

# Thermal Analysis of Polymer Blends

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*One of the major disadvantages of epoxy resins when they are used to impregnate a fabric or when they are used to obtain laminates is their rigidity that leads in loading conditions to the matrix fracture followed by breaking of fabric due to a shearing mechanism in which the two free parts of the matrix fracture acts as a scissor. During the design of a composite material or structure such behavior of the matrix has to be taken into account and the problem could be solved if the rigidity of the matrix is reduced. The present study is about changing the value of this parameter by using an organic polymer solvent and a thermoplastic polymer to modify the basic properties of an epoxy resin. At this time an analysis of thermal properties of polymer blends is done to determine the effect of solvent and thermoplastic polymer presence inside the epoxy matrix.*

*Keywords: epoxy resin, polyvinylpyrrolidone, 1-methyl-2-pyrrolidinone, specific heat, thermal expansion coefficient*

Epoxy systems are relatively low molecular weight pre-polymers able to be processed under various conditions. These systems have two important advantages in comparison with unsaturated polyester resins: they can be partially treated and stored in this state and they exhibit a low contraction during the curing process. Epoxy composites are one of the most important classes of thermosetting materials and they are widely used due to their strong soldering resistance, high insulation and thermal resistance. These epoxy resins systems provide characteristic properties that can be combined with the outstanding properties of liquid crystalline polymers [1], [2]. Approximately 45% of the total amount of produced epoxy resin systems is used in protective coatings, while the rest of these systems is used in structural applications, such as laminates and composites, tools, casting, construction, adhesives and so on [3]. A wide range of raw materials can be used for the preparation of epoxy resins, thus offering a variety of resins with highly controllable performance characteristics. These resins are generally prepared by reaction of poly-functional amines or phenols with epichlorohydrin in the presence of a strong base [4] - [15]. Nowadays epoxy resins systems are widely used in a wide range of applications as fiber-resistant composite materials forming, general purpose adhesives, high performance coatings and encapsulating materials due to their high adhesion to many substrates and chemical resistance, [16] - [18]. Many researchers had investigated the mechanical, chemical and thermo-mechanical properties of different epoxy resins systems by different methods [19]. Graur et al. [20] studied specific heat and coefficient of thermal expansion of epoxy systems doped with ionic substances. It was analyzed the effect of the ions presence inside of epoxy matrix. It was found that the presence of ions inside of epoxy composites improved their thermal behavior by decreasing values of investigated parameters. Munteniță et al. [21] analyzed the specific heat of modified composite materials with nanoparticles of barium and strontium ferrites by means of a differential scanning calorimetry method (DSC). It was determined that the modification of epoxy composites with nanoparticles of barium and strontium ferrites leads to an increasing of specific heat. Also, the epoxy systems are used as matrix for fiber and/or fabric reinforced composites. So, Ștefănescu et al. [22] used the modified epoxy resin (Epiphen RE 4020 - DE 4020 system) as a stratified epoxy matrix reinforced with different fabrics. It was investigated the specific heat and coefficient of thermal linear expansion of fabric reinforced hybrid epoxy composites. Bunea et al. [23] analyzed the thermomechanical and electrical properties of stratified hybrid epoxy materials. The epoxy matrix of four composites materials was made of Epiphen resin system RE4020 - DE4020. In many other researches it was used Epiphen resin system RE4020 - DE4020 to investigate the electrical, thermal, tribological and mechanical properties fiber or fabric reinforced epoxy composites [24], [25] and filled epoxy materials such as clay [26].

The aim of this paper is to analyze the specific heat and coefficient of thermal linear expansion of modified epoxy composites made of Epiphen RE4020 - DE4020 system by adding of solvated polyvinylpyrrolidone (PVP) powder in 1-methyl-2-pyrrolidinone solvent at different concentrations.

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## Experimental part

### Materials and methods

As epoxy matrix it was used Epiphen system consisting of RE4020 (resin) and DE4020 (hardener). This system was used to form polymer mixtures with the polyvinylpyrrolidone (PVP) (powder) and 1-methyl-2-pyrrolidinone (1M2P) solvent. Four materials were formed for this study. As molds it was used the cylindrical polypropylene tubes with 8 mm diameter and 220 mm length. The reference material was composed of RE 4020 epoxy resin and DE 4020 hardener with 100:30 ratio and it was denoted M0. The other three materials were formed using the RE 4020-DE 4020 epoxy system, which was modified by adding of different concentrations of polyvinylpyrrolidone powder and 1-methyl-2-pyrrolidinone solvent. The concentrations of the used components to form the mixtures are shown in Table 1. The composite materials modified with (PVP) powder and (1M2P) solvent was mixed mechanically with the resin for one hour and then the right amount of hardener was added continuing the stirring for 15 minutes. The final mixture has a gel time of about 30 minutes and during this period the liquid mixture was placed into the molds. As it easily to notice the concentration of PVP in 1M2P solution is the same for all the materials but at the final material level the epoxy resin is diluted by the presence of 5%, 10% or 15% PVP solution in 1M2P.

**Table 1**  
MATERIALS USED TO FORM POLYMER BLENDS COMPOSITES

Sample code	Resin RE4020 [ml]	Hardener DE4020 [ml]	PVP [g]	1M2P [ml]	%
M0	136.67	45.55	-	-	0%
M1	130.76	43.58	1	9	5%
M2	123.07	41.00	2	18	10%
M3	107.70	35.90	3	27	15%

The thermal measurements were performed by using Differential Scanning Calorimeter (DSC) for specific heat analysis and Thermo-Mechanical Analyzer (TMA SDTA 840) for investigation of coefficient of thermal linear expansion. The acquisition and evaluation of data was realized with STARE software. The specific heat of epoxy composite materials was measured by two methods. In first method the samples were subjected to two heating-cooling cycles on temperature interval  $-60^{\circ}$  to  $180^{\circ}\text{C}$  with  $10^{\circ}\text{C}/\text{min}$  and four isothermal processes with 3 minutes duration at each  $-60^{\circ}$  and  $180^{\circ}\text{C}$  temperatures. In second method the samples were subjected just to one heating-cooling cycle on temperature interval  $-60^{\circ}$  to  $180^{\circ}\text{C}$  with  $10^{\circ}\text{C}/\text{min}$  and two isothermal processes of 3 minutes duration at each  $-60^{\circ}$  and  $180^{\circ}\text{C}$  temperatures. For investigation of thermal expansion coefficient of epoxy composites, it was applied a heating-cooling cycle on the temperature interval from  $30^{\circ}$  to  $180^{\circ}\text{C}$  with  $10^{\circ}\text{C}/\text{min}$  and three isothermal processes with 3 minutes duration at each  $30^{\circ}$  and  $180^{\circ}\text{C}$  temperatures.

A Raman spectrophotometry analysis had been done in order to realize a qualitative evaluation of the polymer blends modifications and eventually to identify the effect of PVP-1M2P solution.

## Results and discussions

The Raman spectrophotometry had provided the spectra showed in fig. 1. and fig. 2., once again it is very difficult to interpret the results for the Epiphen epoxy system since there is not available information regarding the chemical structure of the liquid components, but it is noticeable that the resin and the hardener have some common peaks. The same thing is observable for PVP and 1M2P but, in this case it is about pure substances. In solution the peaks of PVP ( $145, 400, 416,$  and  $431\text{cm}^{-1}$ ) are disappearing (the solution concentration is the same of 10%) and is low with respect to the 1M2P presence. The same situation is visible in the case of epoxy system where the polymer peaks are almost identical with the RE4020 (resin) and the peaks of DE4020 (hardener) are not appearing on the polymer spectrum ( $127, 178, 262, 304,$  and  $415\text{cm}^{-1}$ ). All the spectra were obtained by the same setting of Raman spectrophotometer and it is easily to notice that in the case of the solution the intensity decreases from 1M2P to the solution while in the case of the epoxy resin the intensity is higher in the case of solid polymer (in solid phase the signal is much clear). In the case of the solution (PVP in 1M2P) the absence of the PVP peaks into the solution might be explained by the fact that in solution there are monomers (the PVP Raman analysis was done on powder) and not PVP chains. In the case of epoxy resin the fact that the hardener peaks are not appearing could be explained through the chemical interaction between the two components (resin and hardener). In fig. 3. The Raman spectra of the three formed materials (M1, M2, M3) are presented together with the Raman spectrum of the solid epoxy resin. It is easily to observe that the peaks of epoxy resin are not affected by the presence of 1M2P and PVP inside the its matrix excepting the fact that a higher concentration diminishes the peak amplitude.

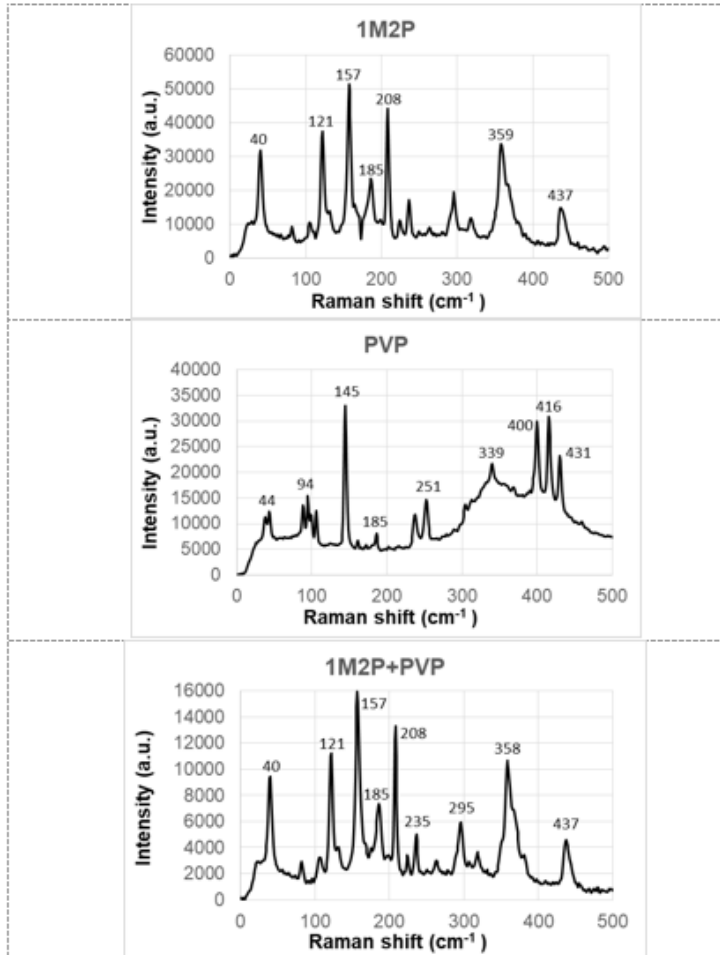


Fig. 1. Raman spectra of 1M2P, PVP and the solution 10% of PVP in 1M2P

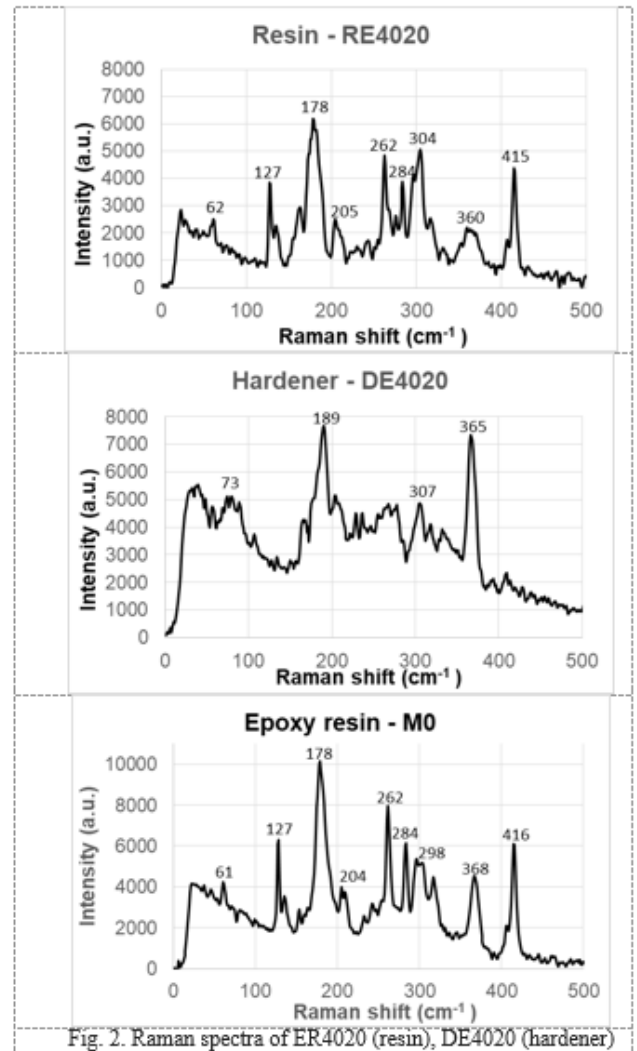


Fig. 2. Raman spectra of ER4020 (resin), DE4020 (hardener) and solid polymer (epoxy - M0)

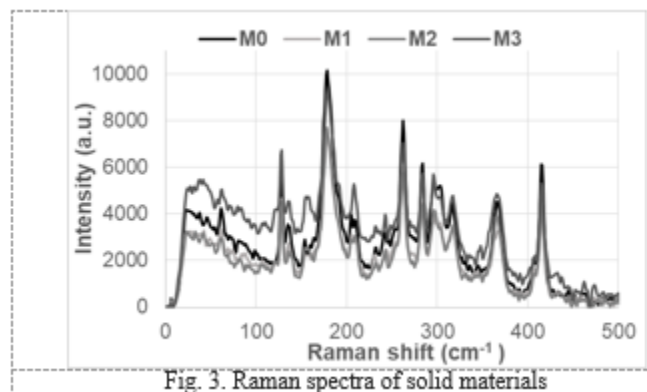


Fig. 3. Raman spectra of solid materials

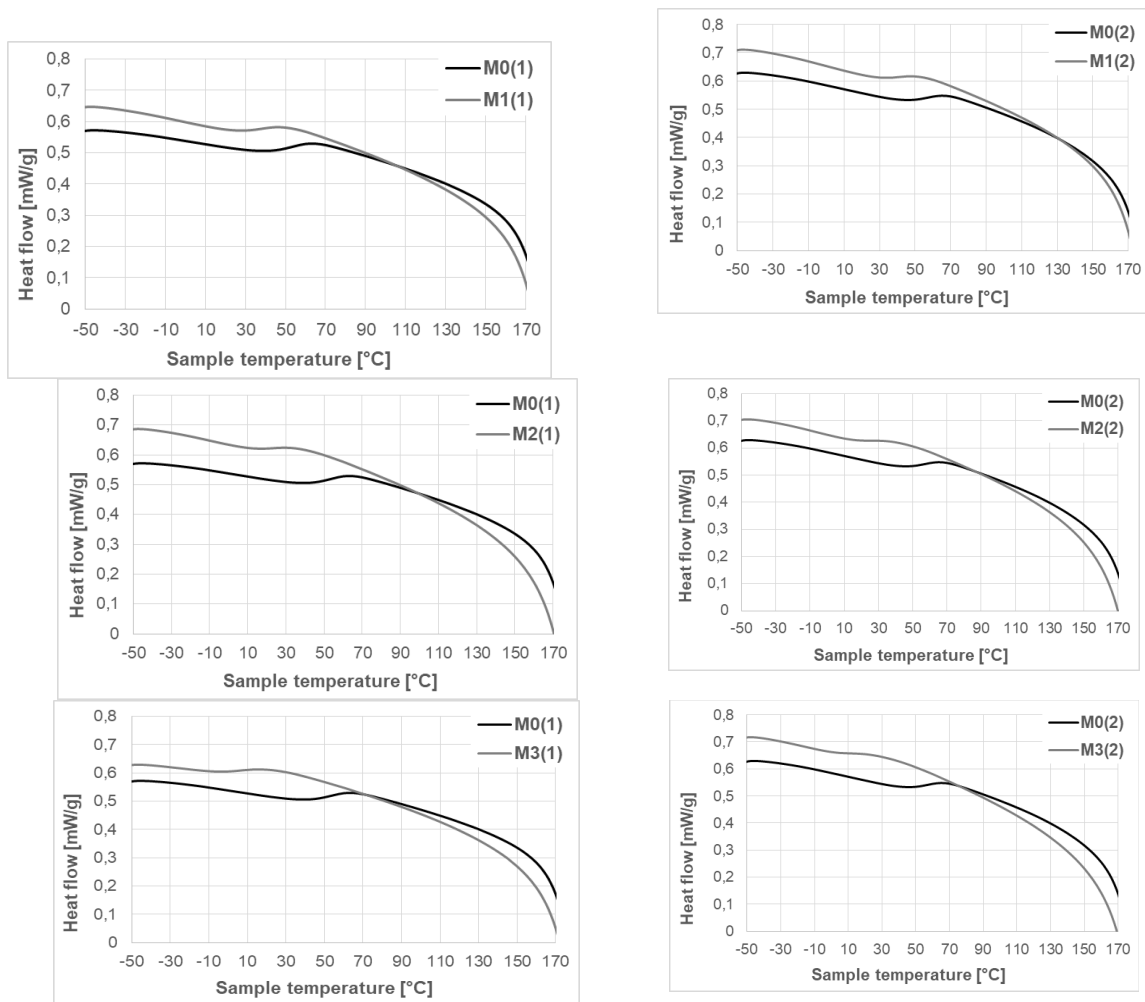
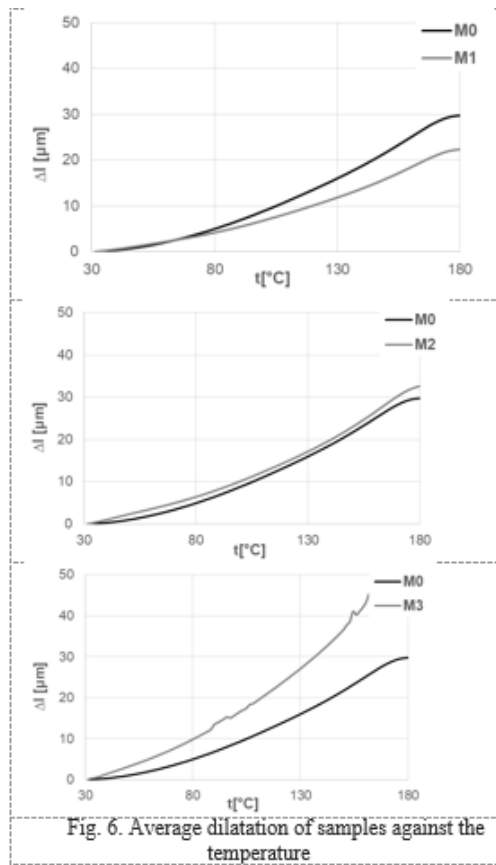
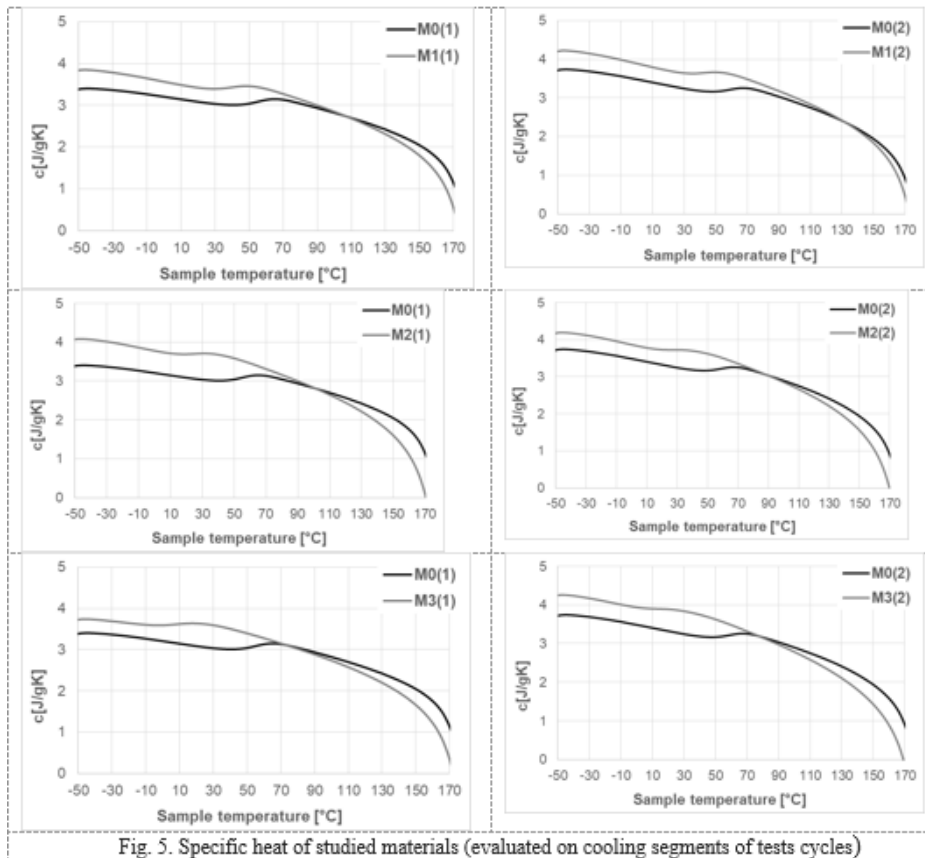


Fig.4. The DSC normalized heatflow through sample for the studied materials

The specific heat analysis of formed materials is also presented together with the reference material (M0). For each studied sample the weight was measured before and after the test to determine the loss of substance (volatile components) since the specific heat was determined in isobar conditions. In fig. 4. the heatflow vs. sample temperature curves are presented for each material but it is about the weight normalized heatflow *i.e.* the heatflow through the mass unit of the sample. In this case it is important to notice that the normalization is taking into account the initial value of the sample mass because, as it is easily observable, for the second testing cycle the value of the normalized heatflow is higher than the value of the same parameter during the first cycle. Together with the DSC analysis a weight analysis of the samples was made and the loss of weight of each sample is presented in Table 2. It seems that the amount of loss weight is directly related with the amount of 1M2P or PVP but in this respect it has to be said that the samples were not thermally treated according to the epoxy system producer recommendations and since the DSC test temperatures are above the vaporization point of 1M2P it is suitable to admit that the solvent is not chemically bonded to the epoxy resin. However, it is also possible to notice that there is a loss of weight even for the epoxy resin but this loss is smaller if the material is thermally treated (is polymerized in optimal conditions).

**Table 2**  
THE LOSS OF WEIGHT FOR STUDIED MATERIALS DURING DSC TESTING

Material	One cycle test	Two cycles test
M0	0.58%	0.78%
M1	0.73%	1.25%
M2	2.34%	3.42%
M3	3.32%	4.31%



	M0	M1	M2	M3
(30-40)°C	5.57E+01	1.44E+02	1.95E+02	1.79E+02
(40-50)°C	9.19E+01	1.59E+02	1.84E+02	1.76E+02
(50-60)°C	1.25E+02	1.50E+02	1.60E+02	1.68E+02
(60-70)°C	1.42E+02	1.42E+02	1.53E+02	1.71E+02
(70-80)°C	1.55E+02	1.44E+02	1.53E+02	1.77E+02
(80-90)°C	1.61E+02	1.50E+02	1.60E+02	1.81E+02
(90-100)°C	1.65E+02	1.55E+02	1.64E+02	1.85E+02
(100-110)°C	1.65E+02	1.58E+02	1.69E+02	1.88E+02
(110-120)°C	1.68E+02	1.61E+02	1.70E+02	1.91E+02
(120-130)°C	1.71E+02	1.66E+02	1.78E+02	1.99E+02
(130-140)°C	1.77E+02	1.72E+02	1.88E+02	2.09E+02
(140-150)°C	1.84E+02	1.83E+02	2.00E+02	2.23E+02
(150-160)°C	1.90E+02	1.92E+02	2.13E+02	2.56E+02
(160-170)°C	1.97E+02	2.05E+02	2.38E+02	3.43E+02
(170-180)°C	3.94E+02	4.74E+02	6.51E+02	9.14E+02

**Table 3**  
LINEAR EXPANSION COEFFICIENT FOR  
STUDIED materials  $\alpha$ [ppm/°C]

The results regarding the specific heat of studied materials are given in fig. 5. and it is noticeable that the value of the specific heat of each material is lower than the value for epoxy resin at elevated temperatures (after the peak presented by the specific heat of epoxy resin at about 65°C) and is higher at lowered temperatures (before the peak presented by the specific heat of epoxy resin). What it is interesting is the fact that after the second cycle of heating the specific heat values of the modified materials are practically identical. Also it is observable that the peak (of modified materials and corresponding to the 65°C for the resin -  $T_g$ ) is moving to the left proportionally with the modifying agent presence. That is indicating an alteration of  $T_g$  leading to poorer properties of obtained materials.

The thermomechanical analysis reveals that the higher is the amount of modifying agent the higher is the dimensional instability of materials as it might be noticed in fig. 6. that reveals the increase of the material thickness against the temperature value. Regarding the values of linear thermal expansion they are presented in the Table 3. and they are averaged values over three samples all tested in the same conditions but having different initial dimensions. There are some contradictory data on the first two temperature intervals and on the last one but they can be explained as transitory states even the testing program was designed with initial and final isothermal segments. It seems that the M2 material is almost identical to the epoxy resin meaning that the amount of added modifying agent is not changing the dimensional stability of the material (very good for epoxy resins). It is easy to notice that in the case of M3 material there are some asperities on the dilatation vs. temperature curve that could be interpreted both by massive loss of weight (with volume consequences) or reaching of softening point (lowered by the presence of modifying agent).

## Conclusions

The study was initiated to analyze the modifications regarding the thermal response induced by the presence of another polymer inside the epoxy polymer matrix. The other polymer is polyvinylpyrrolidone and in order to place it into the epoxy matrix was solubilized in 1-methyl-2-pyrrolidinone. Of course it is expected that mechanical properties of the polymer blends to be lowered comparing with the ones of the epoxy resin but this could be an advantage in the case of properties design when some structures need less brittle matrix in some areas (as in the case of car bodies).

The idea is also to use 1-methyl-2-pyrrolidinone to solubilize some inorganic substances in order to try to get ceramic nanostructures directly into a polymer (like in the method of citric gels). In this case the polyvinylpyrrolidone is used to avoid the saturation of inorganic salt solution in the mentioned solvent.

The Raman spectrophotometry does not emphasized any spectral modification but this does not mean that inside the mixture some reactions did have not place but the amount of modifying agent is too low to determine a signal high enough to be visible throughout the epoxy resins signals (peaks). It is possible to admit that, regarding the Raman spectra of modified materials, that the correspondent peaks of 175cm<sup>-1</sup> of 1M2P are appearing proportionally with solvent concentration inside the 178cm<sup>-1</sup> peak of Epiphen RE 4020.

From the thermal point of view, on one hand, it is observable the vaporization of the solvent (due the fact that the materials were not thermally treated) and the amount of vaporized substance is proportional with the amount of modifying agent. On another hand the analysis revealed the fact that adding the modifying agent the glass transition of the material is moving toward lower values of the temperature. In the case of double cycles DSC tests the value of the specific heat of

modified materials is practically the same meaning that thermal treatment could lead to better materials (considering that first testing cycle is the thermal treatment).

The thermomechanical analysis showed that the material modified with the intermediary amount of modifying agent has almost the same dimensional stability as the epoxy resin. Also for this type of analysis was noticed the fact that despite the isothermal segments included into the automatic analysis there are some transition effects at the beginning and at the end of temperature interval what it is observable at the level of the linear expansion coefficient values over these intervals.

For sure mechanical analysis of modified materials has to be performed in order to fully describe the material properties. Also taking into account the above results it is possible to test the hypothesis regarding the nano-structuration of epoxy resin by developing isolated (by the polymer) chemical reactions inside the liquid (viscous) state of the two main components of the epoxy system.

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