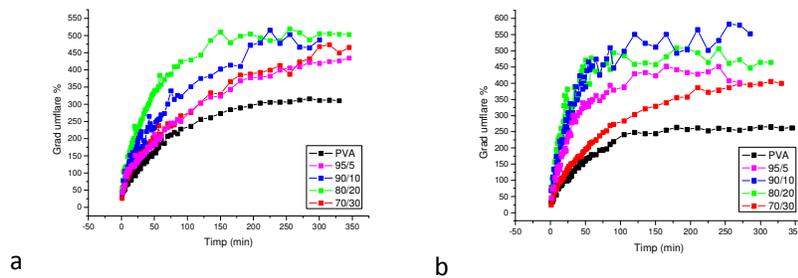


Fig.6. Swelling degree for PVA/ β -CD membranes: (a) at 25 °C, (b) at 37 °C

The swelling process is slightly influenced by temperature, a significant decrease of swelling degree being noticed at 37°C for membrane comprising 30% β -CD.

An increase of swelling degree with increasing β -CD content up to 20% is observed, while it decreases for membrane with 30% β -CD, probably due to a phase separation occurring at a high concentration value of β -CD.

2.4. Investigation of polymer structures was performed by spectral, morphological, thermal (calorimetry) rheological analyses, as well as by determination of water uptake evolution using simulated biological media.

The cross-linking reaction occurred between pNIPAM and DEGDA was confirmed by appearance of a new absorption band at 1731 cm^{-1} , attributed to the C=O group from the structure of cross-linking agent (**Fig. 7**).

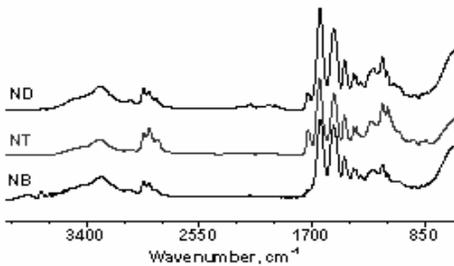


Fig. 7. FT-IR spectra for cross-linked polymer networks

FT-IR spectra recorded for hydrogels based on collagen and pNIPAM after cross-linking using different cross-linking agents present absorption bands at 2855 , 1366 and 838 cm^{-1} , respectively. FT-IR spectrum for NB polymer network type present absorption bands at 3645 - 3839 , 2361 and 1338 cm^{-1} , respectively.

Fig. 8 present the SEM micrographs recorded for the transversal sections of cross-linked polymer networks based on pNIPAM and collagen. The observed morphological differences due to the cross-linking agents are obvious. The SEM images show clearly the collagen fibres embedding within the polymer networks.

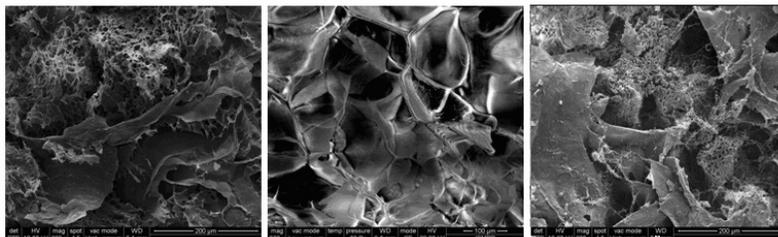


Fig.8. SEM images for polymer networks

The average pores dimension, randomly measured for 12 pores within the polymer networks, indicates a value of $3 \div 6\ \mu\text{m}$ for ND hydrogels, $10 \div 15\ \mu\text{m}$ for NT hydrogels, and $2 \div 4\ \mu\text{m}$ for NB hydrogels, respectively.

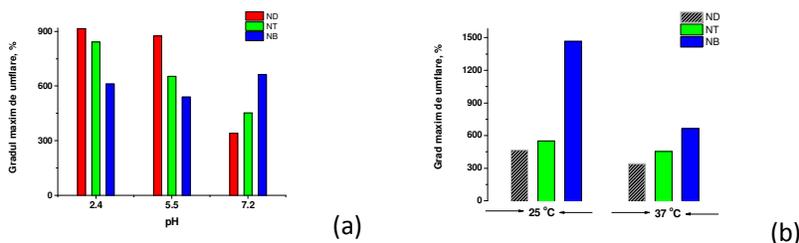


Fig. 9. Swelling degree of polymer networks at equilibrium state: (a) influence of pH and (b) influence of temperature

The hydrogels swelling occurs rapidly in the first 10 min. then the swelling degree remains approximately constant.

The NT hydrogels present a uniform structure and good pores dispersion with very-well individualized walls, while the ND polymer networks exhibit an adequate embedding of collagen fibers within the pNIPAM polymer matrix. The NB hydrogels have a similar morphology with that of ND polymer networks, excepting the pores dimension which is smaller and a weak embedding of the two polymers. The presence of some supplementary functional groups (isopropyl, NH_2 , CO) influences directly the swelling capacity due to the degree of ionization as a function of solution pH (**Fig. 9**). The polymer networks present a pseudo-plastic behavior (**Fig. 10 a-c**), evidenced by viscosity decreasing with strain increasing.

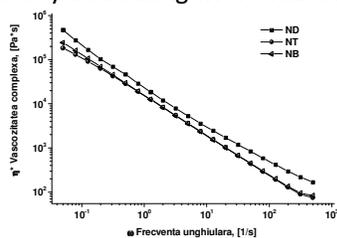


Fig. 10a. Complex viscosity behavior

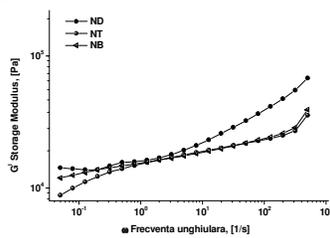


Fig. 10b. Storage modulus evolution

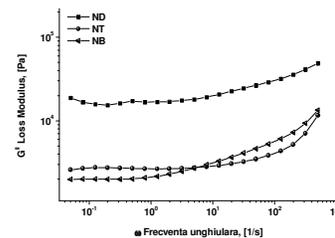


Fig. 10c. Loss modulus evolution

The mechanical properties of hydrogels were described considering both the storage modulus (G') and the loss modulus (G''). The polymer networks exhibit a viscous behavior at lower strain values and an elastic behavior at high strain values. The complex viscosity of hydrogels depends on the composition of each hydrogel type, the polymer structure, and the structural changes occurred during synthesis, respectively.

2.5. The chemical pre-treatment of wood was performed using a solution of succinic anhydride SA at 100°C , under continuous stirring (200 rpm) for 1h. There were applied 3 values of concentration as follows: 60%, 80%, and 120% (w/w), respectively. After chemical modification reaction, wood samples coded as MW(60), MW(80) and MW(120), were kept at room temperature. Further, wood samples were immersed in ESO in the presence of 5% TEA at 100°C for 1h. There were considered 40 wood samples as follows: 10 non-treated samples coded as R (control), and 10 wood samples treated with SA and coated with ESO, for each SA concentration value, coded as MW(60)CESO, MW(80)CESO and MW(120)CESO, respectively. Structural changes were evidenced by FT-IR spectroscopy method. Thermal behavior of wood samples was investigated by thermal analysis (TG-DTG). After chemical reaction of wood with SA, the weight percent gain value (WPG) increased from approx. 11% up to 39%, depending on the SA concentration. The WPG values calculated for wood samples after pre-treatment with SA and coating with ESO varied from 3.25% to 4.74% (**Table 2**).

Table 2. WPG evolution (%) for softwood samples after chemical pre-treatment and coating

Sample	R	MW(60)CESO	MW(80)CESO	MW(120)CESO
wood treated with SA	0	10.93	21.83	39.45
wood treated with SA, coated with ESO	4.74	4.53	3.56	3.25

Fig. 11 show the FT-IR spectra recorded for initial wood samples (A), wood samples modified with SA (B) and wood samples modified with SA and coated with ESO (C). The spectrum A presents absorption bands specific to wood: 3330 cm^{-1} (attributed to the $-\text{OH}$ groups valence vibrations), 2890 and 2918 cm^{-1} (characteristic to C-H from CH_3 and CH_2 groups), between 1800 and 1100 cm^{-1} (attributed to the main polymer components from wood structure). In spectrum B, the intensity of absorption band from 3330 cm^{-1} decreases and shifts to lower wavenumber values, evidencing a lower amount of OH groups in wood structure after chemical reaction with SA. The band from 1736 cm^{-1} , attributed to the carbonyl groups $\text{C}=\text{O}$, significantly increases as intensity. All these spectral changes evidence the occurrence of the chemical reaction between wood and SA. In spectrum C, the signals from 2918 , 2890 and 1736 cm^{-1} , respectively, increase as intensity due the reaction occurred between succinic monoester and ESO.

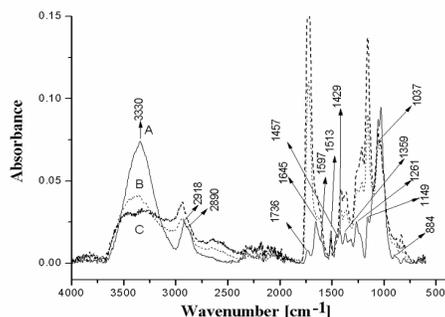


Fig. 11. FTIR spectra for non-treated wood (A), wood treated with SA (B) and wood treated with SA and coated with ESO (C)

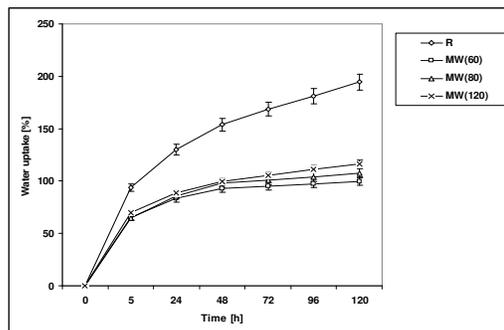


Fig. 12. Water absorption evolution for non-treated wood (R) and wood treated with SA (MW)

The chemical pre-treatment of wood can reduce its hydrophilic properties. A significant decrease of water absorption is noticed (**Fig. 12**) when hydrophilic OH groups are substituted with hydrophobic succinyl groups by increasing SA concentration in reaction medium. Thermal analysis evidenced that chemical pre-treatment of wood with SA influence its thermal stability, wood becoming more susceptible to degradation as a function of SA concentration value. Wood properties under environmental factors action (humidity, UV radiation) can be improved by chemical modification and coating with ESO (on-going study).

3. Dissemination of results

There were elaborated and presented 11 oral papers and 16 posters at:

- national scientific symposia: 21st Symposium on Thermal Analysis and Calorimetry, Feb. 17, 2012, Bucuresti; Seminary "Thermal analysis: Characterization of materials by using thermal analysis techniques", May 24, 2012 Iasi (organized in cooperation with Netzsch Company); National Conference on Chemistry Valcea, Oct. 3–5, 2012
- international scientific symposia: Fifth Cristofor I. Simionescu Symposium "Frontiers in Macromolecular and Supramolecular Science", June 11–13, 2012, Bucuresti; COFrRoCA – 2012, Septième Colloque Franco-Roumain de Chimie Appliquée, 27–29 Jun 2012, Bacau; 7th MoDeSt Conference, 2-6 Sept., 2012, Prague, Czech Republic; 15th International Conference Polymeric Materials, Halle, Germany, Sept. 12-14, 2012; 4th Bilateral Symposium on Functional Heterocyclic and Heterochain Polymers for Advanced Materials, Iasi; 2^{eme} Colloque Franco-Roumain de Chimie Medicinale, CoFrRoCM 2012, Iasi, Romania. The detailed informations are presented on the project's web page mentioned below.

Considering the obtained results, there were published and submitted for publication the following scientific papers:

1. C.-D. Varganici, A. Durdureanu-Angheluta, D. Rosu, M. Pinteala, B.C. Simionescu; Thermal degradation of magnetite nanoparticles with hydrophilic shell; *J. Anal. Appl. Pyrol.* **96** 63–68 (2012) (IF: 2.487)
2. D. Rosu, L. Rosu, F. Mustata, C.-D. Varganici; Effect of UV radiation on some semi-interpenetrating polymer networks based on polyurethane and epoxy resin; *Polym. Degrad. Stab.* **97** 1261–1269 (2012) (IF: 2.769)
3. O.M. Paduraru, D. Ciolacu, R.N. Darie, C. Vasile; Synthesis and characterization of polyvinyl alcohol/cellulose cryogels and their testing as carriers for a bioactive component; *Materials Science and Engineering C.* **32**, 2508–2515 (2012) (IF: 2.686)
4. C.-D. Varganici, O. Ursache, C. Gaina, V. Gaina, B.C. Simionescu; Studies on new hybrid materials prepared by both Diels-Alder and Michael addition reactions; *J Therm Anal Calorim.* **2012**, <http://dx.doi.org/10.1007/s10973-012-2532-y> (IF: 1.604)
5. S.F. Patachia, M.-T. Nistor, C. Vasile; Thermal behavior of some wood species treated with ionic liquid; *Industrial Crops and Products*, Available online 29 October 2012, <http://dx.doi.org/10.1016/j.indcrop.2012.10.003> (IF: 2.469)
6. D. Rosu, L. Rosu, C.-D. Varganici; The thermal stability of some semi-interpenetrated polymer networks based on epoxy resin and aromatic polyurethane; *J. Anal. Appl. Pyrol.*, **2012**, <http://dx.doi.org/10.1016/j.jaap.2012.12.003> (IF: 2.487)
7. C.-A. Teaca, D. Rosu, R. Bodirlau, L. Rosu; Structural changes in wood under artificial UV light irradiation determined by FTIR spectroscopy and color measurements –a brief review; *BioResources*, **2012**, submission needing revision 1 (IF: 1.328)
8. O. Ursache, C.Gaina, V.Gaina, C.-D.Varganici; New hybrid materials obtained by Diels-Alder and Michael addition reactions. A comparative study; *Polym. Bull.*, **2012**, submitted (IF: 1.532)

9. M.-T. Nistor, C. Vasile; TG/FT-IR/MS study on the influence of nanoparticles content on the thermal decomposition of the starch/poly(vinyl alcohol) montmorillonite nanocomposites; *Iranian Polymer Journal*, **2012**, submitted (IF: 0.936)

10. C.-D. Varganici, L. Rosu, D. Rosu, B.C. Simionescu; Miscibility studies of some semi-interpenetrating polymer networks based on an aromatic polyurethane and epoxy resin; *Composites Part B*, **2012**, submitted (IF: 1.731)

It was elaborated the project's web page: <http://www.icmpp.ro/grants/Dan%20Rosu/PN-II-ID-PCE-2011-3-0187-ro.pdf>

4. Re-actualization and consolidation of managerial and administrative plan

The research team involved in the project has performed the following activities:

- monthly working meetings with research team members;
- advisory activities performed by senior researchers for training PhD students ;
- establishment of panels by senior researchers for solving scientific issues;
- writing and submission of scientific articles for publication in ISI journals;
- establishment and providing the materials' supply for development of research program;
- planning the human, material and financial resources for the next stage;
- planning of acquisition activity, elaboration of documentation for acquisitions;
- following the supply chain and the mode of implementation project's funds;
- elaboration of the stage report (scientific, financial).

In order to develop and implement the management structure, the research team members have established monthly meetings for elaborating the detailed activities plan. It was envisaged an efficient and operational communication of administrative, technical and financial issues both within the research team, and with the contracting authority. All research team was involved in elaboration of the stage report. It was completed the documentation necessary for independent audit report related to financial statements 2011-2012.

The research team has fulfilled the proposed objectives with a full degree of implementation.

Stage 2013

Objectives:

1. Study of the influence of controlled environmental factors upon obtained multicomponent polymer systems.
2. Kinetic modeling of thermal degradation reactions.
3. Modification of properties during photochemical degradation of multicomponent polymer systems.

Durability of multicomponent polymer systems (MPS) is diminished as a result of their exposure to aggressive elements of the external environment. Degradation of polymer materials represent all complex processes, reactions and changes that occur in chemical structure, morphology and their properties under the action of various agents of environmental degradation. In the process of degradation under environmental factors results products that retain their macromolecular character, but whose physical and chemical properties are changed. During decomposition new structures are obtained which may resume up to the monomeric unit or even to mineralization. Degradation processes are irreversible and may occur under the action of heat, UV radiation and/or humidity. These processes occur in all life stages of polymeric materials, sometimes initiated just before use. Each degradation process has its own particular characteristics.

1. Influence of environmental factors on multicomponent polymer systems

1.1. Exposure to UV radiation. The majority MPS are affected by ultraviolet radiation. Depending on the wavelength, the radiation intensity, exposure time and chemical structure, respectively, MPS exposed to UV radiation can undergo photo-degradation processes. These processes involve both color and gloss changes that only affect the a esthetic appearance of MPS and major structural changes such as cleavage of macromolecules and Mesh, signified affecting physical-mechanical properties. The latter can affect property to such an extent that cause premature aging or even scrapping of MPS. Photochemical degradation effects of MPS which require long periods of exposure may be tracked by putting samples through accelerated aging tests performed in clean rooms and irradiating them with high intensity UV lamps. Aging speed if MPS can be by significant values (over 60 times). Knowledge of photo-degradation mechanisms and identifying the active species affecting MPS structure is very useful in choosing the most appropriate and effective methods of photo-stabilization.

1.2. Exposure to temperature. MPS thermal stability is important as it determines the maximum processing temperature and environmental conditions under which the materials can be used without spoiling. As long as thermal stability is related to the initial temperature of degradation and the degradation rate of MPS, the determination of kinetic parameters associated with degradation processes under the influence of temperature is

a major topic of interest. The results may provide useful information in defining specific processing conditions of MPS for different applications and can establish a correlation between thermal stability and material structure. The data could also be useful for predicting the lifetime of MPS at different temperatures and in the recovery/destruction of polymer waste by pyrolysis or combustion.

1.3. The effect of humidity. Under the action of humidity the degradation MPS is rapid. As a consequence of this process, there result free radicals that can enhance the degradation reactions, affecting both the thermal stability of the MPS and their structure. When wood is exposed to environmental factors conditions without any protection, for example humidity and/or sunlight (especially UV) - its surface is deteriorating rapidly. Action of environmental factors upon wood can cause micro-cracks that subsequently induce cracks in wood mass due processes of swelling and shrinkage of wood as a result of water absorption and drying process. Under the action of humidity, photo-degraded fragments of wood (mainly from lignin) are removed and therefore increase the surface roughness of wood. It is known that low resistance to moisture is one of the main disadvantages of wood, and this can be improved by chemical modification. Wood reaction with succinic anhydride significantly reduced hydrophilic nature of its constituents (**Table 3**). A decrease in the values of water absorption was recorded for modified wood compared with the initial sample.

Table 3. Water absorption values for chemically treated wood samples

Sample/ soak time	5 h	24 h	48 h	120 h
LB	92	128	153	178
LB60	64	82	90	98
LB80	60	76	85	90
LB120	58	75	84	87

Chemical and physical treatment and/or wood surface coating are effective methods that can be applied to protect the wood surface from damage. In this way the dimensional stability, resistance to moisture and to fungi action are improved. By chemical treatment, the initial structure of biopolymeric components of wood is influenced and some of its properties can be modified (for example, hydrophilicity).

2. Kinetics of thermal degradation reactions

2.1. Study of thermal transformations that occur in polymers. MPS heating may cause phase transitions, phenomenon indicated by the glass transition temperature (T_g). T_g values can provide an indication of the miscibility of the MPS components. In the case of MPS that have not undergone cross-linking (e.g. mixtures of linear polymers) there may be determined the melting and crystallization temperatures. Heat curing and crosslinking kinetics studies may be undertaken. Via thermogravimetric studies the MPS thermal stability may be monitored by correctly assessing the initiation of the thermal decomposition process. Also kinetic studies on the rate of decomposition reaction may be undertaken and feedback on different thermal decomposition mechanisms may be obtained. The apparent kinetic parameters of the decomposition reaction can also be set to develop a kinetic model. Using coupled techniques (TG/FT-IR, TG/MS) allows qualitative evaluation of volatile products evolved during thermal decomposition, depending on the temperature. The semi-interpenetrated polymer networks (S-IPNS) based on polyurethane (PU) and epoxy resin (ER) obtained during the stage of 2012 show a single composition-dependent T_g . T_g values move slightly towards higher values as crosslinked resin content increases. This is due to the reduction of free volume between chain segments, restricting the movement of polymer chains by steric hindrance. The melting/crystallization profiles of pure PU decrease in intensity with increasing crosslinking density up to a 30% ER content. This is a sign of compatibility between components of S-IPN structures. Miscibility studies were conducted by applying Fox and Gordon-Taylor equations and the results were in good correlation with those obtained from experiments. Crosslinking densities were determined and their values increased with heat capacity values decrease, as expected.

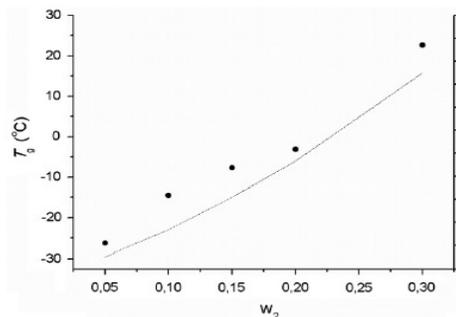


Fig. 13

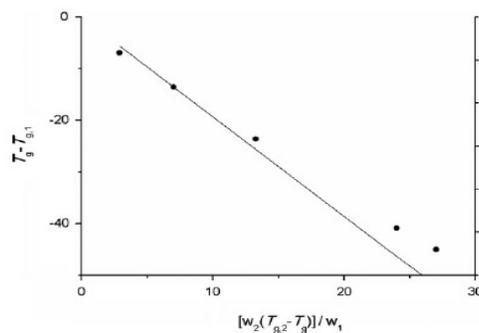


Fig. 14

Applying the equation of Fox (**Fig. 13**) has revealed the presents of specific interactions between the components of SIPN networks by obtaining a positive deviations between experimental and theoretical data. An appreciation of the strength of these bonds was achieved by Gordon-Taylor equation (**Fig. 14**). Gordon-Taylor experimental constant value was close to 2 values, suggesting the presence of strong interactions between the two components of the networks.

Heat capacity values and cross-linking density values are given in **Table 4**. It can be observed that T_g and cross linking density values increase with the heat capacity values decrease, as expected. The heat capacity is an energetic characteristic of the chain segments movement. Upon increasing values of the cross-linking degree, reduction of free volume between chain segments sterically hinders their movement, thus lowering the heat capacity values (**Table 4**).

Table 4. Heat capacities and related cross-linking data.

Sample	Heat capacity, C_p ($J g^{-1} ^\circ C^{-1}$)	ρ'_c ($mol cm^{-3}$)
PU	1.485	-
S-IPN-1	1.466	0.0128
S-IPN-2	1.417	0.0458
S-IPN-3	1.335	0.101
S-IPN-4	1.290	0.131
S-IPN-5	1.172	0.210

2.2. Calculation of kinetic parameters for establishing reaction mechanisms.

Thermogravimetric analysis conducted in an inert atmosphere (N_2) and at 4 heating rates (5, 10, 15 and $20^\circ C/min$) in a temperature range between 30 and $700^\circ C$ was used for the determination of the apparent kinetic parameters (activation energy, pre-exponential factor, conversion function form) of the MPS thermal decomposition reactions (**Fig. 15** and **Fig. 16**).

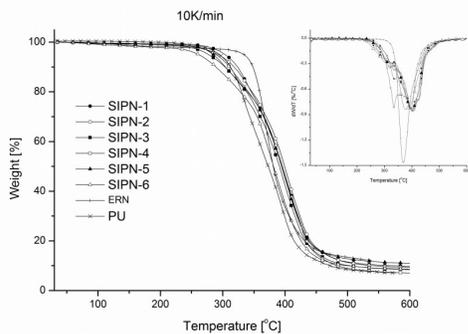


Fig. 15

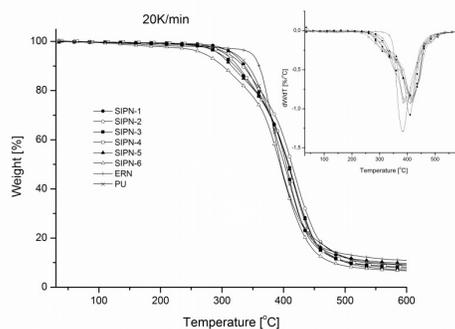


Fig. 16

Initial decomposition temperatures, the temperatures corresponding to each stage of decomposition and the residual masses were also determined. Global kinetic parameters were calculated by isoconversional methods of Friedman (**Fig. 17**) and Ozawa-Flynn and Wall (**Fig. 18**) which use the thermograms registered at four different heating rates. The conversion function was determined by multiple nonlinear regression method.

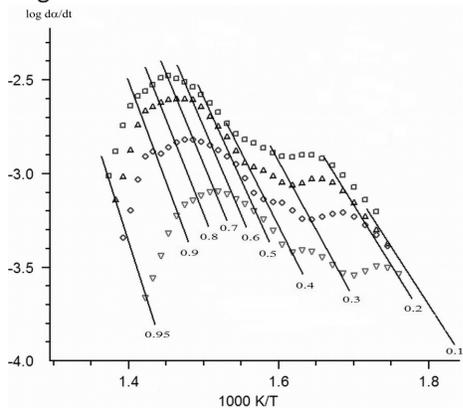


Fig. 17

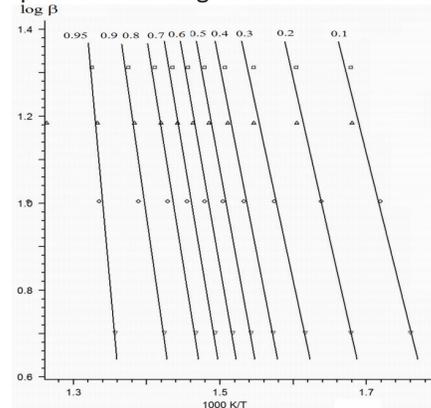


Fig. 18

2.2.1. Semi-interpenetrated polymer networks (IPN-S) based on polyurethane (PU) and epoxy resin (ER)

It was found that thermograms shifted towards higher temperature domains with heating rate increase. Based on those shifts the values of global kinetic parameters were calculated (**Table 5**).

Table 5. Values of global kinetic parameters

α	Kinetic parameters		Flynn-Wall-Ozawa	
	Friedman		Flynn-Wall-Ozawa	
	Log A (s ⁻¹)	E (kJ mol ⁻¹)	Log A (s ⁻¹)	E (kJ mol ⁻¹)
0.1	12.56	121	6.64	107
0.2	20.86	136	8.11	126
0.3	18.5	166	7.63	123
0.4	12.71	177	7.65	125
0.5	16.46	181	8.92	141
0.6	23.40	186	10.02	155
0.7	30.73	177	10.72	166
0.8	30.45	192	10.79	168
0.9	36.65	199	10.70	170
0.95	36.48	211	14.66	230

Kinetic parameters values increased with conversion degree, thus suggesting a complex mechanism of thermal degradation in three successive stages. After testing 14 kinetic models by multivariate linear regression method, it was found that the overall process of thermal decomposition is characterized by a kinetic model of n order:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E/RT} (1 - \alpha)^n$$

2.2.2. Cryogels obtained from polyvinyl alcohol (PVA) and microcrystalline cellulose. Cryogels containing PVA and cellulose show 4 stages of thermal degradation. The residual mass depends on the amount of cellulose in the composition of cryogels and the DTG curves peaks decrease for all stages of thermal degradation with natural polymer content increase. These issues highlight the presence of hydrogen bonding interactions between the two components, leading to an increase in the thermal stability in the presence of cellulose. **Figs. 19** and **20** show the graphs obtained with the Friedman (**Fig. 19**) and Flynn-Wall-Ozawa (**Fig. 20**) methods at the conversion degree (α) values between 0.1 and 0.9. Both isoconversional methods indicate the dependence of activation energy (E) on the conversion degree.

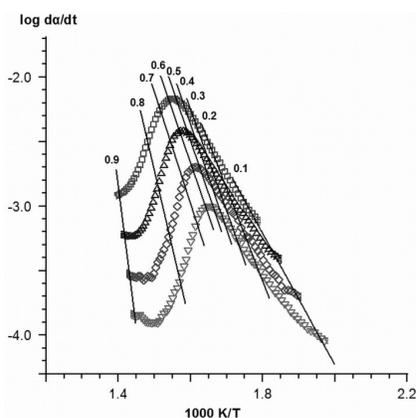


Fig. 19

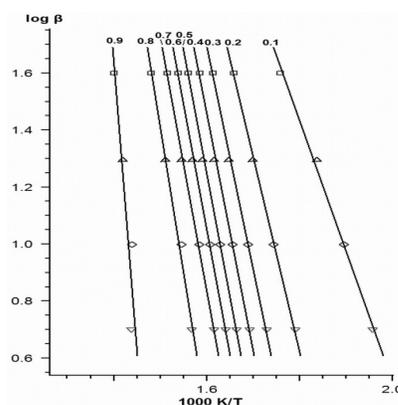


Fig. 20

2.2.3. Wood – a multicomponent polymer system.

2.2.3.1. Study of thermal stability of treated wood surface with succinic anhydride (SA).

Thermal degradation of wood is a very complex process, given its chemical structure. **Fig. 21** shows the TG curves (**Fig. 21A**) and DTG curves (**Fig. 21B**).

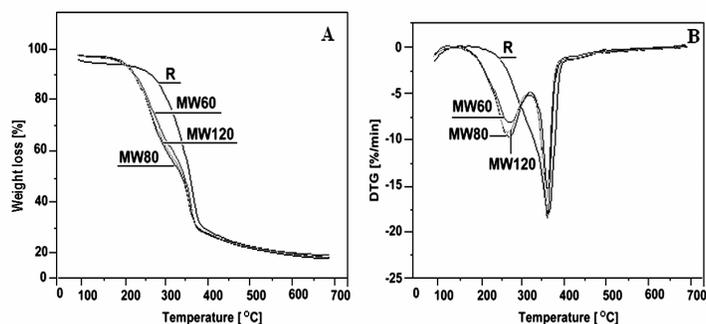


Fig.21

Data on behavior of wood thermal degradation are presented in **Table 6**. Chemical modification of wood favorably influenced thermal stability, especially at high concentrations of SA.

Table 6. Data resulted from the analysis of thermal degradation behavior of wood

Wood sample	T _i (°C)	T _{50%} (°C)	T _{ml} (°C)	W _{ml} (%)	T _{mII} (°C)	W _{mII} (%)	T _f (°C)	T _f -T _i (°C)	W _{Tf-Ti} (%)	W _{rez} (%)
R	109	365	372	75.5	-	-	388	229	75.5	19.4
MW60	203	355	279	33.7	368	43.9	383	180	77.6	19.3
MW80	199	352	276	38.2	368	41.50	380	181	78.7	19.0
MW120	196	350	277	38.8	368	40.0	381	185	78.8	19.1

2.2.3.1. Study of thermal stability of wood treated with the ionic liquid.

Thermal analysis of wood species showed that the effect of ionic liquid is dependent on the type of wood (for example its chemical composition). Ionic liquid lowers the specific energy of water removal process. This is due to the ability to transform ionic liquid bound water into free water, helping the release of water from wood. The ionic liquid increased the initial temperature of the beechwood by changing the reaction mechanism of decomposition. The new compounds were identified, and the time of initiation of the evolution of volatile compounds was delayed for beechwood. Identification of volatile compounds resulting from thermal degradation was performed using 3D FT-IR spectroscopy (Fig. 22). It may be observed that signals intensity change with wood degradation temperature.

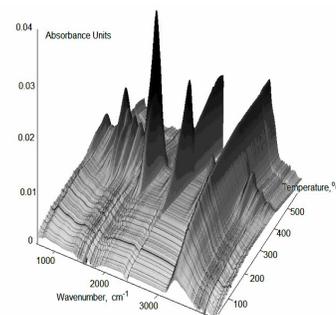


Fig.22

2.3. Determination of the factors influencing the results of thermogravimetric analysis.

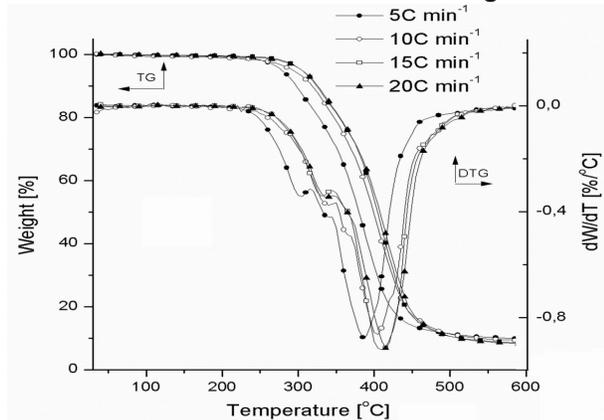


Fig.23

Thermogravimetric analysis results can be influenced by: the shape of analyzed samples and rate of heating. Sample characteristics exert a complex influence on TG curves. It was found that the thermal properties of powders differ substantially from those of larger samples. Effect of heating rate on the position and shape of TG curves is explained by the fact that the change of this parameter affects the processes of heat and mass transfer. In general thermograms shift towards higher temperatures with heating rate increase (Fig. 23).

3. Properties modification during photochemical degradation of multicomponent polymer systems

3.1. Establishment of the influence of wavelengths and doses of radiation on the studied polymers

Sunlight and especially the UV component of the sunlight spectrum are responsible for initiating photochemical degradation. In principle, photo-degradation of polymers is an effect of energy dissipation of photo-chemically excited molecules and is one of the primary photochemical process steps. This can lead to either to the split of the excited macromolecule, with the emergence of new macromolecular fragments with low molecular weights, which modifies the system polydispersity, or formation of interchain chemical bonds with neighboring polymer chains and the formation of crosslinked structures, resulting in increased final molecular weight and low solubility. Once initiated in this manner, degradation of polymers usually continues through secondary photochemical processes (e.g. photo-oxidation) in which also participates, together with the initial polymer chains, oxygen and substances derived from primary photochemical process. The structure of most polymers consists mainly of covalent bonds of C-X type (where X can be: C, O, halogen, N or P) and these bonds absorb more or less radiation with wavelengths higher than 200 nm.

3.2. Photodegradation kinetics study

In the photo-degradation kinetic studies of semi-interpenetrated polymer networks (IPN-S) based on polyurethane (PU) and epoxy resin (ER), there were followed by FT-IR technique the signals variation in the

specific wavenumber range 1492-1570 cm^{-1} and 1750-1716 cm^{-1} , specific to urethane bond and ester entities from polyurethane.

The highest changes occurred in the first 25h of irradiation. After 200h irradiation times the most important loss of urethane bonds occurred in the PU structure due to photo-Fries rearrangement. One explanation of this behavior may be related to the high transparency of the PU film compared to the studied networks that are more opaque, UV radiation causing a more advanced penetration of the PU film than for the networks. The significant decrease in the absorbance value at 1727 cm^{-1} specific to ester structure may be observed in the first 25 hours of irradiation (**Fig. 24**).

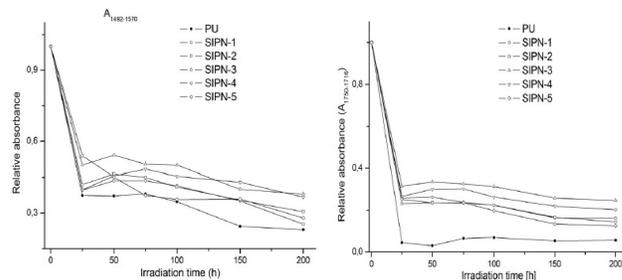


Fig. 24

The highest loss of ester linkages have been identified for the network comprising 40% cross-linked ER. It may be observed (**Fig. 24**) that above 20% cross-linked ER concentration, there occurs a protection phenomenon of the PU "soft" segments, due to increasing opacity with cross-linked ER content increase and micro phase separation. This may explain a decreasing trend in the concentration of carbonyl entities of soft segments of PU from the sample containing 40% crosslinked ER during irradiation.

3.3. Establishment of photodegradation mechanisms.

After 200h irradiation time the most important loss of urethane bonds occurred in PU structure due to photo-Fries rearrangement, which consists of formation of ortho-amino ester structure and chain branching. This process leads to an increase in affinity of S-IPNs for water molecules. Photodegradation of ester structures by Norrish type reactions occurs by CO_2 elimination, leading to mass variations in the studied structures, reducing of molecular weight and polydispersity increase.

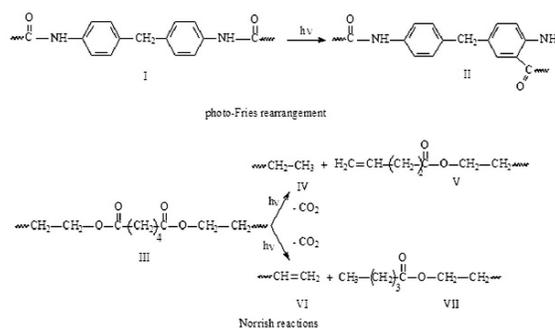


Table 7. The variation of chromatic coefficients with irradiation time

Samples	a*							b*						
	0	25	50	75	100	150	200	0	25	50	75	100	150	200
PU	-0.576	1.563	2.135	3.750	4.243	4.314	4.421	11.680	30.864	31.001	31.371	31.790	34.532	35.012
S-IPN-1	0.291	0.868	0.902	1.003	1.063	3.241	7.194	13.503	22.103	23.798	24.802	25.5583	27.101	29.798
S-IPN-2	-2.499	1.257	1.474	2.003	2.273	5.668	6.001	16.795	22.343	23.111	26.115	27.972	28.003	28.595
S-IPN-3	-2.202	0.013	0.423	0.585	0.814	0.951	0.963	15.928	17.324	19.235	22.043	24.143	25.005	25.870
S-IPN-4	-1.493	0.023	0.520	1.243	1.827	3.353	5.380	11.959	19.222	23.384	25.252	26.0957	27.312	28.2248
S-IPN-5	2.2785	2.345	2.446	2.502	2.5884	4.582	6.3001	16.9252	17.555	22.128	25.399	29.2824	28.887	28.4201

The lightness factor decreased for all the studied samples during irradiation (**Fig. 25**). The behavior is an indication of the darkening of all samples after UV irradiation. The irradiation caused the increase of chromatic coefficients values (a^* and b^*) for all the studied samples (**Table 7**). The chromatic coordinates variation shows the tendency of reddening and yellowing of the irradiated samples. The gloss decreased during the irradiation of the studied samples (**Fig.26**).

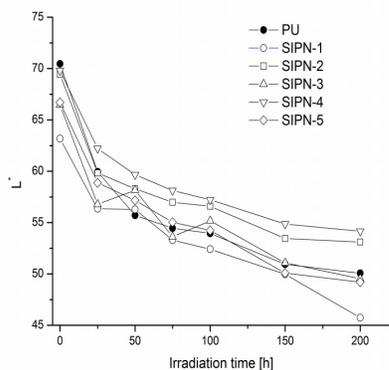


Fig. 25

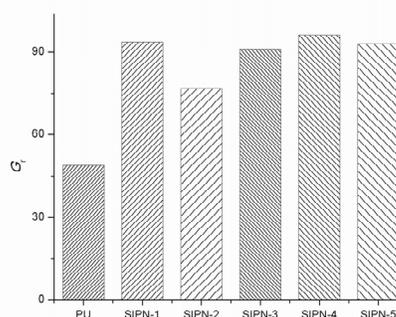


Fig. 26

The gloss decrease on the surface during irradiation can be explained by changing their roughness because there is a direct relationship between gloss and roughness. It is well known that the rough surfaces are less glossy.

4. Insurance framework of the project. Improving the implementation process.

4.1 Completing the project web database.

Project database has been updated and can be found at: <http://www.icmpp.ro/mcps/ro/index.php>

4.2. Dissemination of the results.

Scientific papers: 12

1. D. Rosu, L. Rosu, C.-D. Varganici, The thermal stability of some semi-interpenetrated polymer networks based on epoxy resin and aromatic polyurethane, *J. Anal. Appl. Pyrol.* 100, 103-110 (2013); IF=2,560; SI=1,244
2. C.-D. Varganici, O. Ursache, C. Gaina, V. Gaina, B.C. Simionescu, Studies on new hybrid materials prepared by both Diels-Alder and Michael addition reactions, *J. Therm. Anal. Calorim.* 111(2), 1561-1570 (2013); IF=1,982; SI=0,548
3. C.-A. Teaca, D. Rosu, R. Bodirlau, L. Rosu, Structural changes in wood under artificial UV light irradiation determined by FTIR spectroscopy and color measurements – A brief review, *BioResources* 8(1), 1478-1507 (2013); IF=1,309; SI=1,322
4. S.F. Patachia, M.-T. Nistor, C. Vasile, Thermal behavior of some wood species treated with ionic liquid, *Ind. Crops and Prod.* 44, 511-519 (2013); IF=2,468; SI=1,731
5. M.-T. Nistor, C. Vasile, TG/FT-IR/MS study on the influence of nanoparticles content on the thermal decomposition of the starch/poly(vinyl alcohol) montmorillonite nanocomposites, *Iranian Polym. J.* 22(7), 519-536 (2013); IF=1,053; SI=0,540
6. C.-D. Varganici, L. Rosu, D. Rosu, B.C. Simionescu, Miscibility studies of some semi-interpenetrating polymer networks based on an aromatic polyurethane and epoxy resin, *Composites Part B: Eng.* 50, 273-278 (2013); IF=2,143; SI=2,722
7. O. M. Padurararu, A. Bosinceanu, G. Tantaruu, C. Vasile, Effect of hydroxypropyl- β -cyclodextrin on the solubility of an antiarrhythmic agent, *Ind. Eng. Chem. Res.* 52, 2174-2181 (2013); IF=2,206; SI=1,911
8. C.-D. Varganici, O. Ursache, C. Gaina, V. Gaina, D. Rosu, B.C. Simionescu, Synthesis and characterization of a new thermoreversible polyurethane network, *Ind. Eng. Chem. Res.* 52(15) 5287-5295 (2013); IF=2,206; SI=1,911
9. R. Bodirlau, C.-A. Teaca, D. Rosu, L. Rosu, C.-D. Varganici, A. Coroaba, Physico-chemical properties investigation of softwood surface after treatment with organic anhydride, *Central Eur. J Chem.* 11(12), 2098-2106 (2013), IF=1,167; SI=0,655
10. M.-T. Nistor, A. Chiriac, L. Nita, I. Neamtu, C. Vasile; Semi-interpenetrated network with improved sensitivity based on poly(N-isopropylacrylamide) and poly(aspartic acid), *Polym. Eng. Sci.* (2013), publication on-line, DOI: 10.1002/pen.23488; IF=1,243; SI=1,349
11. M.-T. Nistor, C. Vasile, A.P. Chiriac; Hybrid collagen-based hydrogels with embedded montmorillonite nanoparticles, *Appl. Clay Sci.* (2013), sent to publication; IF=2,342; SI=1,268
12. O. Ursache, C. Gaina, V. Gaina, N. Tudorachi, A. Bargan, C.-D. Varganici, New Diels-Alder thermoresponsive networks based on ether-urethane bismaleimide-functionalized poly(vinyl alcohol), *Ind. Eng. Chem. Res.* (2013), sent to publication; IF=2,206; SI=1,911

Papers presented at scientific conferences: 9 (communications: 3 and posters: 6)

European Polymer Congress – EPF 2013, Pisa, Italia, 16-21 June, 2013

1. C.-D. Varganici, L. Rosu, D. Rosu, B.C.Simionescu; Semi-interpenetrating polymer networks based on an aromatic polyurethane and epoxy resin. Miscibility studies (**COMMUNICATION**)
2. D.Rosu, C.-C.Gavat, L.Rosu, C.-D.Varganici; Cellulose fabrics painted with some reactive azotriazine dyes. Photochemical behaviour (**POSTER**)
3. L. Rosu, C.-D. Varganici, D. Rosu; Semi-interpenetrating polymer networks based on an aromatic polyurethane and epoxy resin. Surface properties modifications (**POSTER**)
4. F. Mustata, I.Bicu, D. Rosu, C.-D.Varganici; Epoxy monomers based on methyl ester of corn oil (**POSTER**)
5. R. Bodirlau, C.-A. Teaca, D. Rosu; Organic anhydride treatment of softwood to improve its weathering protection (**POSTER**)
6. C.-A. Teaca, R. Bodirlau, I. Spiridon, N. Tudorachi; Multi-component polymer systems comprising modified starch microparticles and different natural fillers (**POSTER**)

Academic Days Iasi, A XXIV Scientific Session of the Institute of Macromolecular Chemistry "Petru Poni", "PROGRESS IN SCIENCE AND MACROMOLECULAR ORGANIC COMPOUNDS", Iasi, 3-5 Oct.2013

7. C.-D. Varganici, A. Coroaba, R. Bodirlau, C.-A. Teaca, L. Rosu, D. Rosu; Study of structural and thermal properties of chemically modified wood (**POSTER**)
8. C.-D.Varganici, D. Rosu, L. Rosu, B.C. Simionescu; Epoxy and polyurethane based S-IPNs as coating materials. Miscibility through thermal studies (**COMMUNICATION**)
9. O.-M. Mocanu (Paduraru), C.-D. Varganici, L. Rosu, D. Rosu; Study of thermal degradation of the hydrogels of poly (vinyl alcohol) / cellulose by analyzing TG/FTIR-MS (**COMMUNICATION**)

Other activities:

This Research project supported the following doctoral stages:

1. **Miscibility studies of semiinterpenetrating polymer networks based on aromatic polyurethane and crosslinked epoxy resin**, PhD. Cristian-Dragos Varganici
2. **Thermal stability of semi-interpenetrated based aromatic epoxy resin and polyurethane**, PhD. Cristian-Dragos Varganici

Public doctoral thesis:

1. **Interpenetrated networks based on collagen or polyaspartic acid with applications in medicine and pharmacy**, June 18, 2013, PhD. Manuela-Tatiana Nistor
2. **Multicomponent polymer systems containing polysaccharides**, June 20, 2013, PhD. Oana-Maria Paduraru

Masters Dissertation thesis:

X ray diffractometry study of polymers and polymer composites, June 2013, Masters Elena Marlica

Part of these theses represents results obtained and reported in this project.

3.3. Ensure resources. Preparation of report stage

The involved research team in the project realized the following activities:

- Monthly work sessions with team members;
- Counseling activities for doctoral/postdoctoral students by senior researchers;
- Organizing panels of senior scientific team problem solving;
- Elaboration and submitting articles for publication in ISI journals;
- Establishing and procurement of the necessary materials for the development research program;
- Human resource, financial and material planning for the next stage;
- Acquisition activity planning, preparing documentation for procurement;
- Tracking the supply flow and the use of funds;
- Preparing stage report 2014 (scientific, financial)

In order to develop and implement management structure, team members met monthly and established detailed activity plans. It was followed effective and efficient communication of administrative, technical and financial research both within the team, and with the contracting authority. The entire research team was involved in drafting the report stage. It was compiled the file necessary to achieve independent financial audit in 2013.

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

Stage 2014 Objectives:

1. Physico-chemical characterization of multicomponent polymeric systems aged under controlled conditions
2. Selection criteria establishment for the studied multicomponent polymeric systems, considering specific applications
3. Insurance of the project implementation framework. Improving the implementation process

The obtaining of multicomponent polymeric systems is important for a sustainable evolvement, taking into account aspects regarding environmental protection and waste management. Polymeric semi-interpenetrating networks (SIPN) are particular blends formed from one linear and one cross-linked polymer without chemical bonds established between components. Cross-linked epoxy resins and polyurethanes (PU) may form semi-interpenetrating polymer networks with interesting combinations of properties which make them excellent coating materials. Polyvinyl alcohol (PVA) possesses high capacity of hydrogen bonding with other polymers and at the same time being biodegradable, biocompatible and water soluble. All these properties recommend PVA as a candidate for the obtaining of films in blends with other natural polymers, such as cellulose. PVA and cellulose based cryogels may assure mass transport of micro- and nanoparticles, as well as making possible the immobilization of different cells and biomolecules on their surfaces. Such materials may be destined for some specific applications, such as: tissue engineering, biodegradable food packaging, membranes for biosensors or wound dressings, assuring an appropriate level of moisture necessary for cauterization. Natural fibres textiles, such as cotton, silk and wool offer weak protection of human skin from solar spectrum light due to reduced light absorbing capacity of these materials. Improvement of light absorbing capacity is possible by painting the textiles with different coloured dyes. Wavelengths in the range 300-400 nm (\approx 5% of the solar light spectrum which reaches the Earth surface), having high energy, act in a destructive manner to both human skin and textiles. Recent studies in the field of composites generate opportunities for the obtaining of materials with significantly improved properties by efficiently exploiting renewable resources and with a wide range of applications. Such systems are obtained based on matrices from renewable resources – biopolymers – having a positive impact on the environment.

1. Physico-chemical characterization of multicomponent polymeric systems aged under controlled conditions

1.1. Evaluation of optical properties (colour, gloss) and physico-mechanical properties modification

Five semi-interpenetrating polymer networks based on PU and increasing content of cross-linked epoxy resin were synthesized and characterized. Based on the percent content of cross-linked epoxy resin, the networks were noted as SIPN1 (5% resin), SIPN2 (10% resin), SIPN3 (15% resin), SIPN4 (20% resin) and SIPN5 (30% resin). The photochemical behaviour of SIPNs under UV irradiation with $\lambda > 300$ nm is interesting from both practical point of view, especially when the increase of materials photochemical stability is sought, and theoretical point of view, in order to gain new knowledge on different photochemical decomposition mechanisms of polymers, finding of adequate photostabilizers or obtaining of photodegradable materials. Concerning the photochemical stability studies of SIPNs, irradiation was made on 40 mm² surfaces with a medium pressure Hg vapour lamp of 100 W, model OSRAM HQE-40 with an emission spectra range between 340-370 nm. Irradiations were undertaken in air atmosphere. The more energetic radiations with $\lambda < 300$ nm, absent in natural light spectra, were eliminated with a quartz/borosilicate filter with a maximum transparency at 365 nm. Colour variation analysis (ΔE) was evaluated with Eq.1, where L^* is the lightness factor, a^* is the chromatic coefficient of redness-greening and b^* is the chromatic coefficient of yellowness-blueness.

Indexes 2 and 1 in Eq.1 represent the parameter values measured after and before irradiation, respectively.

$$\Delta E = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad \text{Eq.1}$$

Gloss variation on the surfaces of the samples was determined at 60° by comparing the intensity of luminous reflection on the sample surface with the value obtained for the standard (polished black glass). The surface gloss retention (G_r) was calculated with Eq. (1) where G_i and G_f represent the initial and the final gloss values.

$$G_r = \frac{G_f}{G_i} \cdot 100 \quad \text{Eq. 2}$$

Figs. 27 and **28** show the variations of colour differences and gloss retention with irradiation time. An increase in ΔE values with irradiation time may be observed (**Fig.27**). The most significant increase of these values was observed in the first 25 h of UV irradiation for PU. The ΔE value for PU was 31.1 after 200 h irradiation time,

indicating major colour differences between irradiated and non-irradiated samples. The ΔE values of SIPNs were lower than those recorded for PU at the end of the photo-degradation process. ΔE values increased in the following order: SIPN3 (19.9) < SIPN5 (21.3) < SIPN2 (21.5) < SIPN1 (22.3) < SIPN4 (23.6). The G_r value decreased with irradiation time for all samples (**Fig.28**) with lowest value for PU (48.7), while for the other samples it varied between 76.9 (SIPN2) and 96.1 (SIPN4).

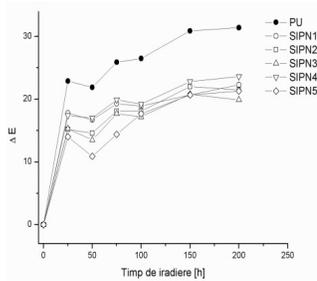


Fig. 27 Colour modifications with irradiation time

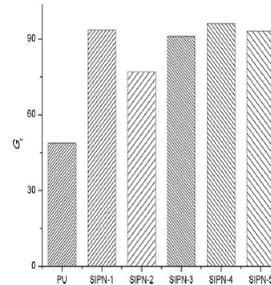


Fig. 28 Gloss retention variation with irradiation time

This decrease in G_r values was explained by a modification in structures roughness, because of presence of a direct relationship between gloss and roughness. An explanation for the decrease in G_r value for PU compared with the other structures is attributed to the high transparency of the polymer structure, because UV light deeper penetrates the sample, thus generating an advanced deterioration. Irradiation significantly modifies the samples resistance to mechanical effort and deformation. **Figs. 29** and **30** show the effort-deformation curves for samples SIPN2 and SIPN5.

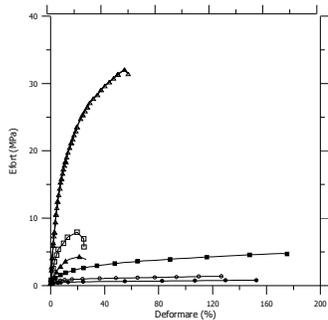


Fig. 29 Effort-deformation curves during SIPN2 irradiation: ● -non-irradiated; ○ -15h; ■ - 80h; □ - 120h

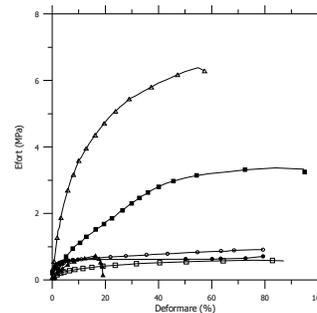


Fig. 30 Effort-deformation curves during SIPN5 irradiation: ● -non-irradiated; ○ - 15h; ■ - 80h; □ - 120h; ▲ - 160 h; △ - 200h

Irradiation of SIPN samples determines a growth of some physical and chemical properties such as: initial elasticity modulus, the resistance of elasticity limit, resistance to shearing and reducing the elongation break at elasticity limit. These properties modifications decrease with cross-linked epoxy resin content increase in SIPNs. This behaviour is explained by a weak photo-stabilizing effect of PU by the cross-linked epoxy resin.

1.2. Establishing interaction types between polymeric components

The influence of the components ratio and that of the interactions established between them on the photochemical stability of cryogels has been studied. The most significant structural modifications consist of macromolecular chain scission, cross-linking and oxidation reactions. During UV irradiation of PVA and cellulose based cryogels there were identified significant colour modifications, evidenced through the increase in lightness factor (L^*) values, accumulation of instable red chromophores (a^*) and surface yellowing (b^*). **Figs. 31-33** show the modification of chromatic coefficients values with irradiation time for the cryogels. Structural modifications during UV irradiation were monitored via FT-IR, UV-Vis and XPS techniques. Due to interruption of oxygen diffusion through the PVA surface, cellulose in the cryogels exhibited a slower photo-oxidation process. Photo-oxidation was possible via intermediate hydroperoxidic structures formation, confirmed through an iodometric method. Individual cellulose has also suffered photo-oxidation phenomena via continuous hydroperoxides formation and depolymerization. Due to its oxygen diffusion barrier properties, PVA protected cellulose fibres from UV radiations up to a concentration of 70% PVA in the cryogel.

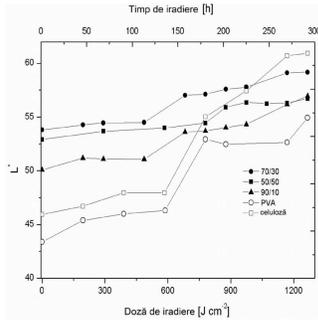


Fig. 31 Variation of lightness factor with irradiation time and dose.

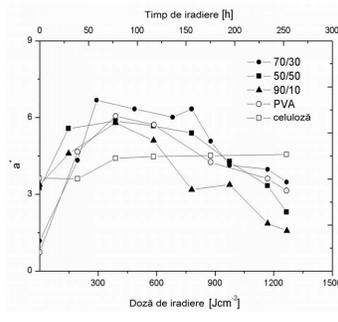


Fig. 32 Variation of chromatic coefficient a^* with irradiation time and dose

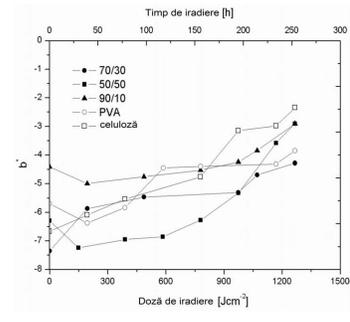


Fig. 33 Variation of chromatic coefficient b^* with irradiation time and dose

SEM micrographs demonstrated that up to a 70% concentration in the cryogel, PVA interacts with cellulose fibers adhering as film to their surface. Above this concentration value, the interactions between components significantly weaken and phase separation phenomenon occurs, each component further photo-degrading via specific mechanisms.

1.3. Crosslinking degree evaluation

In order to determine SIPNs cross-linking density values it is firstly necessary to calculate absolute heat capacity values and introduce them in Eq.3, where C_p^i si C_p^0 are the absolute heat capacities of pure PU and that at a given crosslinking density value (ρ_c)ⁱ.

$$\rho_c = \frac{C_p^i - C_p^0}{C_p^0} = \frac{\Delta C_p^i}{C_p^0} \quad \text{Eq. 3}$$

Determination of absolute heat capacity values may be undertaken via DSC method by recording three consecutive measurements: (1) a scan with empty aluminium crucibles with pierced unsealed lids, (2) a scan with a reference material consisting of pure sapphire and (3) a scan with a same sample mass as that of the reference material. The relationship between the sample caloric capacity, noted C_p (*proba*), which adds up the heat capacity of sample crucible support, that of sample crucible, that of analysed sample and of the reference material, noted C_p (*safir*), which in turn adds up the heat capacity of the reference materials crucible support, that of reference material crucible and that of the reference material and the heating rate, β , is given in Eqs. 4 and 5.

$$C_{1p}(\text{proba}) - C_{1p}(\text{safir}) = (T(\text{proba}) - T(\text{safir})) / \beta \quad \text{Eq. 4}$$

$$C_p(\text{proba}) - C_p(\text{safir}) = kD \quad \text{Eq. 5}$$

Since the caloric capacities of crucible with sample and of crucible with sapphire may be noted with $C_p^h(\text{proba})$ and $C_p^h(\text{safir})$ and specific heat values of sample and sapphire with c_r si c_s and their mass values with m_r and m_s , Eqs. 6-9 may be obtained, in which by D_1 , D_2 si D_3 the thermal displacements between DSC curves of correction, reference and sample were noted.

$$C_p^h(\text{proba}) - C_p^h(\text{safir}) = kD_1 \quad \text{Eq. 6}$$

$$[(C_p^h(\text{proba}) + m_r c_r) - C_p^h(\text{safir})] = kD_2 \quad \text{Eq. 7}$$

$$[(C_p^h(\text{proba}) + m_s c_s) - C_p^h(\text{safir})] = kD_3 \quad \text{Eq. 8}$$

$$\frac{m_s c_s}{m_r c_r} = \frac{D_3 - D_1}{D_2 - D_1} \quad \text{Eq. 9}$$

Since the c values are known, the sample caloric capacity may be calculated with Eq. 10

$$C_p(\text{proba}) = \frac{m_r c_r}{m_s} \cdot \frac{D_3 - D_1}{D_2 - D_1} \quad \text{Eq. 10}$$

The C_p values corresponding to glass transition temperatures (T_g) were thus calculated for the SIPNs (**Table 8**).

Table 8. Absolute heat capacities and crosslinking densities values for SIPN samples

Sample	T_g (°C)	C_p (Jg ⁻¹ °C ⁻¹)	ρ_c (mol cm ⁻³)
PU	-32.7	1.485	-
SIPN1	-29.5	1.466	0.0128
SIPN2	-25.7	1.417	0.0458
SIPN3	-23.5	1.335	0.101
SIPN4	-21.3	1.290	0.131
SIPN5	-15.7	1.172	0.210

One may observe an increase in T_g and ρ_c with C_p values decrease. This behaviour is normal since the caloric capacity represents an energetic characteristic of the segmental chain movement from macromolecular chains. That is why the cross-linking degree increases with cross-linked epoxy resin content increase. As a direct consequence, a reduction in free volume between chain segments occurs due to sequential steric hindering of their movement.

2. Selection criteria establishment for the studied multicomponent polymeric systems, considering specific applications

2.1. Investigations on the effects of immobilized dyes on polymeric substrates in correlation with physical and chemical properties

The influence of UV irradiation time and dose on the interaction of the cellulose substrate (cotton) and 4 different reactive azo-triazine structures with the following commercial names: Reactive Yellow 143 (RY-143), Reactive Orange 13 (RO-13), Reactive Red 183 (RR-183), Reactive Red 2 (RR-2) was studied. These dyes possess the capacity to covalently bond to the textile substrate through stable etheric and/or sulphonic bonds. **Fig. 34** shows the modification in VIS absorbance spectra of the studied dyes after 200 h irradiation time. Studies have demonstrated that UV irradiation affects, depending on the dose, both dye chemical structure, leading to material colour modification, and that of the textile substrate resulting in dye detachment (**Fig. 35**) together with glucose units, offering the possibility of the latter to be solved by human perspiration, thus producing adverse irritable effects on skin.

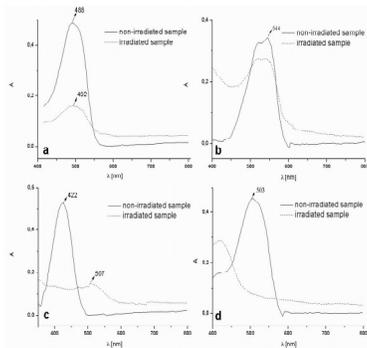


Fig. 34 Modifications of VIS absorbance spectra after 200 h irradiation time: (a) RY-143; (b) RR-183; (c) RR-2; (d) RO-13

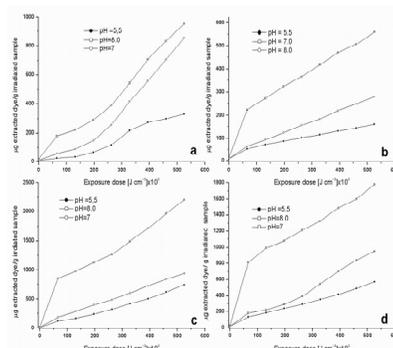


Fig. 35 Released dye quantity per g irradiated sample as a function of irradiation dose and pH: (a) RY-143; (b) RR-183; (c) RR-2; (d) RO-13

2.2. Testing of the multicomponent polymeric systems

Multicomponent polymeric systems based on biopolymeric matrix of plasticized starch (S) and filler materials which include lignocellulosic fibres (fine beechwood sawdust - BS, fir tree needles - FTN) and lignin extracted from the beechwood sawdust (BL) with different concentrations (15%, 30% and 45%). The structure and properties of these materials were investigated via spectroscopy techniques (FT-IR, SEM), X-ray diffraction (XRD) and simultaneous thermal analysis (TG/DTG/DTA) and through determination of surface characteristics (resistance to humidity, transparency). Evaluation of optical properties (transparency/opacity) for the obtained systems is shown in **Fig.36**. **Table 9** shows the results of humidity resistance tests of the multicomponent polymer systems.

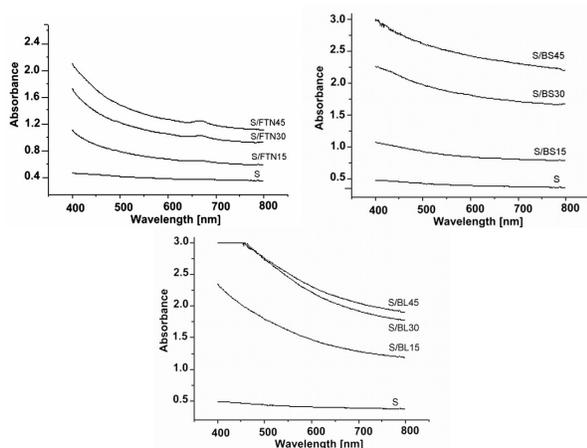


Fig. 36 Evaluation of opacity properties for the polymer matrix (S) and the obtained polymer systems.

Table 9. Evaluation of humidity resistance of the samples

System/ Absorption %	Immersion time			
	5h	30h	50h	125h
S	52.70	58.09	56.36	54.43
S/FTN15	49.51	56.52	58.16	59.91
S/FTN30	45.01	48.47	56.87	56.89
S/FTN45	44.24	44.80	48.59	53.81
S/BL15	41.61	51.12	51.57	52.25
S/BL30	38.88	48.34	47.65	47.79
S/BL45	45.98	45.96	45.98	46.15
S/BS15	32.52	40.28	49.80	53.03
S/BS30	24.55	27.20	33.55	41.42
S/BS45	27.33	32.97	39.49	52.03

The presence of vegetable filling materials in the plasticized starch polymer matrix determines a slight increase in humidity resistance and may improve the application possibilities of these materials. This behavior is due to the presence of interactions consisting in hydrogen bonding formation between the starch polymer matrix, the structural crystalline part of wood (beech wood sawdust) and the fir tree needles (which possess cellulose in their chemical composition).

2.3. Investigations of life cycle assessment (*lifetime prediction*) for the studied polymeric systems

For the estimation of lifetime of the SIPNs, the samples were aged under controlled conditions by exposure to UV irradiation at different temperatures (40°C, 70°C, 100°C si 130°C). A simplified form of the Arrhenius equation was used, based on the time-temperature relationship (Eq. 11), in which t is the lifetime, t_0 is pre-exponential factor, T is aging temperature, E is activation energy and R is the gases constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$).

Table 10. Lifetime estimation of UV irradiated SIPN networks calculated based on colour modifications

Sample code	E (kJ mol ⁻¹)	$\ln t_0$	t at 25°C (h)	Correlation coefficient
SIPN1	19	-3.987	39	0.949
SIPN2	38	-9.580	308	0.861
SIPN3	67	-19.514	1568	0.954
SIPN4	19	-3.955	127	0.837
SIPN5	29	-7.110	116	0.954

$$t = t_0 e^{\frac{E}{RT}} \quad \text{Eq. 11}$$

The period corresponding to an increase in colour difference (ΔE) from 0 to 5, when the modification becomes visible by the human eye, was taken into account. Parameters calculated with Eq. 11 are shown in **Table 10**.

3. Insurance of the project implementation framework. Improving the implementation process

3.1. Completing the project database

Project database has been updated and can be found at: <http://www.icmpp.ro/mcps/ro/>

3.2. Dissemination of the results

Scientific papers: 7

1. Photochemical stability of cellulose textile surfaces painted with some reactive azo-triazine dyes; L. Rosu, D. Rosu, C.–C. Gavat, C.–D. Varganici; *J. Mater. Sci.*, 49(13), 4469-4480 (2014); **IF=2,305; SI=1,371**
2. Multicomponent bio-based polymer systems comprising starch and wood polymers-structure and thermal behavior; C.-A.Teaca, R.Bodirlau, D.Rosu, L.Rosu, C.-D.Varganici; *J. Biobased Mater. Bioenergy*, 8(2), 253-260 (2014); **IF=0,536; SI=0,761**
3. A new way to synthesize of poly(urethane-imide)s based on nitroethyl carbamate intermediary; C.Gaina, O.Ursache, V. Gaina, C.-D. Varganici; *Polym.-Plastics Technol. Eng.*, 53(11) 1160-1168; (2014); **IF=1,481; SI=0,555**
4. Studies on Diels-Alder thermoresponsive networks based on ether-urethane bismaleimide functionalized poly(vinyl alcohol); O. Ursache, C. Gaina, V. Gaina, N. Tudorachi, A. Bargan, C.-D. Varganici, D. Rosu; *J. Therm. Anal. Calorim.*, 118, 1471-1481 (2014); **IF=2,206; SI=0,507**
5. Influence of poly(vinyl alcohol) on cellulose photochemical stability in cryogels during UV irradiation; C.–D. Varganici, L. Rosu, O.-M. Mocanu (Padurarur), D. Rosu; *J. Photochem. Photobiol. A: Chem.* DOI: 10.1016/j.jphotochem.2014.10.00 accepted (2014); **IF =2,291; SI=0,939**
6. On the thermal stability of some aromatic–aliphatic polyimides; C.–D. Varganici, D. Rosu, , C. Barbu–Mic , L. Rosu, D. Popovici, C. Hulubei, B.C. Simionescu; *J. Anal. Appl. Pyrol.*; sent to publication (2014); **IF = 3.070; SI = 1,705**
7. Poly(urethane–benzoxazine)s; C. Gaina, O. Ursache, V. Gaina, C.–D. Varganici; *J. Polym. Res.* 21(11), 586-597 (2014); **IF=1,897; SI=0,967**

Papers presented at scientific conferences: 9 (communications: 3 and posters: 6)

8th International Conference on Modification Degradation and Stabilization of Polymers – MoDeSt 2014, 31 August – 4 September 2014, Portoroz (Slovenia)

1. Accelerated photoaging of dyed textiles; D. Rosu, C.–D. Varganici, L. Rosu (*COMMUNICATION*)
2. On the thermal stability of poly(vinyl alcohol) and cellulose based cryogels; C.–D.Varganici, D.Rosu, O.M.Mocanu (Padurarur), L.Rosu (*COMMUNICATION*)
3. On the photodegradation of poly(vinyl alcohol) and cellulose based cryogels; L.Rosu, C.–D.Varganici, O.M. Mocanu(Padurarur), E.Marlica (*POSTER*)
4. Curing reactions of epoxidized methyl esters of corn oil and thermal characterization of the obtained crosslinked products; F.Mustata, E. Marlica, N. Tudorachi, I. Bicu, C.-D. Varganici (*POSTER*)

5. Starch/wood bio-based polymer systems - structure and thermal properties; R. Bodirlau, C.-A. Teaca, D. Rosu, L. Rosu, C.-D. Varganici (*POSTER*)

6. Investigation of structural changes occurred in wood due to chemical treatment; C.-A. Teaca, R. Bodirlau, D. Rosu, L. Rosu (*POSTER*)

The 2nd CEEP Workshop on Polymer Science, October 24-25, 2014, Iasi, Romania.

7. Thermal behavior of semiaromatic polyimides; C.-D. Varganici, D. Rosu, C. Barbu-Mic, L. Rosu, D. Popovici, C. Hulubei, B. C. Simionescu (*POSTER*)

"Al.I.Cuza" University Days, Iasi, FACULTY OF CHEMISTRY Conference, 2014 Edition; 31 October - 1 November 2014

8. Effect of temperature on aliphatic-aromatic polyimides; C.-D. Varganici, D. Rosu, C. Barbu-Mic, L. Rosu, D. Popovici, C. Hulubei, B. C. Simionescu (awarded *COMMUNICATION*)

9. Wood treatment with vegetable oils and its protective effect under environmental factors action; R. Bodirlau, C.-A. Teaca, E. Marlica, L. Rosu, D. Rosu (*POSTER*)

Other activities:

1. Ph.D. Thesis: **Thermal and photochemical stability of multifunctional polymeric materials;** October 27, 2014; Ph.D. Student C.-D. Varganici.

Part of this thesis represents results obtained and reported in this project. Distinction: **Summa Cum Laude;** Qualificative: **Excellent**

2. **Book Chapter:** Thermal degradation of thermosetting blends; **authors:** D. Rosu, C.-D. Varganici, L. Rosu, O.-M. Mocanu (Paduraru); In:

Thermal Degradation of Polymer Blends, Composites and Nanocomposites; Publisher: Springer-Verlag (2015); **Accepted**

3. **Book Chapter:** Multi-component polymer composite systems using polymer matrices from sustainable renewable sources; **authors:** C.-A. Teaca, R. Bodirlau; In: **Eco-friendly Polymer Nano-composites: Processing and Properties; Publisher:** Springer-Verlag (2015); **Accepted**

3.3. Ensure resources. Preparation of report stage

The involved research team in the project realized the following activities:

- Monthly work sessions with team members;
- Counseling activities for doctoral/postdoctoral students by senior researchers;
- Organizing panels of senior scientific team problem solving;
- Elaboration and submitting articles for publication in ISI journals;
- Establishing and procurement of the necessary materials for the development research program;
- Human resource, financial and material planning for the next stage;
- Acquisition activity planning, preparing documentation for procurement;
- Tracking the supply flow and the use of funds;
- Preparing stage report 2014 (scientific, financial)

In order to develop and implement management structure, team members met monthly and established detailed activity plans. It was followed effective and efficient communication of administrative, technical and financial research both within the team, and with the contracting authority. The entire research team was involved in drafting the report stage. It was compiled the file necessary to achieve independent financial audit in 2014.

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

Stage 2015

Objectives:

1. Photochemical stabilization of multicomponent polymeric systems
2. The thermal stability of the photostabilized multicomponent polymeric systems
3. Dissemination of the results

It is a well known fact that polymeric materials cover almost all of human activity domains. However, such materials possess limited durability, especially during applications which require long exploitation periods. During exposure of polymer based materials to aggressive environmental factors, of which the most significant are solar light (especially the UV component from solar light spectra) and temperature, there occur important structural modifications which lead to loss of properties (optical, mechanical, dielectric), resulting in premature product

failure. That is why predicting the “lifetime” of organic polymeric materials in specific utilization conditions still represents a difficult to resolve complex scientific issue.

1. Photochemical stabilization of multicomponent polymeric systems

Photostabilization methods are generally linked to the photodegradation mechanisms. Taking into account the different mechanisms of photodegradation processes, photostabilization may be made by:

1. *Screening of surfaces exposed to ultraviolet radiations.* Protection is undertaken by coating the surface with some thin layers in order to stop the radiation from penetrating the polymer bulk, through the following mechanisms:

- *absorption of luminous energy* with formation of active species and modification of spin multiplicity, which lose their active character by photochemical transpositions or formation of inert species;
- *transformation of absorbed light* into vibrational energy, without modification of spin multiplicity, the deactivation of excited states being accompanied by thermal effects;

2. *Usage of energetic quenchers of excited states.* Such quenchers are compounds capable to accept energy from photochemically activated molecules before initiation of photodegradation process. An efficient stabilization is reached when the energetic content of the quencher’s excited state is lower than that of the photochemically activated polymer. Once the excited state is transferred from the photochemically active polymer to the photostabilizer molecule, the latter returns to its fundamental state through fluorescence, phosphorescence or heat emission.

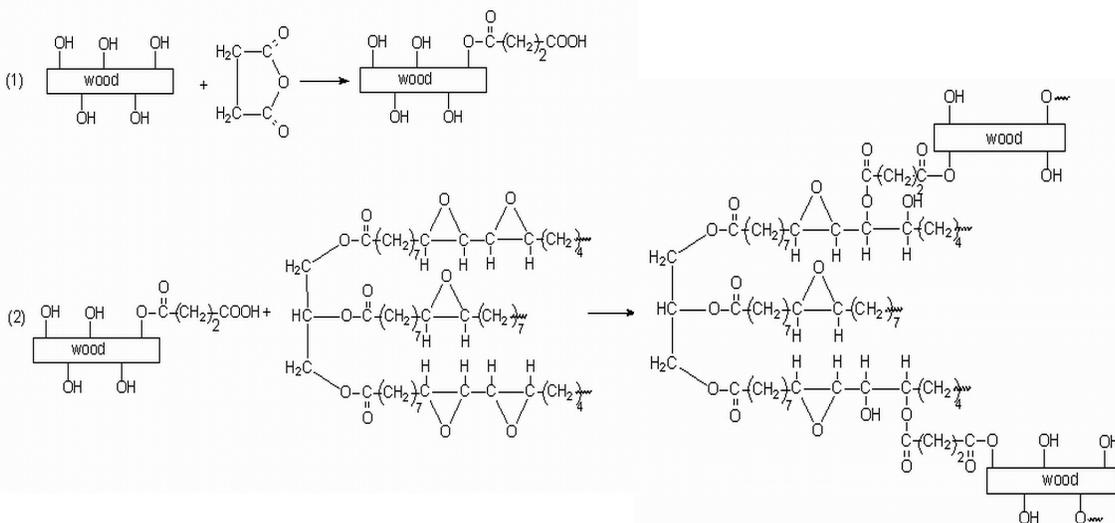
3. *Hydroperoxides decomposition.* During polymers photodecomposition there occur photo-oxidative processes which result in the formation of hydroperoxidic structures. Accumulation of hydroperoxides into materials bulk containing organic polymers must not occur since these structures are highly instable and decompose through thermal or photochemical activation, leading to free radicals formation and thus to depolymerization processes via radicalic mechanism. Since there is evidence of the proportionality between the photodecomposition rate of exposed materials and concentration of free radicals accumulated in bulk, it is appreciated that decomposition of hydroperoxidic structures right after their formation through adding of sulphur or nickel based compounds may prevent free radicals accumulation in critical concentrations.

4. *Caption of radicals formed during exposure and their transforming into chemical species with low reactivity* represents an efficient photostabilization method. The mechanism consists in the introduction of some light sensitive compounds into the material bulk, such as hindered amines (HALS), which act through reactions with active radical species, like peroxides.

1.1. Choosing the adequate photostabilizer depending on the photodegradation mechanism

1.1.1. Wood photostabilization against UV radiations by screening the surface with coating based on succinic anhydride and epoxidized soybean oil

Wood, as natural composite material comprised of cellulose, lignin and hemicelluloses, is sensitive to light, due to the presence of chromophoric entities in its structure, compounds with visible light absorbant capacity which generate photo-oxidative processes, leading to irreversible structural modifications.



Scheme 1. Successive treatment of softwood with SA(1) and ESO(2)

Such modifications are accompanied by changes in optical properties, in a former phase, and significant loss of physico-mechanical properties in the end with shape modification. A efficient method of preventing wood photodegradation implies surface screening either by thin layer coating or by chemical modification. The study presented in the current report is focused on the evaluation of softwood photostability, chemically modified by successive surface treatment with succinic anhydride (SA) and epoxidized soybean oil (ESO) (**Scheme 1**) (Epoxy and succinic anhydride functionalized soybean oil for wood protection against UV light action D.Rosu, R.Bodirlau, C.–A.Teaca, L.Rosu, C.–D.Varganici; *J. Clean. Prod.*, (2015); doi.org/10.1016/j.jclepro.2015.07.092).

The wood photo-oxidation process was investigated by monitoring structural and surface properties (colour). Chromatic coordinates values (specific to surface reddening and yellowing) increased with irradiation time and dose. Lignin exhibited a strong photodegradation tendency, leading to significant surface reddening. It was concluded that the epoxidized soybean oil coating protects wood surface against photo-oxidation reactions by a screening effect. As an exemplification, **Fig. 37** shows the colour difference variation as a result of UV exposure of untreated wood sample and wood sample treated by coating with succinic anhydride and epoxidized soybean oil as a function of time and irradiation dose (Epoxy and succinic anhydride functionalized soybean oil for wood protection against UV light action D.Rosu, R.Bodirlau, C.–A.Teaca, L.Rosu, C.–D.Varganici; *J. Clean. Prod.*, (2015); doi.org/10.1016/j.jclepro.2015.07.092).

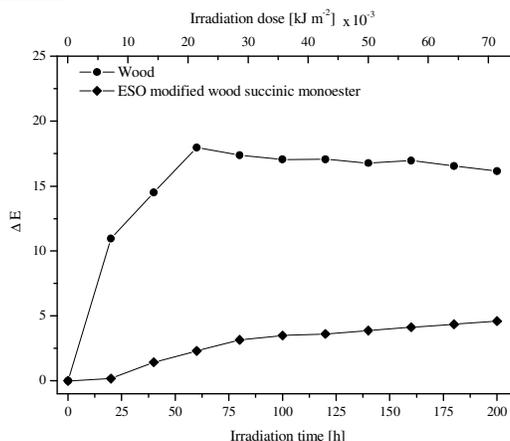


Fig. 37. Variation of colour difference as a function of irradiation time and dose

It may be observed that colour variations measured at coated wood surface are much lower as the ones characterizing unprotected wood surface. Studies regarding colour modifications have evidenced that in the case of unprotected wood there exists a surface darkening tendency, while the surface of wood treated with succinic anhydride and epoxidized soybean oil exhibits a slight decoloration tendency. **Fig. 38** shows the lightness factor variation (ΔL) with irradiation time and dose measured at wood surface before and after protection. Accumulation of chromophores at irradiated samples surface is indicated by the variation of chromatic coordinates a^* and b^* (**Fig. 39**). (Epoxy and succinic anhydride functionalized soybean oil for wood protection against UV light action D.Rosu, R.Bodirlau, C.–A.Teaca, L.Rosu, C.–D.Varganici; *J. Clean. Prod.*, (2015); doi.org/10.1016/j.jclepro.2015.07.092).

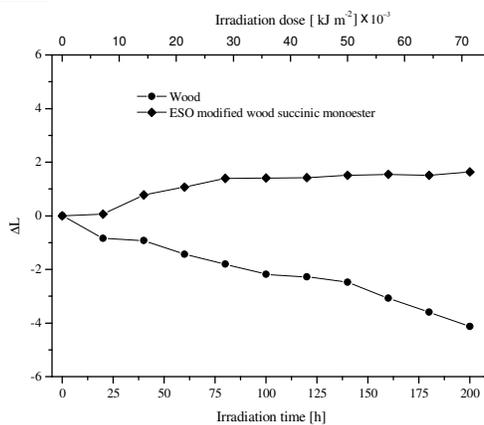


Fig. 38 Variation of lightness factor as a function of irradiation time and dose

The data shown in **Fig. 39** depicts the tendency of red and yellow chromophores accumulation at unprotected wood samples surface. The protective effect of succinic anhydride and epoxidized soybean oil coating is sustained by the accumulation of a lower quantity of chromophores during irradiation.

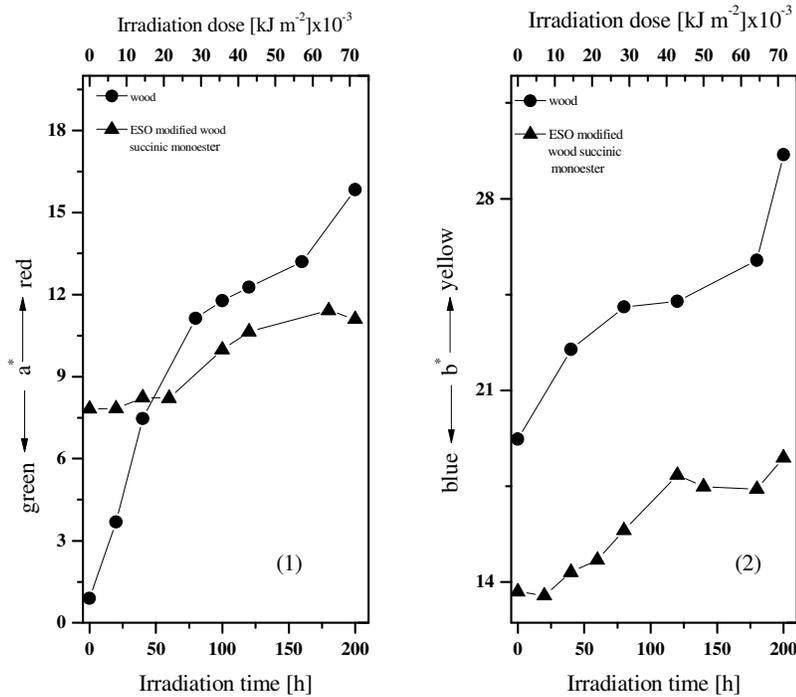


Fig. 39 Modification of chromatic coordinates with irradiation time and dose

Variation of chromatic coordinates characterizing the protected wood samples is much diminished by comparison with that of unprotected samples. Structural modifications during irradiation were monitored by FT-IR technique for both unprotected and coated samples. (Epoxy and succinic anhydride functionalized soybean oil for wood protection against UV light action D.Rosu, R.Bodirlau, C.–A.Teaca, L.Rosu, C.–D.Varganici; *J. Clean. Prod.*, (2015); doi.org/10.1016/j.jclepro.2015.07.092). Comparative evolution of carbonilic and phenolic entities was thusly monitored, as depicted in **Figs. 40** and **41**.

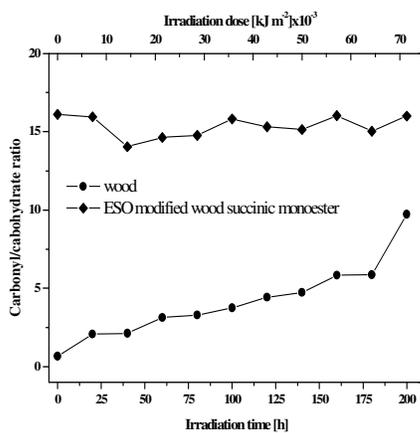


Fig. 40 Modification of carbonyl group content during irradiation of unprotected and coated wood samples

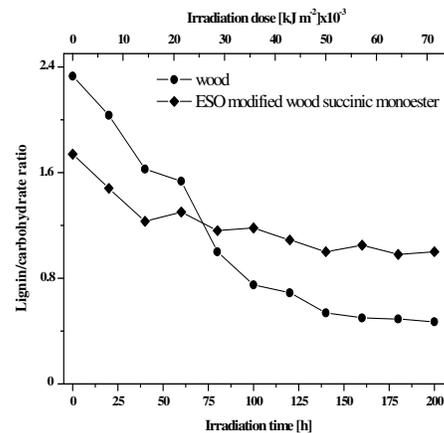


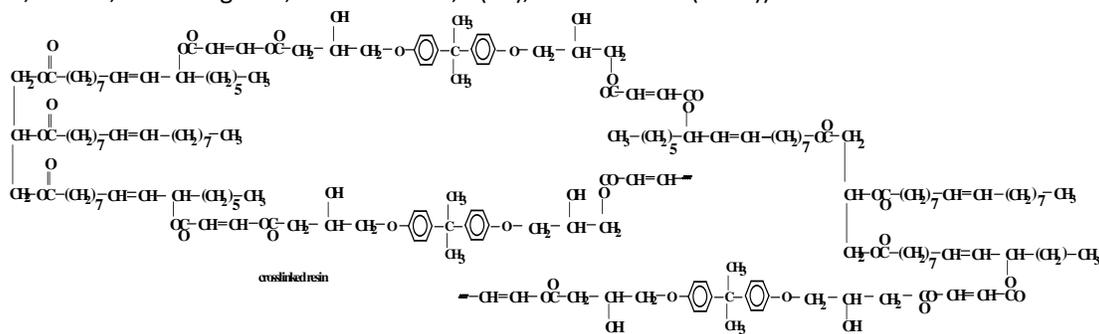
Fig. 41 Modification of lignin content during irradiation of unprotected and coated wood samples

Research has shown that in the case of unprotected wood, the concentration of carbonyl groups increases proportionally with irradiation time, thus sustaining the idea of wood degradation through photo-oxidative

processes. These processes occur throughout the entire exposure period of samples to UV irradiation. It was also demonstrated that, unlike unprotected wood, wood surface coated with succinic anhydride and epoxidized soybean oil manifests chemical inertness during photo-oxidation (**Fig. 40**). The ratio between surface signals in the range 1698-1774 cm^{-1} , corresponding to carbonil groups, and in the range 1343-1396 cm^{-1} , corresponding to carbohydrate structural units from cellulose, remains almost constant. **Fig 41** demonstrates that the photodegradation rate of lignin (most susceptible wood component to light action from whose degradation chromophore structures result) is significantly reduced by coating with succinic anhydride and epoxidized soybean oil. One may observe that the decrease of the ratio between lignin aromatic structural entites signal (1452-1535 cm^{-1}) and the one at 1343-1396 cm^{-1} , specific to carbohydrate units decreases much slowly in the case of protected wood.

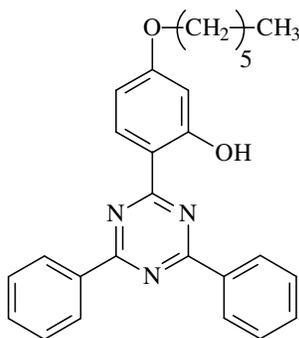
1.1.2. Photostabilization of epoxy resins crosslinked with modified vegetable oils

There were conducted photochemical stability studies concerning some epoxy networks based on bisphenol A crosslinked with modified vegetable oils. The crosslinking agent was obtained by reaction of epoxidized castor oil with maleic anhydride. The structure of the studied network is given in **Scheme 2** (Novel bio-based flexible epoxy resin from diglycidyl ether of bisphenol A cured with castor oil maleate; D.Rosu, F.Mustata, N.Tudorachi, V.E. Musteata, L.Rosu, C.-D.Varganici; *RSC Advances*, 5(57), 45679-45687 (2015)).



Scheme 2 Structure of epoxy resins crosslinked with modified vegetable oils

Preliminary studies have evidenced the obtaining of some good results concerning the photostabilization of the studied material with 2-[2,6-diphenyl-1,3,5-triazin-2-yl]-5-[hexyl]oxy-phenol, commercially known as „Tinuvin 1577 FF”. The photostabilizer is a solid powder (molar mass 425,53), it is very efficient in the photostabilization of polymeric materials and has low toxicity.



Tinuvin 1577 FF

The photostability of the stabilized crosslinked epoxy network was studied by exposure to filtered UV radiations generated by mercury lamps having wavelength maxima located at 254 and 365 nm. Irradiations were conducted in air on 250 μm thick rectangular sample films. The medium irradiance value measured at samples surface was 95 W m^{-2} , while the medium exposure dose was 350 $\text{kJm}^{-2}\text{h}^{-1}$. Photostabilizer concentration in the polymer bulk was 1%. The influence of the Tinuvin 1577 FF product on the photochemical stability of the epoxy network crosslinked with chemically modified vegetable oil was evaluated through thermal analysis methods (TG and DSC),

surface colour variations, gloss measurements, spectral analyses (UV-Vis, FT-IR), SEM micrographs. Variation of carbonyl index with irradiation time for the studied samples is given in **Table 11**.

Table 11. Variation of carbonyl index with irradiation time

Irradiation time (h)	Carbonyl index at 254 nm		Carbonyl index at 365 nm	
	unstabilized	stabilized	unstabilized	stabilized
0	7,8	7,4	7,8	7,5
50	20,6	15,2	10,3	7,6
100	31,2	24,5	10,9	6,7
150	34,8	24,1	10,9	6,6
200	33,2	31,04	10,9	6,6
250	40,8	29,6	9,5	7,1

From the table one may observe the influence of the photostabilizer on the increase in the photo-oxidative stability of the crosslinked network. At both 254 and 365 nm wavelengths it is clear that carbonyl indexes are much lower in the case of Tinuvin 1577 FF treated samples compared to the unstabilized ones.

2. The thermal stability of the photostabilized multicomponent polymeric systems

2.1. Thermal characterization of the photostabilizers

The thermal behavior of the Tinuvin 1577 FF photostabilizer was studied by using coupled thermal analysis techniques TG-DTA (simultaneous TGA-DTA thermal analysis device Jupiter 449 F1, NETZSCH – Germany). **Fig. 42** depicts the TG-DTA thermograms of Tinuvin 1577 FF sample, recorded in the temperature range 32-700⁰ C, at a heating rate of 10 K min⁻¹ and in inert atmosphere (N₂). By analyzing the thermogram of photostabilizer with 2-[2,6-diphenyl-1,3,5-triazin-2-yl]-5-[hexyl]oxy]-phenol, one may observe that the compound is thermally stable up to 338⁰ C when the beginning of mass loss occurs. The photostabilizer thermally decomposes in a single stage with maximum mass loss rate around 452⁰ C, as it may be deduced from the maximum peak temperature in the DTG curve.

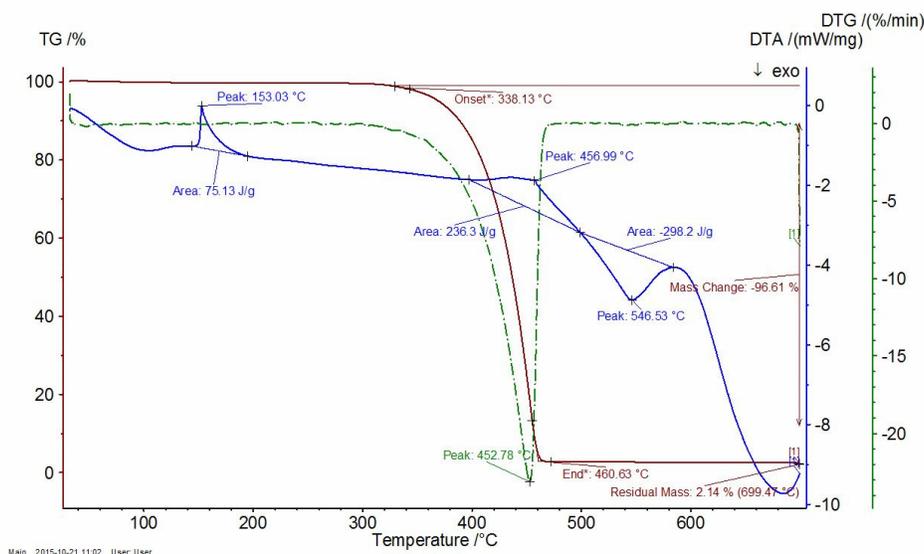


Fig. 42 TG, DTA and DTG curves of Tinuvin 1577FF photostabilizer

The thermal decomposition process ended at around 460⁰C, with over 97,6% mass loss. The residue mass was 2,14% at 700⁰ C. The DTA thermogram indicates two endothermic signals at 153,03⁰ C ($\Delta H = 75,13 \text{ Jg}^{-1}$) and 457⁰ C ($\Delta H = 238,3 \text{ Jg}^{-1}$) and an exothermic one at 546,53⁰ C ($\Delta H = -298,2 \text{ Jg}^{-1}$). The first endothermic process depicts the melting process of the studied compound, whilst the other two accompany the thermal decomposition processes.

2.2. The influence of photostabilizers on the thermal resistance of the studied materials

The thermal stability of the epoxy resin based on bisphenol A and crosslinked with castor oil modified with maleic anhydride and stabilized with „Tinuvin 1577 FF” was study by thermogravimetric analysis. Approximately 10 mg of

sample was weighed in alumina crucibles and heated in inert atmosphere, in the range 30-700⁰ C at a rate of 10 K min⁻¹. Mass variation as a function of temperature is given in **Fig. 43**.

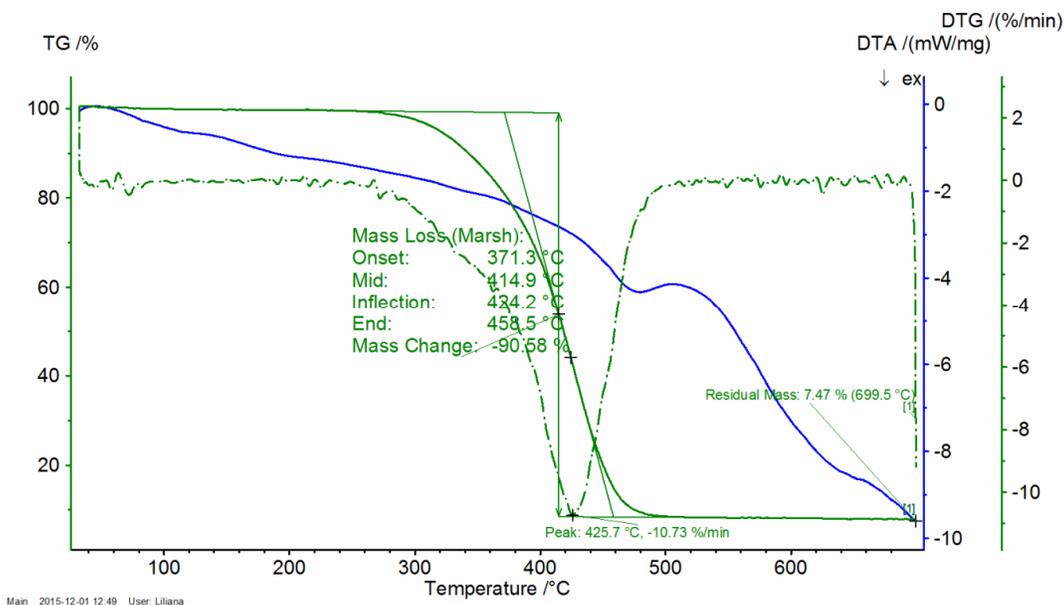


Fig. 43 Thermogram describing the thermal decomposition of epoxy resin based on bisphenol A and crosslinked with castor oil modified with maleic anhydride and stabilized with „Tinuvin 1577 FF”

Fig. 43 demonstrates that the studied sample thermally decomposes in a single stage in the temperature range 371,3 ÷ 458,5⁰ C. Confirmation of this statement is given by the shape of the DTG curve which shows a single maximum at 425,7⁰C. The starting thermal decomposition temperature of the studied sample (T_{onset}), defined as the temperature above which the mass losses become significant, is 371,3⁰C. The final thermal decomposition temperature (T_{endset}), defined as the temperature after which the sample exhibits insignificant mass loss, is 458,6⁰C. Another important parameter which characterizes thermal decomposition processes of polymers is represented by the temperature at which the mass loss rate is maximum (T_m). In the case of the studied sample, the T_m value was found as 425,7⁰C, value corresponding to the DTG curve peak. At this temperature the sample losses mass at a rate of -10.73% min⁻¹. Residual mass at 700⁰C was 7.47%, the sample thus losing 92.5% of its initial mass. As one may observe from the DTA curve shape, the entire process is an exothermic one. By comparing these data with the ones obtained for the unstabilized sample, one may conclude that the presence of the photostabilizer does not greatly influence the thermal stability of the studied polymer.

3. Dissemination of the results

Scientific papers: 7

1. Novel bio-based flexible epoxy resin from diglycidyl ether of bisphenol A cured with castor oil maleate; D.Rosu, F.Mustata, N.Tudorachi, V.E. Musteata, L.Rosu, C.-D.Varganici; *RSC Advances*, 5(57), 45679-45687 (2015); **IF= 3,840; SI= 2,339**.
2. Epoxy and succinic anhydride functionalized soybean oil for wood protection against UV light action D.Rosu, R.Bodirlau, C.-A.Teaca, L.Rosu, C.-D.Varganici; *J. Clean. Prod.*, (2015); doi.org/10.1016/j.jclepro.2015.07.092; **IF= 3,844; SI= 1,621**
3. Influence of poly(vinyl alcohol) on cellulose photochemical stability in cryogels during UV irradiation; C.-D.Varganici, L.Rosu, O.M.Mocanu (Paduraru), D. Rosu; *J. Photochem. Photobiol. A: Chem.*, 297, 20–30 (2015); **IF= 2,495; SI=0,939**
4. On the thermal stability of some aromatic-aliphatic polyimides; C.-D.Varganici, D.Rosu, C.Barbu-Mic, L.Rosu, D.Popovici, C.Hulubei, B.C. Simionescu; *J. Anal. Appl. Pyrol.*, 113, 390–401 (2015); **IF= 3,564; SI=1,705**
5. Influence of two structural phases of Fe₃O₄ and γ-Fe₂O₃ on the properties of polyimide/iron oxide composites; S. Ioan, S. Nica, V. Nica, V.C. Grigoras, C.-D. Varganici, D. Popovici, C. Hulubei; *Polym. Int.*, 64, 1172–1181 (2015); **IF= 2,409; SI= 1,686**

6. TGA/DTA–FTIR–MS coupling as analytical tool for confirming inclusion complexes occurrence in supramolecular host–guest architectures; C.–D.Varganici, N.Marangoci, L.Rosu, C.Barbu–Mic, D.Rosu, M.Pinteala, B.C. Simionescu; *J. Anal. Appl. Pyrol.*, 115, 132–142 (2015); **IF= 3,564; SI= 1,705**
7. Thermal and hydrolytic stability of silver nanoparticle polyurethane biocomposites for medical applications; D.Macocinschi, D.Filip, M.F.Zaltariov, C.–D.Varganici; *Polym. Degrad. Stab.*, 131, 238–246 (2015); **IF= 3,183; SI= 2,291**

Book chapters: 2

1. D.Rosu, C.–D.Varganici, L.Rosu, O.M.Paduraru, Thermal degradation of thermosetting blends, in: **Thermal Degradation of Polymer Blends, Composites and Nanocomposites**, P.M. Visakh, Y. Arao (Editori), Editura Springer International, Elvetia, 2015, pg. 17-50; **ISBN 978-3-319-03463-8 ISBN 978-3-319-03464-5** (eBook).
2. C.-A.Teaca, R.Bodirlau, Multicomponent polymer composite/nanocomposite systems using polymer matrices from sustainable renewable sources, in: **Eco-friendly Polymer Nanocomposites Processing and Properties**; Thakur, Vijay Kumar, Thakur, Manju Kumari (Eds.), Editura Springer India, 2015, pg. 469-494, **ISBN: 978-81-322-2470-9**

Papers presented at scientific conferences: 11 (oral presentations: 2 and posters: 9)

Seventh Cristofor I. Simionescu Symposium Frontiers in Macromolecular and Supramolecular Science, June 4 – 5, 2015; “Petru Poni” Institute of Macromolecular Chemistry of Romanian Academy, Iasi

1. D.Rosu, F.Mustata, N.Tudorachi, C.-D.Varganici, L.Rosu; Bio–based flexible networks from epoxy resin and castor oil maleate (Poster)
2. C.-A.Teaca, R.Bodirlau, D.Rosu, N. Tudorachi; Multi-component polymer systems based on biopolymers from renewable resources – structure and properties (Poster)

Romanian International Conference on Chemistry and Chemical Engineering, RICCE 19, Sibiu, 2-5 September 2015.

3. C.A. Teaca, R. Bodirlau, L. Rosu, C.-D. Varganici; FTIR spectral and colour changes of softwood coated with epoxy functionalized soybean oil and photo-degraded under UV light (Poster)
4. R. Bodirlau, C.A. Teaca, L. Rosu, E. Marlica, D. Rosu; Wood treatment with vegetable oils and its protective effect under environmental factors action (Poster)
5. D.Rosu, C.-D. Varganici, L. Rosu, O.M. Mocanu (Paduraru); Poly(vinyl alcohol)–cellulose cryogels. Photochemical behavior (Poster)
6. C.-D. Varganici, L. Rosu, O.M. Paduraru (Mocanu), D. Rosu; Poly(vinyl alcohol)–cellulose cryogels. Thermal behavior (Poster)
7. F. Mustata, E. Marlica, C.D. Varganici, V.E. Musteata; Thermal and electrical properties of DGEBA cured with maleinized castor oil (Poster)

The 3rd CEEP Workshop on Polymer Science, September 23 - 26, 2015 “Petru Poni” Institute of Macromolecular Chemistry Iasi, Romania

8. C.-D. Varganici, D. Rosu, C.–A. Teaca, L. Rosu, R. Bodirlau; Effect of epoxy and succinic anhydride functionalized soybean oil coating on wood resistance against photodegradation (Oral presentation)
9. C.-A. Teaca, R. Bodirlau, L. Rosu, N. Tudorachi, D. Rosu; Multi-component polymer systems comprising different bio-based fillers (Poster)

"Progress in organic and polymer chemistry", The XXVth Symposium, 24 - 26 September 2015, Iasi

10. C.–D Varganici, N. Marangoci, L. Rosu, C. Barbu–Mic, D. Rosu, M. Pinteala, B.C. Simionescu; Studiul fenomenului de complexare in arhitecturi supramoleculare de tip gazda-oaspete prin TGA/DTA–FTIR–MS (Oral presentation)
11. C.-D. Varganici, D. Rosu, C. Barbu–Mic, L. Rosu, D. Popovici, C. Hulubei, B. C. Simionescu; Studiul comportamentului termic al poliimidelor semi-aromatice (Poster)

3.3. Ensure resources. Elaboration of the report stage.

The involved research team in the project realized the following activities:

- Monthly work sessions with team members;
- Counseling activities for postdoctoral students by senior researchers;
- Organizing panels of senior scientific team problem solving;
- Elaboration and submitting articles for publication in ISI journals;
- Establishing and procurement of the necessary materials for the development research program;
- Human resources, financial and material planning for the next stage;

- Acquisition activity planning, preparing documentation for procurement;
- Tracking the supply flow and the use of funds;
- Preparing stage report 2015 (scientific, financial)

In order to develop and implement management structure, team members met monthly and established detailed activity plans. It was followed effective and efficient communication of administrative, technical and financial research both within the team, and with the contracting authority. The entire research team was involved in drafting the report stage. It was compiled the file necessary to achieve independent financial audit in 2015.

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

Stage 2016

Objectives:

1. Photochemical stabilization of multicomponent polymeric systems
2. The thermal stability of the photostabilized multicomponent polymeric systems
3. Dissemination of the results

1. Photochemical stabilization of multicomponent polymeric systems

Photostabilization methods, as presented in our previous report, are generally related to the photodegradation mechanisms. Taking into account the different mechanisms of photodegradation processes, photostabilization may be accomplished through:

1. *Screening of surfaces exposed to ultraviolet radiations.* Protection is undertaken by coating the surface with some thin layers in order to stop the radiation from penetrating the polymer bulk, through the following mechanisms:

- *absorption of luminous energy* with formation of active species and modification of spin multiplicity, which lose their active character by photochemical transpositions or formation of inert species;
- *transformation of absorbed light* into vibrational energy, without modification of spin multiplicity, the deactivation of excited states being accompanied by thermal effects;

2. *Usage of energetic quenchers of excited states.*

3. *Hydroperoxides decomposition.*

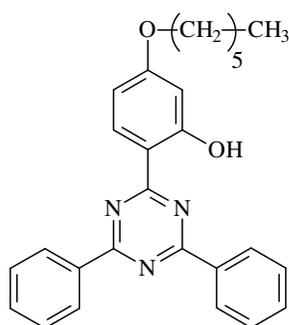
4. *Capture of radicals formed during exposure and their transforming into chemical species with low reactivity* represents an efficient photostabilization method.

1.1. Assessing the optimal concentration of the photostabilizer

In 2015 studies were initiated on the photochemical stabilization of some polymeric epoxide networks based on bisphenol A, crosslinked with epoxidized castor oil modified with maleic anhydride. From preliminary analyses it resulted that the product 2-(4,6-diphenyl-1,3,5-triazin-2-yl)-5-[(hexyl)oxy]-phenol, commercially known as *Tinuvin 1577 FF*, behaved as photostabilizing agent for the polymeric networks in coating applications. It was observed that the presence of triazine photo-stabilizer in low concentration (1% to resin mass) protected the polymeric network against photo-oxidation process during exposure to UV radiations in air and at wavelength values of 254 nm and 365 nm, respectively. The photostabilizing effect was evidenced by FTIR structural analyses conducted at sample surface, through monitoring the carbonyl index together with color and gloss modifications. It was also observed that *Tinuvin 1577 FF* slowed down the photo-oxidative process caused by UV radiations at both studied wavelength values, being more efficient at 365 nm than at 254 nm.

This year's research was oriented to obtaining the optimal concentration of *Tinuvin 1577 FF* in the polymer network bulk, with 1 to 4% crosslinking. Structural modifications were monitored by FTIR structural analyse, as well as some properties, such as color, gloss, mass variation and film thickness were monitored.

Fig. 44 shows as an exemplification, the color parameters variation of initial, non-irradiated samples as function of *Tinuvin 1577 FF* concentration in the polymer.



Tinuvin 1577 FF

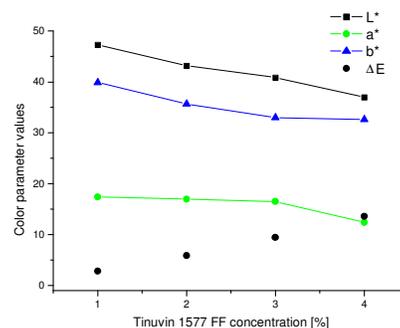


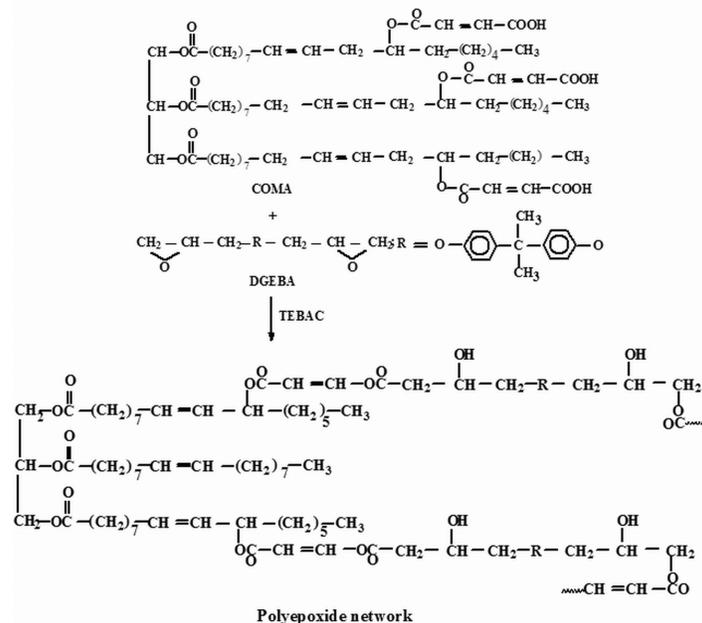
Fig.44 Color parameters variation as function of photo-stabilizer concentration

It may be observed that the photo-stabilizer presence leads to color modifications of the initial samples. The lightness factor (L^*) shows continuous decrease with photo-stabilizer concentration increase, indicating sample darkening. Chromatic coordinates values a^* and b^* also decrease with *Tinuvin 1577FF* concentration increase, indicating accumulation of green and blue chromophores in the studied samples. Color differences (ΔE) increase with *Tinuvin 1577FF* concentration increase. Taking into account the observation that up to 5% color modifications are not visible by the human eye, it was considered that a concentration of *Tinuvin 1577FF* up to 1% may be successfully applied as photostabilizing agent for the studied material, without significantly modifying its optical properties. The data obtained regarding photostabilizer influence on the crosslinked polymer properties are given in the next section.

2. The thermal stability of the photostabilized multicomponent polymeric systems

2.1. The influence of photostabilizers on the resistance of the multicomponent polymeric systems upon environmental factors action

A flexible polyepoxide network was obtained from maleinized castor oil (COMA) and diglycidyl ether of bisphenol A (DGEBA) for potential applications as high performance coating material (**Scheme 3**).



Scheme 3. Structure of the polyepoxide network

Initial and photostabilized networks were exposed to UV irradiation at two different wavelengths of 254 nm, for biomedical (sterilizing) and aeronautic applications, and at 365 nm in order to test material behaviour to outdoor environmental conditions. Both initial and photostabilized samples were evaluated by means of colour, gloss

properties and structural modifications using dielectric measurements, FT-IR, UV-Vis and scanning electron microscopy (SEM) techniques.

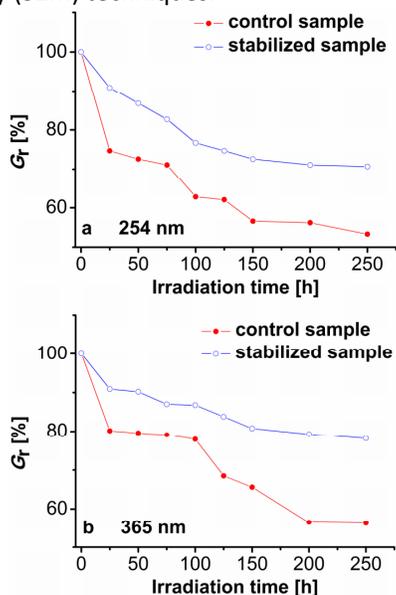


Fig. 45 a,b. Gloss retention as function of irradiation time at 254 nm (a) and 365 nm (b).

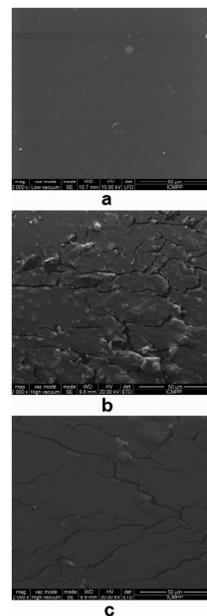


Fig. 46. SEM micrographs of non-irradiated sample (a); sample irradiated at 254 nm for 250 h (b) and at 365 nm for 250 h (c).

The photostabilized sample exhibited lower carbonyl index values compared with the non-stabilized one at all irradiation times. The *Tinuvin 1577 FF* photostabilizing effect on the samples irradiated with $\lambda_{max} = 365$ nm was demonstrated by an almost constant carbonyl index variation throughout the entire irradiation process, thus the photostabilizer absorbance capacity was more pronounced in the UVA region. Gloss retention (G_T) of sample surface decreased during irradiation. It is generally known that surface roughness increases with gloss retention decrease, as shown in **Figs. 45a** and **b** and confirmed by the SEM micrographs in **Fig. 46**.

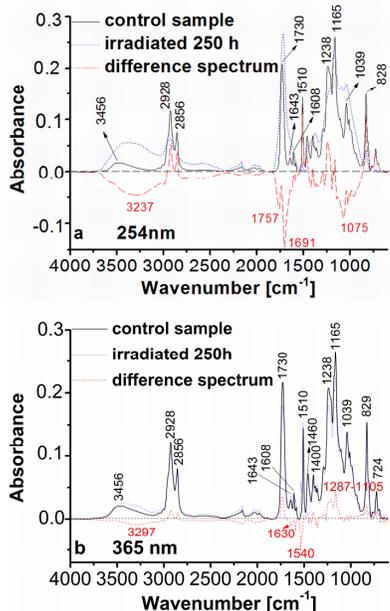


Fig. 47 a,b. Comparison between FT-IR spectra recorded for wavelengths of 254 nm (a) and 365 nm (b) for the photostabilized sample

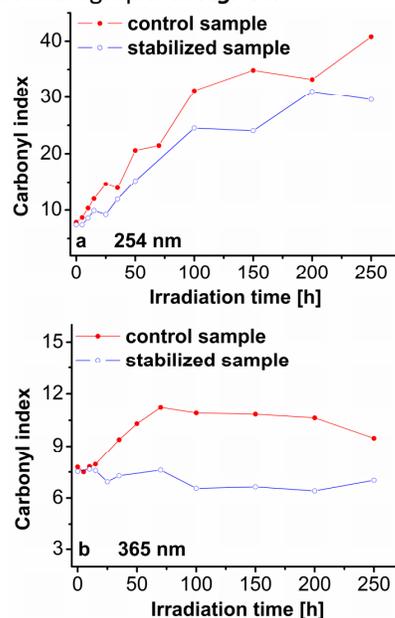


Fig. 48 a,b. Variation of carbonyl index during irradiation for 254 nm (a) and 365 nm (b)

Samples which contain photo-stabilizer were with 17.4% and 21.8% glossier compared with the non-stabilized samples, after an exposure of 250 h at 254 nm and 365 nm, respectively, thus this effect is most visible at 365 nm, due to a stronger destructive effect of UV radiation at lower wavelengths. The new signals from 3237, 1757, 1691 and 1075 cm^{-1} support both photo-oxidative processes with formation of hydroperoxide intermediates and chemical compounds with carboxyl and/or carbonyl groups (**Fig. 47a**) irradiated at 254 nm. Destruction of the ester bonds is indicated by the positive signals from 1287-1105 cm^{-1} which appeared mainly in the difference spectrum of samples irradiated with $\lambda = 365$ nm. The new signal from 1540 cm^{-1} in **Fig. 47b** could be attributed to the formation of some carbonyl conjugated groups during photo-degradation, such as presented in **Scheme 4** as a result of photo-oxidation process.



Scheme 4. Formation of new carbonyl conjugated groups during photodegradation.

The carbonyl index variation with irradiation time for both stabilized and non-stabilized samples is presented in **Figs. 48a** and **b**. The increase is more intense at higher energy radiation (lower wavelengths). Formation of a greater number of active radical species could explain the intensification of photo-oxidation at lower wavelengths. A continuous increase of the carbonyl index may be observed during irradiation with $\lambda = 254$ nm, while at $\lambda = 365$ nm the carbonyl index increased only in the first 70 hours of exposure, slowly decreasing afterwards. In the latter case it seems that the photo-oxidation processes are accompanied by ester structures photo-decomposition through Norrish type reactions that occur at $\lambda = 325$ nm, wavelength which is included in the emission spectrum of the lamp with $\lambda_{\text{max}} = 365$ nm. The photo-stabilizer effect of *Tinuvin 1577 FF* is visible in both cases. **Fig. 48a** shows that the stabilized sample has lower carbonyl index values compared with non-stabilized sample at all irradiation times. The *Tinuvin 1577 FF* photostabilizing action on the samples irradiated with $\lambda_{\text{max}} = 365$ nm is obvious. In this case, the carbonyl index value is almost constant throughout the entire irradiation process (**Fig. 48b**). The UV absorbance capacity of *Tinuvin 1577FF* is more pronounced in the UVA region.

The polyepoxide network is a potential material for coating applications. For this purpose pencil hardness, adhesion, flexibility and solvent resistance studies were undertaken. The sample proved to be highly resistant in aqueous, acid and salt media, and poorly stable in alkaline media. Flexibility decreased during irradiation time due to supplementary photo-crosslinking. The following coating properties of non-irradiated and irradiated sample were evaluated and listed in **Table 12**: pencil hardness, adhesion, solvents resistance and the flexibility.

Table 12. Coating performance of the initial and UV irradiated polyepoxide network

Sample	Properties		
	Pencil hardness	Adhesion	Flexibility
Control sample	4B	5B	3T
250 h at 254 nm	HB	5B	1T
250 h at 365 nm	HB	5B	1T

As one may observe from **Table 12**, both irradiated and non-irradiated samples show a very good adhesion (5B) to aluminium plates, as a consequence of large amounts of hydroxyl groups from the macromolecular chains. Although after irradiation the sample surfaces are affected, this does not influence adhesion, maintaining a value of 5B for both studied samples. It is well known that products obtained via DGEBA crosslinking are rigid, their major defect being their brittleness. The introducing of COMA endows the materials with an internal plasticizing effect, thus obtaining a crosslinked flexible compound. Under UV irradiation, the samples become more rigid with their flexibility decreasing from 3T to 1T. From **Table 13** one may observe that the polyepoxide network possesses a good resistance to HCl, EtOH, NaCl, distilled H_2O and is extremely weak alkaline media (NaOH).

Table 13. Chemical resistance of the polyepoxide network

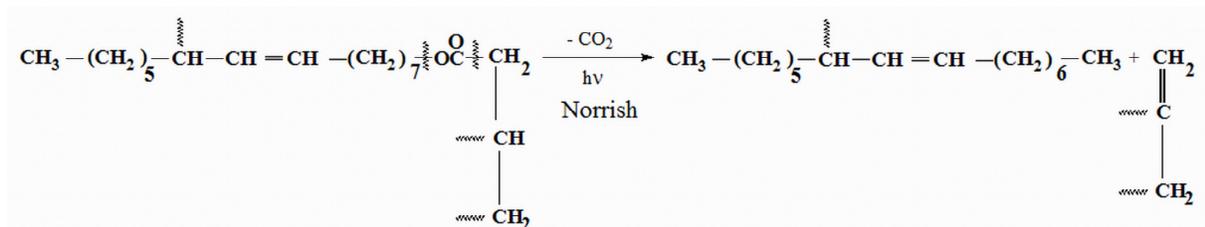
Chemical media	Control sample	Irradiated 250 h at 254 nm	Irradiated 250 h at 365 nm
NaOH (aq. 3 wt %)	complete film degradation	complete film degradation	complete film degradation
HCl (aq. 5 wt %)	film remains unaffected	film remains unaffected	film remains unaffected
NaCl (aq. 10 wt %)	film remains unaffected	film remains unaffected	film remains unaffected
EtOH (aq. 20 wt %)	film remains unaffected	film remains unaffected	film remains unaffected
distilled H ₂ O	film remains unaffected	film remains unaffected	film remains unaffected

The formation possibility of some crosslinked structures in these circumstances has been confirmed by hardness, dielectric and DSC measurements. In **Table 14** the hardness values for irradiated and non-irradiated samples are shown.

Table 14. Hardness values for irradiated and non-irradiated samples obtained by measuring the depth penetration in the tested sample of the device head

Sample	Control	Irradiated 250 h at 254 nm	Irradiated 250 h at 365 nm
Hardness (Shore A degree)	22	67	52

It can be therefore seen that the photodegradation mechanisms of the studied sample are dependent on the wavelength of UV radiation. Thus the photodegradation of samples irradiated at 254 nm occurred by hydroperoxide intermediates, while at 365 nm structural degradation of ester entities was carried out principally based on Norrish type reactions (**Scheme 5**).

**Scheme 5.** Photodegradation through Norrish reactions

- The *Tinuvin 1577 FF* photostabilizing effect on the samples irradiated with $\lambda_{\text{max}} = 365$ nm was demonstrated by an almost constant carbonyl index variation throughout the entire irradiation process, thus the photostabilizer absorbance capacity was more pronounced in the UVA region.
- Variation of physico-mechanical properties (toughness) and optical properties (colour, gloss) was explained in connection with the structural changes arising from UV light exposure. The photo-stabilized sample exhibited lower, almost constant carbonyl index values and a lower decrease in gloss retention throughout the whole irradiation process.

3. Insurance of the project implementation framework. Improving the implementation process

3.1. Dissemination of the results

Scientific papers: 2

1. Epoxy and succinic anhydride functionalized soybean oil for wood protection against UV light action; D.Rosu, R.Bodirlau, C.-A. Teaca, L.Rosu, C.-D.Varganici; *J. Clean. Prod.*, 112, 1175-1183 (2016) doi.org/10.1016/j.jclepro.2015.07.092; (IF=4.959) (SI=1.470)
2. A study on coating properties of an epoxy system hardened with maleinized castor oil; D.Rosu, F.Mustata, N.Tudorachi, C.-D. Varganici, L.Rosu, V.E.Musteata; *Prog. Org. Coat.*, 99, 480-489 (2016) doi.org/10.1016/j.porgcoat.2016.07.009; (IF=2.632) (SI=1.561)

Book chapters: 1

Chapter 19. Biopolymers from Renewable Resources and Thermoplastic Starch Matrix as Polymer Units of Multi-component Polymer Systems for Advanced Applications; C.-A.Teacă, R. Bodîrlău; Handbook of Composites from Renewable Materials, Volume 6: Polymeric Composites; Eds. V. K. Thakur, M. Thakur, M. R. Kessler; Wiley-Scrivener Publishing LLC, ISBN: 978-1-119-22380-1 (500 pages), 2016

Papers presented at scientific conferences: 9 (oral presentations: 1 and posters: 8)

25th "Symposium of Thermal Analysis and Calorimetry – Eugen Segal" organized by the Commission of Thermal Analysis and Calorimetry of the Romanian Academy, 15 April 2016, Bucuresti

1. Thermal behaviour of supramolecular inclusion complexes; C.-D.Varganici, N.Marangoci, L.Rosu, C.Barbu-Mic, D.Rosu, M.Pinteala, B.C.Simionescu (POSTER)
2. Structure–thermal properties relationship in semi-aromatic polyimides; D.Rosu, C.–D.Varganici, C.Barbu-Mic, L.Rosu, D.Popovici, C.Hulubei, B.C.Simionescu (POSTER)
3. Thermal behaviour of a flexible biobased epoxy resin network; L.Rosu, F.Mustata, N.Tudorachi, D.Rosu, C.-D.Varganici (POSTER)

The 9th International Conference on Modification, Degradation and Stabilization of Polymers, Cracow, Poland, September 4-8, 2016

4. Photochemical resistance of epoxy and succinic anhydride functionalized soybean oil coated wood; C.-D.Varganici, D.Rosu, C.-A.Teacă, L.Rosu, R.Bodîrlău (Communication)
5. Thermal stability investigation of epoxy resin based on castor oil maleate and diglycidyl ether of bisphenol A; E.Marlica, F. Mustata, N.Tudorachi, D.Rosu, C.-D.Varganici (POSTER)
6. Effect of thermal aging on the optical properties of poly(ester urethane) elastomers; L.Rosu, S.Oprea, D.Rosu, C.-D.Varganici (POSTER)
7. Photochemical behaviour of biobased epoxy matrix from maleinized castor oil and diglycidyl ether of bisphenol A; D.Rosu, F.Mustata, C.-D.Varganici, E.Marlica, N.Tudorachi, L.Rosu (POSTER)
8. Bio-based polymer composites – structure and properties investigation; C.-A.Teacă, R. Bodîrlău, N. Tudorachi, L. Rosu, E. Marlica, D. Rosu (POSTER)

The XXXIV Romanian Chemistry Conference, Calimanesti-Caciulata, Valcea, Romania, 04-08 October 2016

9. Biobased epoxy matrix from maleinized castor oil and diglycidyl ether of bisphenol A; E.Marlica, F.Mustata, C.-D. Varganici, D.Rosu (POSTER)

3.2. Completing the project database

Project database has been updated and can be found at: <http://www.icmpp.ro/mcps/ro/>

3.3. Elaboration of the project's report stage

The involved research team in the project realized the following activities:

- Monthly work sessions with team members;
- Counseling activities for postdoctoral students by senior researchers;
- Organizing panels of senior scientific team problem solving;
- Elaboration and submitting articles for publication in ISI journals;
- Establishing and procurement of the necessary materials for the development research program;
- Human resources, financial and material planning for the next stage;
- Acquisition activity planning, preparing documentation for procurement;
- Tracking the supply flow and the use of funds;
- Preparing synthetic report for all project's period.

In order to develop and implement management structure, team members met monthly and established detailed activity plans. It was followed effective and efficient communication of administrative, technical and financial research both within the team, and with the contracting authority. The entire research team was involved in drafting the final synthetic report. It was compiled the file necessary to achieve independent financial audit in 2016.

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

Main indicators of the results obtained during project implementation between 2011-2016:

Indicators type	Name	No./year						Total
		2011	2012	2013	2014	2015	2016	
Indicators of results	Accepted and published articles in ISI journals		3	10	6	6	2	27
	Book chapters				1	2	1	4
	Participation to scientific symposia	4	27	9	9	11	9	69
	Other results:							
	Doctoral thesis			2	1			3
Research project		1	1				2	
Research report			1				1	
Master dissertation thesis			1				1	

Project Director,
Dr. Dan Rosu

