

Scientific Report

regarding project implementation in the period January – December 2015

Project Title: **“Advanced researches related to the behavior of multi-component polymer systems under simulated environmental factors action”**

Activities of the proposed objectives were accomplished and are summarized in this report.

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.

Objective 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.

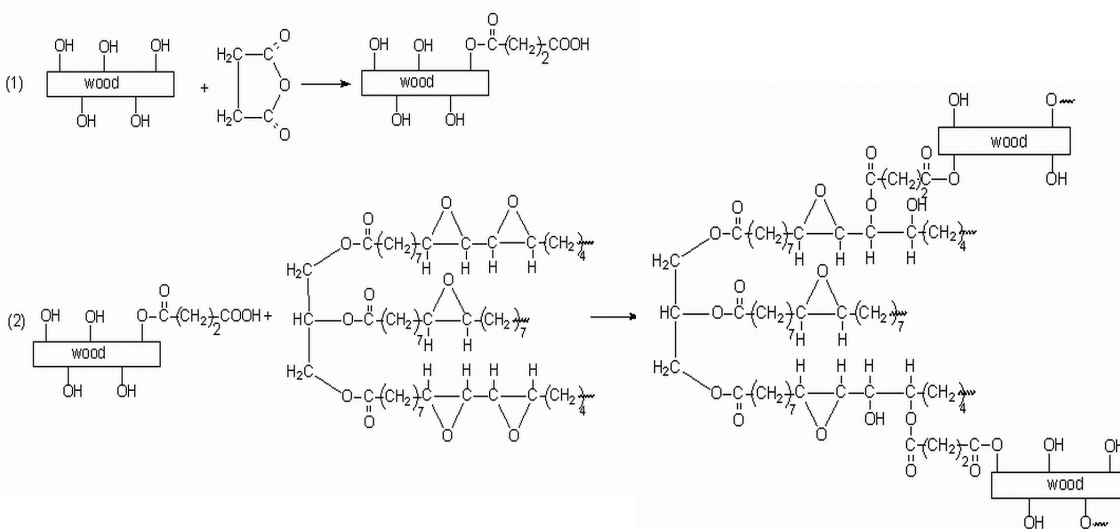
4. *Capture of radicals formed during exposure and their transforming into chemical species with low reactivity* represents an efficient photostabilization method. The mechanism consists in the introduction of some light sensitive compounds into the material bulk, such as hindered amines (HALS), which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



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

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. 1** 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).

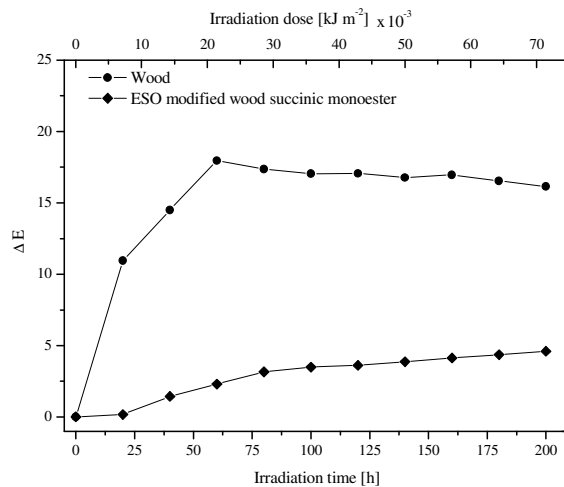


Fig. 1 Variation of colour difference as a function of irradiation time and dose

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. 2** 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. 3**). (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).

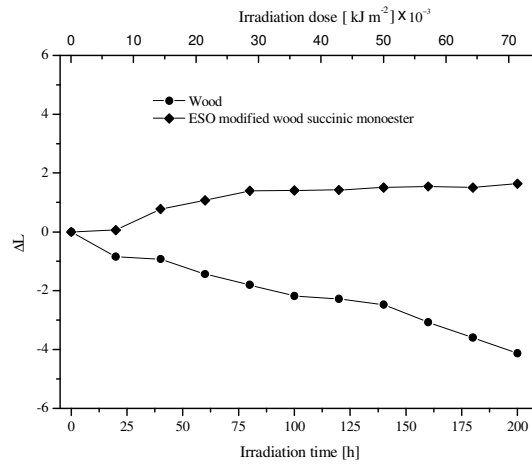


Fig. 2 Variation of lightness factor as a function of irradiation time and dose

The data shown in **Fig. 3** 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.

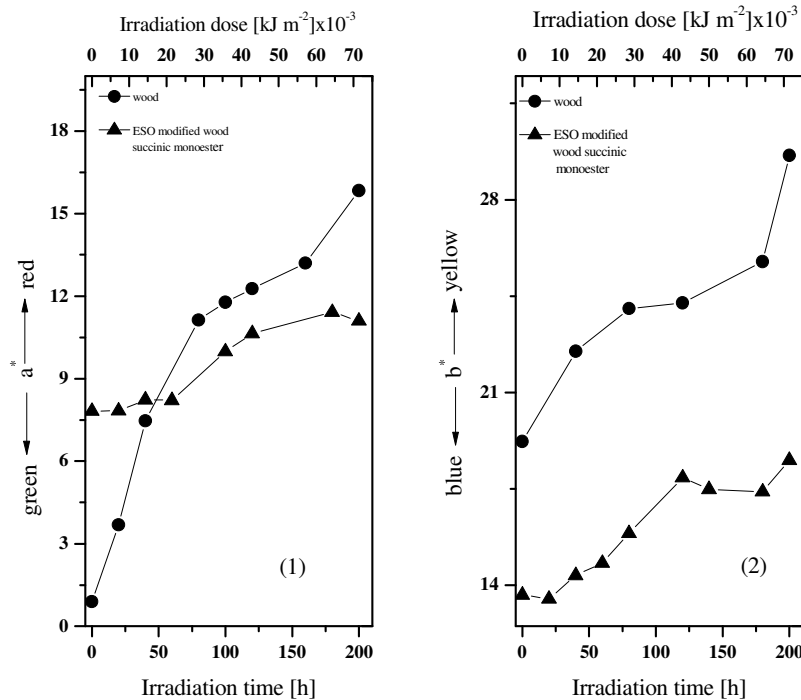


Fig. 3 Modification of chromatic coordinates with irradiation time and dose

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 FTIR 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. 4** and **5**.

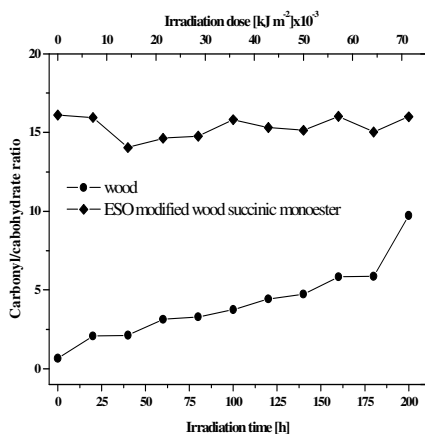


Fig. 4 Modification of carbonyl group content during irradiation of unprotected and coated wood samples

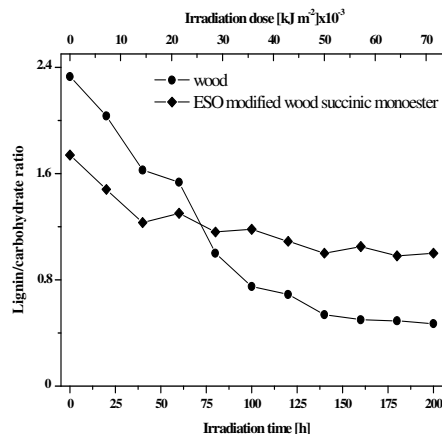
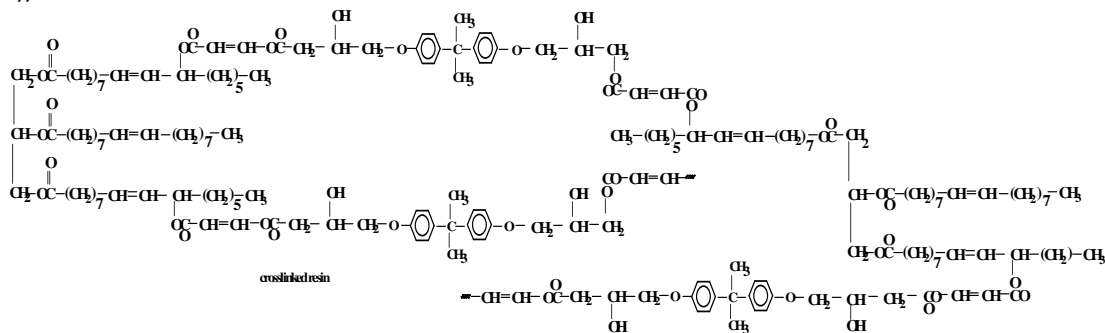


Fig. 5 Modification of lignin content during irradiation of unprotected and coated wood samples

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. 4**). The ratio between surface signals in the range $1698\text{--}1774\text{ cm}^{-1}$, corresponding to carbonil groups, and in the range $1343\text{--}1396\text{ cm}^{-1}$, corresponding to carbohydrate structural units from cellulose, remains almost constant. **Fig 5**. 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 ($1452\text{--}1535\text{ cm}^{-1}$) and the one at $1343\text{--}1396\text{ cm}^{-1}$, specific to carbohydrate units decreases much slowly in the case of protected wood.

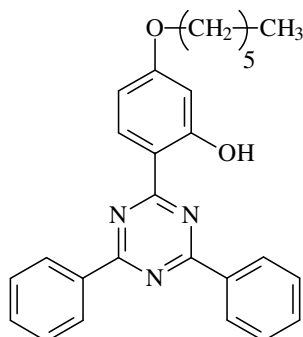
1.1.2. Photostabilization of epoxy resins crosslinked with modified vegetable oils

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, FTIR), SEM micrographs. Variation of carbonyl index with irradiation time for the studied samples is given in **Table 1**.

Table 1. Variation of carbonyl index with irradiation time (unpublished data)

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.

Objective 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. 6** depicts the TG-DTA thermograms of Tinuvin 1577 FF sample, recorded in the temperature range $32\text{-}700^\circ \text{C}$, at a heating rate of 10 K min^{-1} and in inert atmosphere (N_2). 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 338°C when the beginning of mass loss occurs. The photostabilizer thermally decomposes in a single stage with maximum mass loss rate around 452°C , as it may be deduced from the maximum peak temperature in the DTG curve.

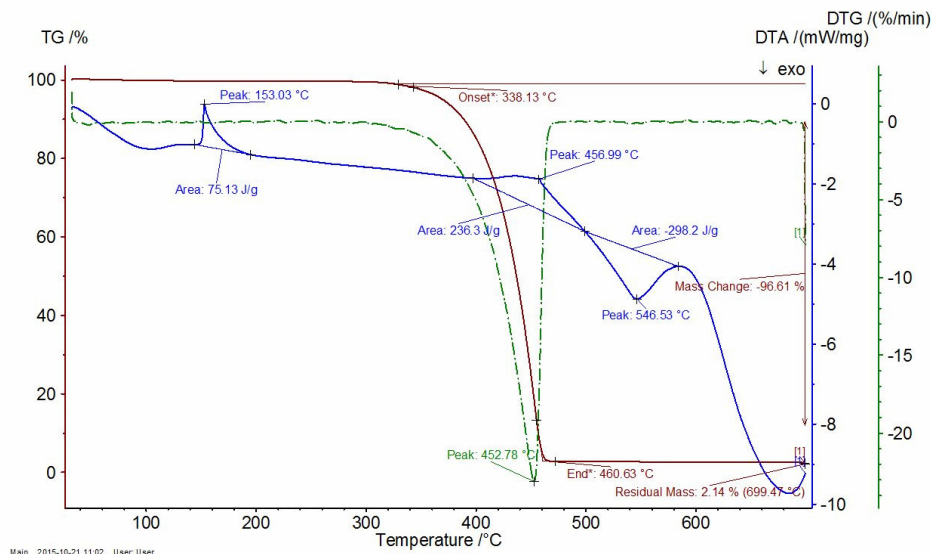


Fig. 6 TG, DTA and DTG curves of Tinuvin 1577FF photostabilizer

The thermal decomposition process ended at around 460°C, with over 97,6% mass loss. The residue mass was 2,14% at 700°C. The DTA thermogram indicates two endothermic signals at 153,03°C ($\Delta H = 75,13 \text{ Jg}^{-1}$) and 457°C ($\Delta H = 238,3 \text{ Jg}^{-1}$) and an exothermic one at 546,53°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 (*unpublished data*).

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 (*unpublished data*). Approximately 10 mg of sample was weighed in alumina crucibles and heated in inert atmosphere, in the range 30-700°C at a rate of 10 K min⁻¹. Mass variation as a function of temperature is given in **Fig. 7**.

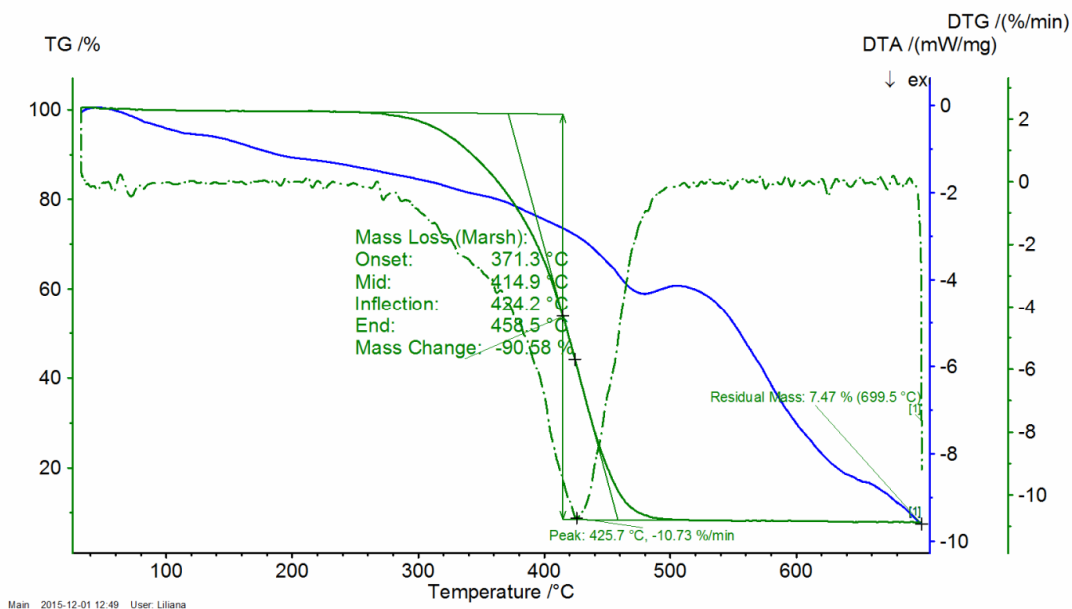


Fig. 7 Thermogram describing the thermal decomposition of epoxy resin based on bisphenol A and crosslinked with castor oil modified with maleic anhydride and stabilized with „Tinuvin 1577 FF”

Fig. 7. demonstrates that the studied sample thermally decomposes in a single stage in the temperature range $371,3 \div 458,5^{\circ}\text{C}$. Confirmation of this statement is given by the shape of the DTG curve which shows a single maximum at $425,7^{\circ}\text{C}$. The starting thermal decomposition temperature of the studied sample (T_{onset}), defined as the temperature above which the mass losses become significant, is $371,3^{\circ}\text{C}$. The final thermal decomposition temperature (T_{endset}), defined as the temperature after which the sample exhibits insignificant mass loss, is $458,6^{\circ}\text{C}$. 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 $425,7^{\circ}\text{C}$, value corresponding to the DTG curve peak. At this temperature the sample losses mass at a rate of $-10.73\% \text{ min}^{-1}$. Residual mass at 700°C 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.

Objective 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 (Padurarur), 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 Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ 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.Padurarur, 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, RICCCCE 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 (Padurarur); Poly(vinyl alcohol)-cellulose cryogels. Photochemical behavior (Poster)
6. C.-D. Varganici, L. Rosu, O.M. Padurarur (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 poliimididelor 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.

Project director,
Dr. Dan Rosu

