# Thermal Analysis of Ionic Substances Doped Epoxy

**IULIA GRAUR, IOAN BOSOANCA, RADU BOSOANCA, MARIUS BODOR, ADRIAN CIRCIUMARU***
S.C. Diagnose and Mesurement Group S.R.L., Galati, 41 Rosiori Str., Bl. Pin1, Ap. 29, 800055, Galati, Romania

*Polymer composites represent one of the most important parts of composites research due to the fact that these types of composites are the most spread in industrial applications. The thermoset polymer composites occupy a leading position on the composites market both to their properties and their prices. Comparing with the thermoplastic matrix composites the thermoset matrix composites involve cheaper technology and more reliable properties (especially the thermal ones) due to polymer properties. An important disadvantage of polymer is connected to their low electric conductivity and that is constitutes a barrier against their spreading in more and more applications that is way many studies concern with finding the ways to increase the value of this parameter. In this paper a method to place metallic ions inside a polymer matrix is presented and formed materials are analysed form the thermal point of view. Specific heat and coefficient of thermal expansion are targeted to point out the effect of ions presence inside the polymer matrix.*

*Keywords: epoxy resin, sodium dichromate, potassium dichromate, specific heat, linear expansion*

One of the most common methods to change the basic properties of a polymer (starting with its colour and ending with its electrical [1] or thermal conductivity) is to place an appropriate substance inside the polymer [2] without respect for dimensions or geometrical form of these substances constituents [3, 4]. These substances contribute to the change not only of the targeted property but also they are changing all the properties of the material including the valuable ones such as mechanical properties [5]. In fact through introduction of a different phase inside the polymer the development of polymer chains are blocked and the final material has not a continuous distribution of its properties (of course that depends on the dimensions of added substance constituents) [6].

First of all, one may observe that the scientific literature regarding the polymer composites is containing some essential terms as reinforcement (reinforced composites or polymers), filler (filled composites) [7, 8], additives, and, now, doped polymers. Is it necessary to specialize the terms? Do the four terms have different meanings or should they have different meanings? Basically as it is very well known, a composite is, at least, a combination of minimum two phases the matrix (ensuring the shape of final material and almost the majority of its properties [9,10]) and the immersed phase which is placed into the matrix with a certain aim. Regarding the immersed phase there are some ambiguities regarding the use of the terms. According to [11] all the references to reinforced materials are regarding fibre or fabric or class mat reinforced polymers while in [12] the reference is regarding the reinforcement is *CNT* reinforced polymer [13]. Generally the reinforcement is a made of long fibres (even they are aligned or randomly distributed) as in [14]. Suitable materials for the reinforcements are surface-treated glass, aramid, and carbon fibres manufactured specifically for this purpose. The same meaning is given also in [15, 16] but in [15] the definition is prolonged to fibres and particles. In [11] the term of filler is analysed as particulate fillers denoting powders used to fill the polymer. In essence one might observe that a classification of substances used in composite formation could be done by their role inside the matrix as [17, 18] : fillers particles with large dimensions that are replacing the polymer to reduce the costs or the material specific weight [19]; additives with considerably reduced dimensions (less than 20μm) used to change some physical properties of polymers but without affecting the basic mechanical properties of polymer and doping agents that acts at atomic level to change the polymer physical properties at orbitals level (such as ions). In the case of fillers large amounts of polymer are replaced due the presence of fillers particles and the material is losing some of its mechanical properties because of the matrix discontinuities. In the case of additives their dimensions are not blocking the development of polymer chains and the mechanical properties remain unchanged. In the case of doping agents the action is only at orbitals or atoms level and depending on doping agent concentration the mechanical properties of polymer remain also unchanged.

One important goal of research today is to find cheap ways to modify the electric conductivity of polymers. One approach is to fill the polymer with conductive powders with strong effects on polymer mechanical properties (all the filler particles will act as structural defects) [20]. Another way to use additives as CNTs or other nano-sized particles (especially nano-ceramics or nano-metals) with the reserve that this type of particles tends to aggregate inside the polymer matrix leading to large structures which act as defects in polymer. To avoid that the particles are functionalized or the polymer is changed by using of other powders to avoid the aggregation. Both filler strategy and additive strategy require large values of immersed phase concentration and that is leading to high value of specific weight of formed materials with less value from the mechanical point of view.

The strategy described here is to change the physical properties of polymer (epoxy resin) by means of ionic substances. This type of strategy is more accurate regarding the dosage of modifying agent and might constitute a strategy to obtain more changeable polymers.

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* *email: acirciumaru@ugal.ro*

## Experimental part

*Materials and methods*

The basic polymer is the WWA-WWB4 (Resoltech) which a bisphenol A based epoxy resin with a gel time of about 45 min. As doping agents potassium dichromate and sodium dichromate were chosen due to their properties. On one hand the properties of sodium and potassium ions nearly alike and the properties of dichromate ion (especially its colour as its presence indicator). More than that due the presence of the oxygen atoms on the bisphenol A molecule these complex ions could chelate and remain in the polymer structure changing the orbital structure and leading to different properties.

Both salts were solubilized in an organic solvent – commercial name nitro-diluent D209, available on the Romanian market that contains acetone, toluene, butanol, and butyl acetate in unmentioned fractions and the solution was mixed in the WWA part of the epoxy system. The concentration of the solution is computed according to the intended level of doping in terms of number of ions/ number of bisphenol A molecules.

At the beginning the largest amount of solvent was evaluated in order to form all the materials in the same conditions. This amount of solvent was mixed with the WWA component of the epoxy system and vaporized. The vaporization conditions were set by trial and error as: mechanical stirring at 200 rotations/min, 60°C, and continuous ventilation above the pot. In this manner the entire amount of solvent (20 cm$^3$) is vaporized in 150 min.

The doping levels were set at 1 alkaline ion at 5000 molecules of bisphenol A (1 chromium ion at 2500 molecules of bisphenol A) and by decreasing the amount of bisphenol by 1000 (1 alkaline atom at 4000, 3000, 2000, 1000 bisphenol A molecules) and 1/500 and by decreasing by 100, 1/400, 300, 200, 100 bisphenol molecules. According to these levels the amounts of dehydrated salts were computed and each solution was made in the same amount of solvent. Each solution was mixed into the right amount of WWA and the solvent had been removed by vaporization in above mentioned conditions. The final mixture was mixed with the required amount of WWB4 (the hardener) and stirred for 15 min. The materials were formed in cylindrical moulds with 11 mm diameter and 200 mm height. To avoid the gaseous intrusions all the moulds were vibrated by use of ultra sounds on a granular bed. After the polymerization, 24 h, all the samples were removed from moulds and the recommended thermal treatment was applied – 8 h at 60°C, 4 h at 80°C, and finally 1 h at 90°C.

Visual inspection of samples showed that the orange specific colour of dichromate ion disappeared for doping levels higher than 1/1000. Also there were not noticed gaseous intrusions.

To facilitate the presentation the following notations had been made: 0000 for the epoxy resin, 0001 for the diluted epoxy resin (the epoxy resin in which the solvent was mixed and then removed by vaporisation), N500 epoxy resin doped at a level of 1 sodium ion/5000 molecules of bisphenol A and descending to N100 for 1/1000, N050 corresponds to 1 sodium ion at 500 molecules of bisphenol A while the highest doping level is N010, 1 sodium ion/100 molecules of bisphenol. All the materials denoted with K present the mentioned doping levels but the sodium ion is replaced by potassium ion as the N materials are doped with sodium dichromate and K materials are doped with potassium dichromate.

## Results and discussions

Specific weight, specific heat and thermal expansion of materials [21, 22, 23] were studied to identify the changes induced by the ions presence inside the polymer matrix. The specific weight was determined by the common method of direct measurement of sample volume and weight and for each material six samples were analysed. As it can be seen in figure 1 for N-type materials and in figure 2. For K-type materials there are not large variations of this parameter due the small amount of salt (milligrams) reported to the amount of resin (hundreds of grams).

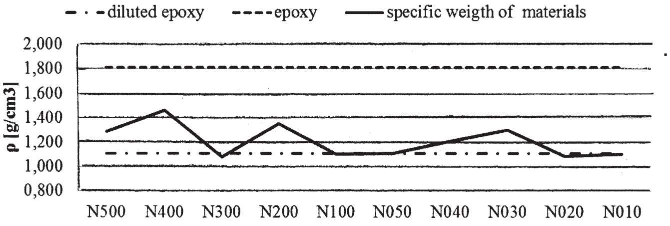

Fig.1. Specific weight of N-type materials

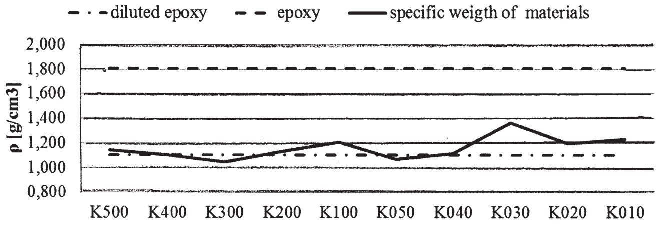

Fig. 2. Specific weight of K-type materials

Also one may observe that the values of specific weight of doped materials are generally comparable with the value of specific weight of epoxy resin while the value of specific weight of diluted epoxy is high. The largest amount of salt is about 3% of material weight and the bisphenol A and the two salts have comparable molecular weights so even the mixing rule leads to close values of materials specific weight. Noticeable is also the fact that the specific weight of materials reaches a lower value for the 1/500 doping level and a higher value for 1/300 doping level. Taking into account the fact that the two salts are sodium dichromate and potassium dichromate similar values of the same parameter for the two types of doped resin might be connected with the presence of chromium ions while dissimilar values might be attributed to alkaline ions.

The situation is not the same in the case of the specific heat of materials. The parameter was measured by means of Differential Scanning Calorimetry on DSC-1 (Mettler Toledo) and using the dedicated software Star*e* provided by the DSC-1 manufacturer.

In this case the evaluation of the specific heat by mixing rule should give values comparable with the ones of epoxy resin or the modified epoxy resin (the one in which the solvent was mixed and then removed) but the results in figures 3 - 6 are generally far from estimated values. For these estimations the weight fractions of matrix and salt had been computed and the specific heat values of epoxy resin and of salts have been determined also by means of DSC analysis using the same method as in the case of doped resins. For each material six samples were analysed and presented results are average values obtained by statistical analysis. Since the materials were formed separately it is possible that the results to be affected by the temporary conditions as air humidity or air temperature.

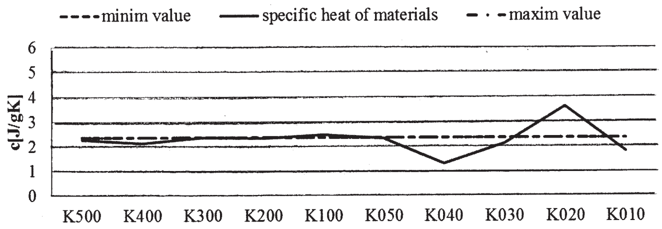

Fig.3. Specific heat of K-type materials for first frame

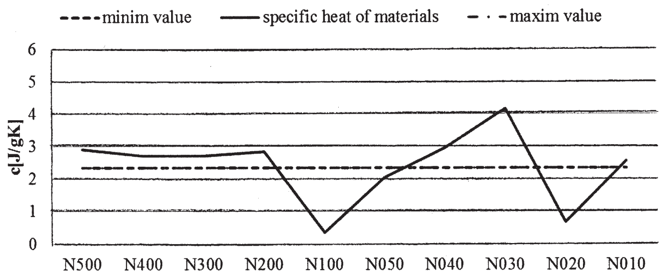

Fig.4. Specific heat of N-type materials for first frame

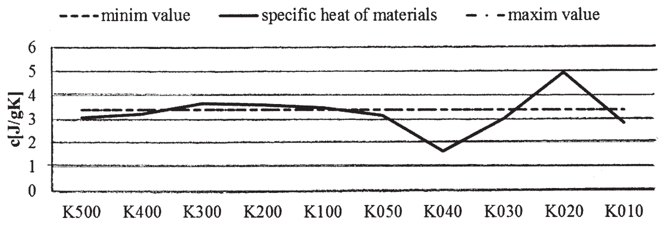

Fig. 5. Specific heat of K-type materials for second frame

The mixing rule provides calculus algorithms for minim and maxim values of a parameter by means of values for the component parameters. These limits were evaluated for each material and they are marked in the graphs as a single line due their close values. According the mixing rule the effect of salts presence inside the polymer should not affect the specific heat of materials but the results are different leading to the idea that the ions are interacting with the polymer and are changing polymer basic properties.

The linear expansion of materials was studied by TMA [24] (Thermo-Mechanical Analysis) means with TMA/SDTA 840 (Mettler Toledo) and dedicated software – Star*e*.

The results presented in figure 7 and figure 8 are showing a more stable response of doped materials (low values of the coefficient of thermal expansion). For the samples with doping level between 1/5000 and 1/1000 the behaviour is dominated by the presence of alkaline ions while the other materials are dominated by the presence of chromium ions – the two curves have almost the same profile especially at high doping level 1/200.

## Conclusions

A method of placing metallic ions into the network of an epoxy resin was configured using organic solvents. The method allows precise determination of ions concentration when the formula of epoxy resin is known. Technically the method consists of solving the salt into an organic solvent (water is excluded due to the reactivity of epoxy groups with it), mixing the solution with the epoxy resin and vaporizing the solvent. An epoxy resin with a known contain of ions is obtained and is stable. The mixture is mixed with the hardener and polymerization is started leading to solid materials (there were not observed phase separations during the pre-polymer preparation).

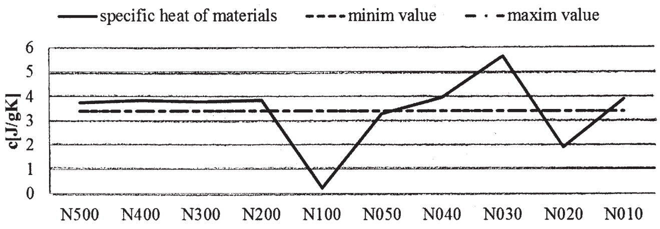

Fig. 6. Specific heat of N-type materials for second frame

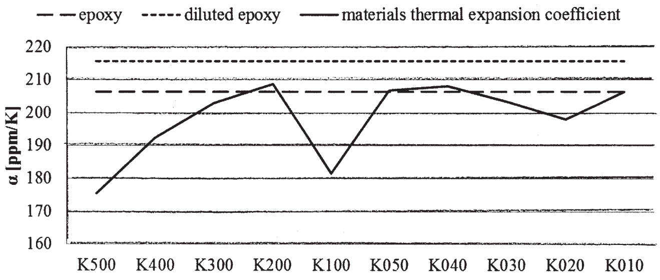

Fig. 7. Coefficient of thermal expansion for K-type materials

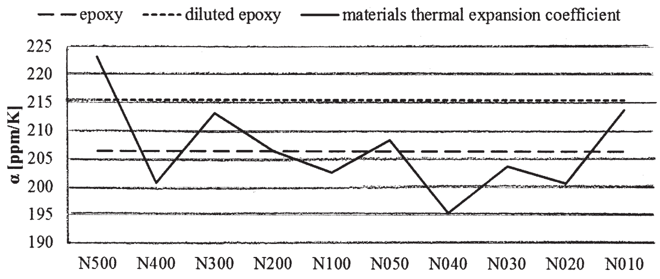

Fig. 8. Coefficient of thermal expansion for N-type materials

The formed materials, with known doping levels, were analysed from thermal point of view by means of DSC and TMA (respecting the international standards requirements) targeting the specific heat and the coefficient of thermal expansion. Two materials had been used as whiteness materials namely the epoxy resin (formed according to producer recommendations) and the diluted epoxy that is the epoxy system in which the solvent was mixed and then removed by vaporization after that the epoxy resin was mixed with the hardener (according to the producer recommendation) and the solid material was formed. The measured values for targeted parameters were compared with the values of the two parameters for epoxy resin and for diluted epoxy resin to identify the effect of metallic ions presence.

The diluted epoxy resin shows highest values of studied parameters signalizing changes at the molecular level while the presence of ions is leading generally to lower values of parameters. Based on the fact that the specific colour of dichromate ion disappears for doping levels higher than 1/1000 the effects of salts may be imparted in alkaline ions presence effects and chromium ions presence effects.

This type of modified polymer could be used as matrix fibre reinforced composites or to form additives modified composites with epoxy matrix being known the fact that constituents of powders tend to aggregate inside the polymer matrix leading to clusters with damaging effect on the mechanical properties of formed materials. One method to avoid this is to modify the powders properties by chemical intervention, generally by deposing metals on the surface of powder constituents. The ions doped epoxy should be a solution for this problem due to the presence of ions. The presented results are representing just the beginning of the materials analysis mechanical, electrical and wear tests must be conducted to completely characterize the materials. Also other solvents have to be studied in order to use them without vaporization to place metallic ions inside the polymer network. Also organic complexes of metals could be used to place metallic ions inside the polymer structure based on organic-organic compatibility of thermoset polymers and organic complexes.

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