# Scientific report

*Regarding the project implementation during the period January-December 2013*

**Project title**: "***Advanced research related to the behavior of multicomponent polymer systems under simulated environmental factors action***"

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

### Introduction

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-degradative processes. These processes involve both color and gloss changes that only affect the aesthetic 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 (Fig. 1). A decrease in the values of water absorption was recorded for modified wood compared with the initial sample.

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).
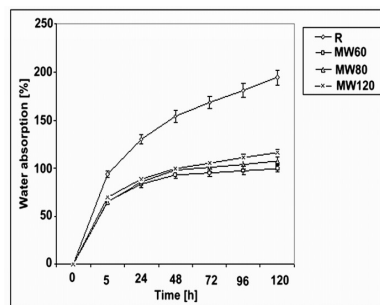


Fig. 1

## 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 (Tg). Tg values can provide an indication of the miscibility of the MPS components. In the case of MPS that have not undergone cross-linking (eg. 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/FTIR, TG/MS) allows qualitative evaluation of volatile products evolved during thermal decomposition, depending on the temperature. The semi-interpenetrated polymer networks (SIPNs) based on polyurethane (PU) and epoxy resin (ER) obtained during the stage of 2012 show a single composition-dependent Tg. Tg 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.

### 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 $20^0$C/min) in a temperature range between 30 and $700^0$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. 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 and Ozawa-Flynn and Wall which use the thermograms registered at four different heating rates. The conversion function was determined by multiple nonlinear regression method.

### 2.2.1. Semi-interpenetrated polymer networks (SIPNs) 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 1).

| $\alpha$ | Kinetic parameters | | | |
| | 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. 2 and 3 show the graphs obtained with the Friedman (Fig. 2) and Flynn-Wall-Ozawa (Fig. 3) methods at the conversion degree ($\alpha$) values between 0.1 and 0.9. Both isoconversional methods indicate the dependence of activation energy (E) on the conversion degree.
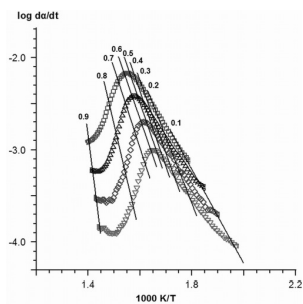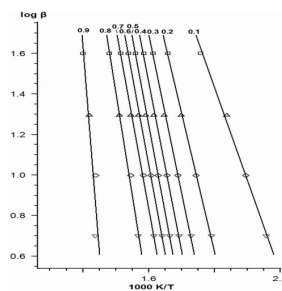.

Fig. 2



Fig. 3

### 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. 4 shows the TG curves (Fig. 4A) and DTG curves (Fig. 4B). Data on behavior of wood thermal degradation are presented in Table 2. Chemical modification of wood favorably influenced thermal stability, especially at high concentrations of SA.
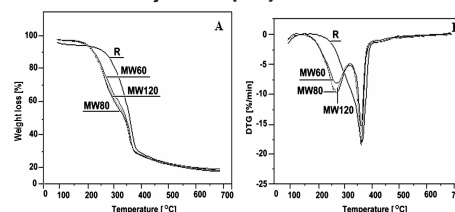


Fig.4

**Table 2.** *Data resulted from the analysis of thermal degradation behavior of wood*

| Wood sample | $T_i$ (°C) | $T_{50\%}$ (°C) | $T_{mI}$ (°C) | $W_{mI}$ (%) | $T_{mII}$ (°C) | $W_{mII}$ (%) | $T_f$ (°C) | $T_{f\text{-}T_i}$ (°C) | $W_{Tf\text{-}Ti}$ (%) | $W_{rez}$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| 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 FTIR spectroscopy (Fig. 5). It may be observed that signals intensity change with wood degradation temperature.
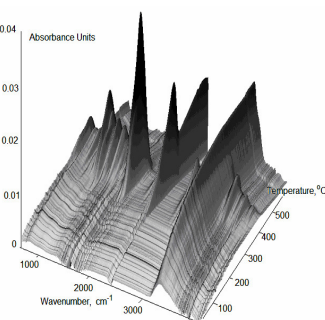


Fig.5

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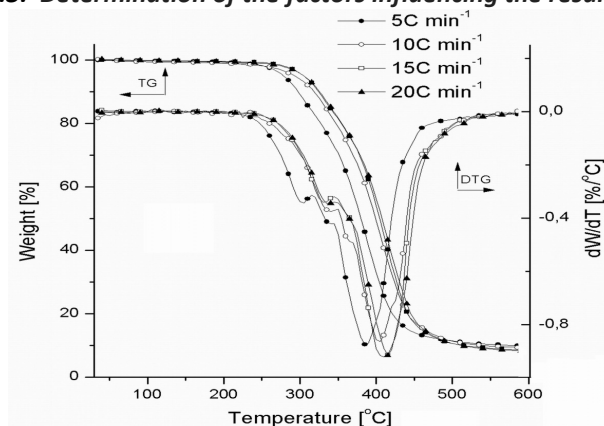


Fig.6

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. 6).

### 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, photodegradation of polymers is an effect of energy dissipation of photochemically 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 interchange 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 (eg. photooxidation) 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. Photo-degradation kinetics study

In the photo-degradation kinetic studies of semi-interpenetrated polymer networks (SIPN) based on polyurethane (PU) and epoxy resin (ER), there were followed by FTIR 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.
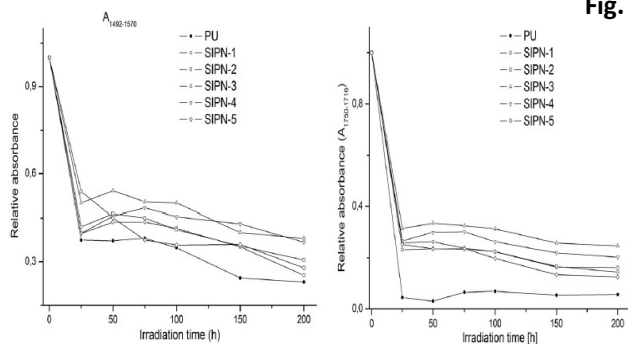


**Fig. 7** The highest changes occurred in the first 25h of irradiation. After 200h irradiation times the most important loss of urethane bonds occurred in the PU structure due to photo-Fries rearrangement. One explanation of this behavior may be related to the high transparency of the PU film compared 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. 7).

The highest loss of ester linkages have been identified for the network comprising 40% cross-linked ER. It may be observed 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 SIPNs 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.
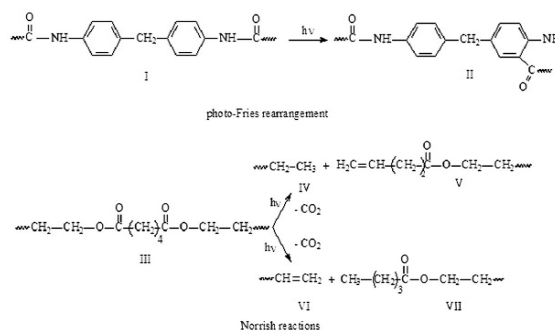


## 4. Insurance framework of the project. Improving the implementation process
### 4.1 Completing the project web database
Project database has been updated and can be found at: http://www.icmpp.ro/mcps/ro/

### 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. Paduraru, A.Bosinceanu, G. Tantaru, C. Vasile, Effect of hydroxypropyl;-cyclodextrinon 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

Master Dissertation thesis:

**X ray diffractometry study of polymers and polymer composites**, June 2013, Master 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.

**Project director,**
Dr. Dan Rosu