

STUDIES ON EPOXY RESIN MODIFIED WITH ORGANIC AGENTS

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ABSTRACT

Epoxy composites are one of the most versatile thermosetting polymers widely used due to their strong soldering resistance, high insulation, and thermal resistance. 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. Essentially, epoxy resins are low molecular weight liquids with two or more epoxide functional groups. To get superior properties of the composite material, a broad variety of inorganic and organic modification agents are used. For this study, two protein substances, gelatin, and wheat gluten were used to change the basic properties of three types of epoxy resins. The specific heat of modified epoxy resin materials was performed by using Differential Scanning Calorimetry (DSC) instrument. The thermal analysis was developed on two heating-cooling cycles and the specific heat was evaluated for each segment of the cycle analysis. Also, the mechanical behavior of organic modified polymers subjected to compression was studied using INSTRON compressive testing machine.

KEYWORDS: epoxy resins, organic compounds, thermal properties

1. Introduction

Epoxy resins as important organic matrices, thanks to their chemical structure and the possibility of modification, have unique properties, which contribute to the fact that these materials have been used in many composite industries for many years. [1]. Epoxy resins are repeatedly used in exacting applications due to their exquisite mechanical properties, thermal stability, scratch resistance, and chemical resistance. Moreover, epoxy materials also have really strong resistance to solvents, chemical attacks, and climatic aging [2-3]. The presented features confirm the fact that there is a constant interest of scientists in the modification of resins and understanding their mechanisms, as well as in the development of these materials to obtain systems with the required properties.

Protein polymers are natural macromolecules derived from plants and animals which makes them an easily obtainable, renewable resource. Therefore, the development of environmentally friendly epoxy systems is of great importance for designing green and biocompatible materials in many applications.

Wheat gluten is a plant protein that is unique among plant proteins, because of its availability, good

biodegradability, low price, unique viscoelastic properties, and ability to crosslink on heating [4, 5]. Gelatin is a natural mixture of polypeptides that is obtained from collagen Type I. Collagen used for gelatin extraction that can be isolated from bones, tendons, and skin of animals, but it is especially obtained from bovine and porcine [6]. Also, gelatin is a low-cost and abundantly available protein biopolymer obtained from partial hydrolysis of collagen found in various biomaterials [7]. It has been widely explored in biomedical applications such as tissue engineering, drug delivery, and wound healing [8]. The cross-linked gelatin nanofibers showed environmental stability, better mechanical properties, and comparable filtration performance [9].

Many researchers had investigated the mechanical, chemical, and thermo-mechanical properties of different epoxy resins systems by different methods [10-12].

Thermal analysis with DSC 1 Mettler Toledo (Differential Scanning Calorimetry) is used to calculate the degree of crystallinity and its composites, but account must be taken for melting and recrystallization that simultaneously occur when heating [13, 14].

The specific heat of a certain material is a physical quantity that is characterized by the energy exchange between the respective material and the environment, energy exchange that has the effect of changing the temperature value of the material. To determine the specific heat of the polymeric materials, the heat flux signal emitted by the specimen to be analyzed is compared with the known signal of the reference specimen.

Application of the DSC test method to polymer matrix composites may also encounter difficulties due to specimen mass loss from either moisture evolution or material decomposition, but this problem can be overcome by taking proper precautions [15-17].

The main purpose of this study was to analyse the composite materials modified with organic agents (wheat gluten and gelatin) with a matrix made from three different epoxy resins, in particular specific heat. There is a multitude of mechanical tests, and because the stresses to be transposed are diverse, they can be performed in static or dynamic conditions, at ambient temperature, as well as at high or low temperatures, in air or in corrosive environments, etc. The determination of the mechanical properties of compression of the composite materials modified proteins was performed as experiments, on the mechanical testing machine INSTRON 8030.

2. Materials and methods

The study was carried out using three epoxy resins, namely Epiphen RE4020-DE 4020, Epoxy Resin C, and Epoxy Resin HT2 [18-20]. Wheat gluten and gelatin were purchased from Sigma-Aldrich and were used as received. The preparation of the modified composites consists of the addition of a quantity of modifying agents in the form of wheat gluten powder and gelatin to the epoxy matrix.

The first step in the process of forming protein-modified composites is to establish the preparation protocols of the moulds (cylindrical polypropylene tubes). These types of moulds were chosen precisely so that the materials could be easily extracted after the period of polymerization (hardening), without being damaged. The modification of the epoxy system consisted of the introduction of a quantity of modifying agents (gluten and gelatin) in the proportion of 1%, 2%, and 3% weight ratios. The resulting mixture was mixed mechanically (500 rpm) for 24 hours at 60 degrees Celsius.

The next step in the process of forming the materials was the actual pouring of the mixture into moulds. Twenty-four hours later, the materials were extracted from the polypropylene tubes. In the final step, the polymerized materials are treated in the heat treatment furnace. The parameters after which the heat treatment was carried out were established by

working protocols, namely: heating the enclosure to a temperature of 60 degrees Celsius, maintaining the time for 8 hours, raising the temperature to 80 degrees Celsius, maintaining it for 2 hours, and finally, the last stage consisted of heating to a temperature of 90 degrees Celsius for 1 hour. The purpose of applying the heat treatment is to eliminate the residual stresses that can appear in the material during casting or during the polymerization period, giving it a necessary state of equilibrium. After the materials had cooled, specimens were extracted (according to the standards in force), in order to determine the parameters that will characterize the composite materials formed depending on the type and quantity of the modifying agent used.

The thermal measurements were performed by using Differential Scanning Calorimeter (DSC) for specific heat analysis. This device is equipped with a sensor that checks the atmosphere inside the cell and provides a balance between the sample to be analyzed and the reference sample. The specific heat was determined from the heat absorption curve and/or the released heat for each type of material. The specific heat of epoxy composite materials was investigated by heating the samples at temperature intervals of -60 to 150 °C and by cooling at temperature intervals of 150 to -60 °C, with 10 °C/min, and the cycle is repeated. Both heating and cooling DSC curves can provide information on the nature of samples.

The behavior of the composite material to the mechanical stresses produced by external forces depends on certain specific properties of it, called mechanical properties. Most tests involve the application of test tubes until the material yields and the strength limit is reached. Also, the mechanical tests were performed on an Instron testing machine and the conditions for testing were established at a speed of 55 mm/min and the stop condition was set at a 40% drop of the loading force. The applied load was 2 kN for bending and 25 kN for the compression test. Samples extraction for the mechanical analysis was performed after the thermal treatment. They have been of 160 mm in length ensuring a length of 10 mm as an engagement zone.

3. Results and discussion

In order to determine the specific heat of the polymeric materials, the heat flux signal emitted by the specimen to be analyzed is compared with the known signal of the reference specimen. This process consists in recording an isothermal curve at low temperature, after which, as the temperature increases, another isotherm is recorded. The specific heat is determined by the quantitative measurement of the energy absorbed by the material, depending on the temperature.

Analyzing the data in the diagram of the unchanged C resin and the modified one with an organic modifying agent, we noticed that after the first heating there is a keeping of the test specimens,

which means the removal of organic modifiers from the epoxy resin. Thermal analysis was performed at different temperature ranges, starting from -50, 50 °C, values that are shown in the diagrams.

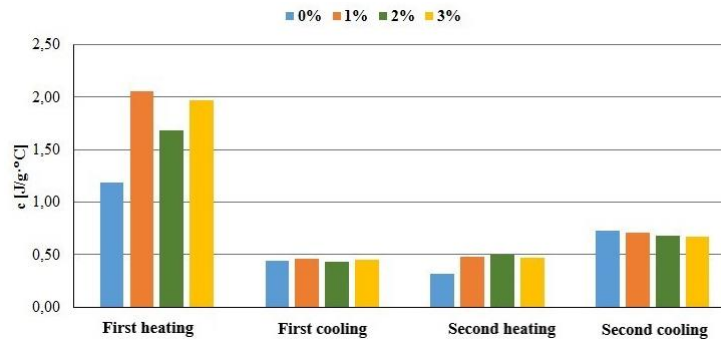


Fig. 1. Specific heat values of C modified epoxy resin materials (-50, 50 °C temperature interval)

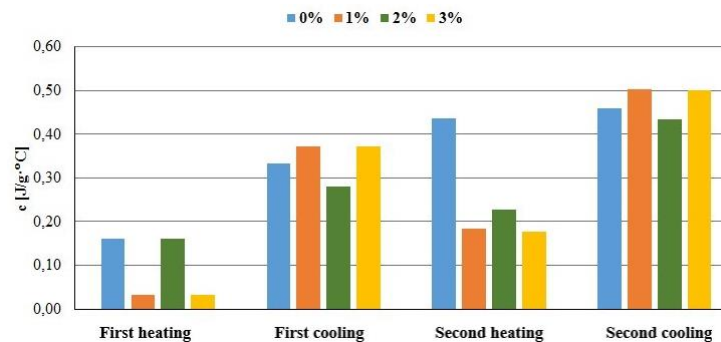


Fig. 2. Specific heat values of E modified epoxy resin materials (-50, 50 °C temperature interval)

In the case of materials formed with epoxy resin E, a considerable change is observed at the second cooling, in which all the resins are almost identical, which means that the modifiers give the material high thermal properties.

In Figure 3, we observed an almost identical behavior of the material at the first heat of the modified material with gelatin and gluten, as well as the unmodified one, as a result of which at the first

cooling there are improved values compared to the control specimen.

According to the type C epoxy resin diagram at 90, 140 °C, the value of the specific heat at the first heating, still shows a significant increase, especially the control C0 and C2, which has very good property compared to the epoxy matrix materials of the same category. The highest specific heat values were obtained for modified and unmodified type C epoxy composites.

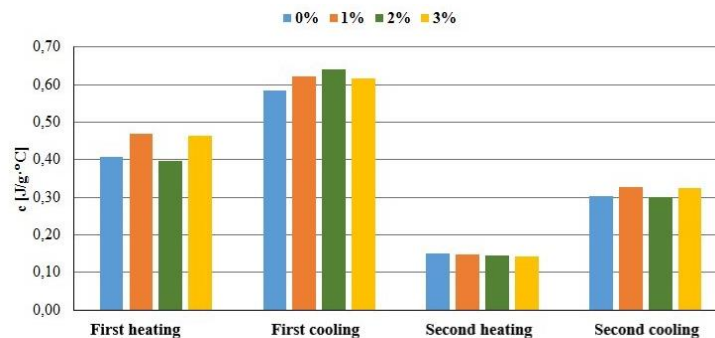


Fig. 3. Specific heat values of HT modified epoxy resin materials (-50, 50 °C temperature interval)

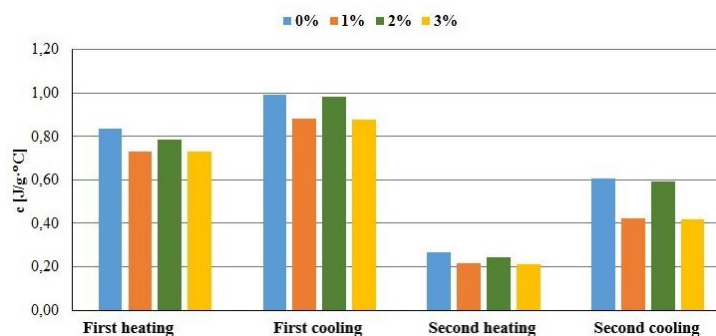


Fig. 4. Specific heat values of C modified epoxy resin materials (90, 140 °C temperature interval)

In the case of materials with epoxy matrix type E, it is observed that combustion occurs in materials E0 and E2 at the first heating.

Thus, higher values of specific heat for E3 material were obtained. No significant variations in the specific heat values of the type E epoxy materials were observed during cooling.

HT type epoxy matrix composite materials showed variations in specific heat values depending on the type of modifying agent used in the structure of the studied materials. We observed higher values

of the resin after the first heating showing high thermal stability, where HT0 and HT2 have similar values, as well as HT1 and HT3.

Before and after determining the specific heat values of the materials, the samples were weighed to determine the loss of substance caused by the increase in temperature. This loss is due to: polymer wastewater, small amounts of diluent or other volatile compounds, which are in the mass of the polymer in the form of oxygen and carbon dioxide resulting from chemical reactions, being represented graphically.

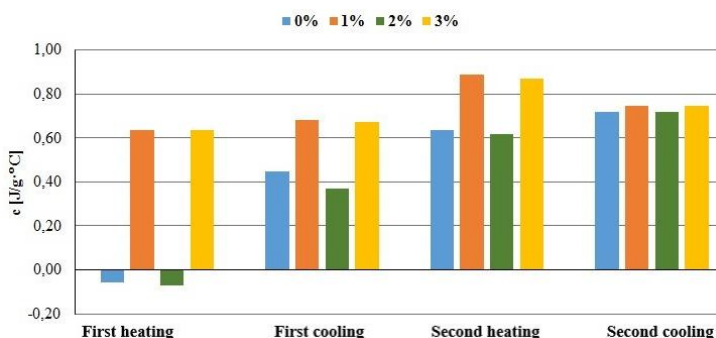


Fig. 5. Specific heat values of E modified epoxy resin materials (90, 140 °C temperature interval)

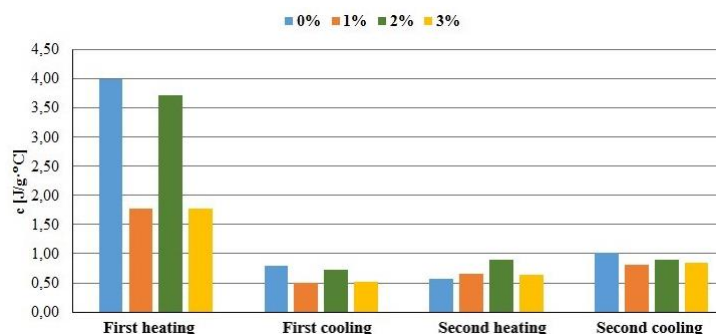


Fig. 6. Specific heat values of HT modified epoxy resin materials (90, 140 °C temperature interval)

Following the analysis of the diagram, we noticed that the highest mass losses were suffered by the materials with epoxy matrix type C and especially with the highest concentration of C3 modifier,

presenting the highest mass loss of all the studied materials. The lowest losses were in the case of epoxy type E materials, but of the HT specimens, the most significant was HT0.

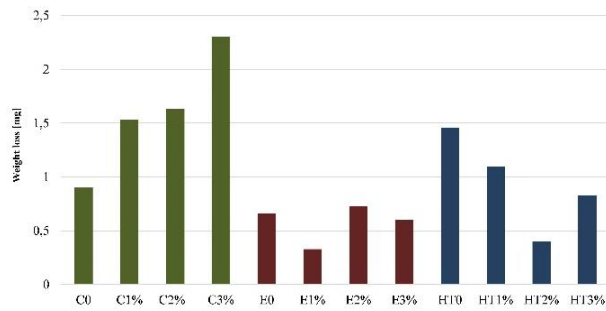


Fig. 7. Mass loss of polymeric materials

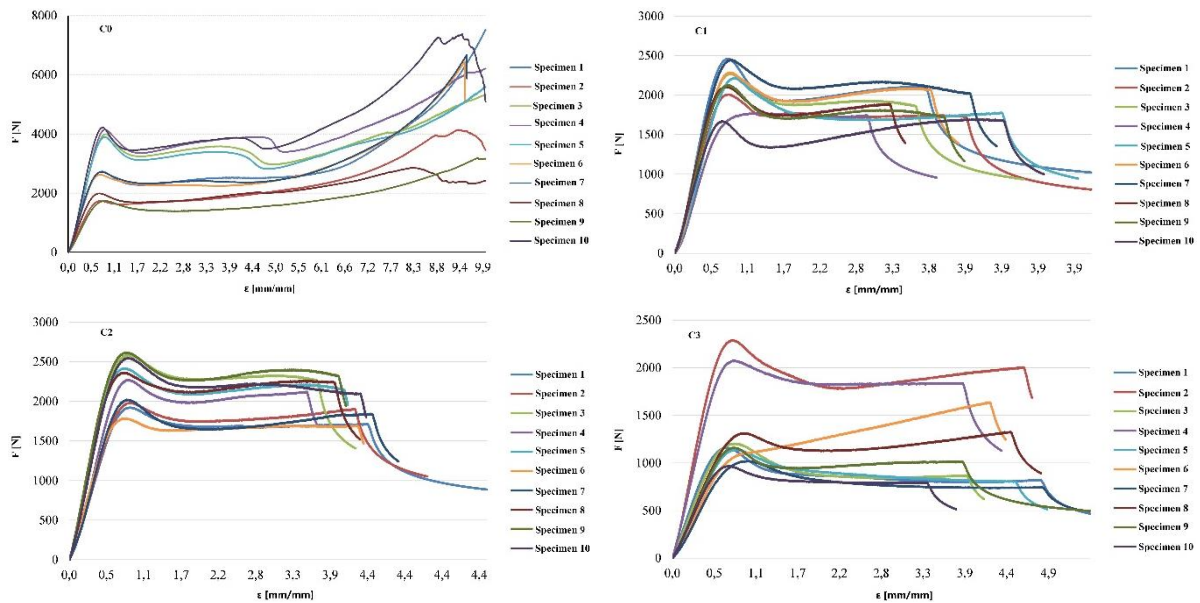


Fig. 8. Compressive behavior for C materials

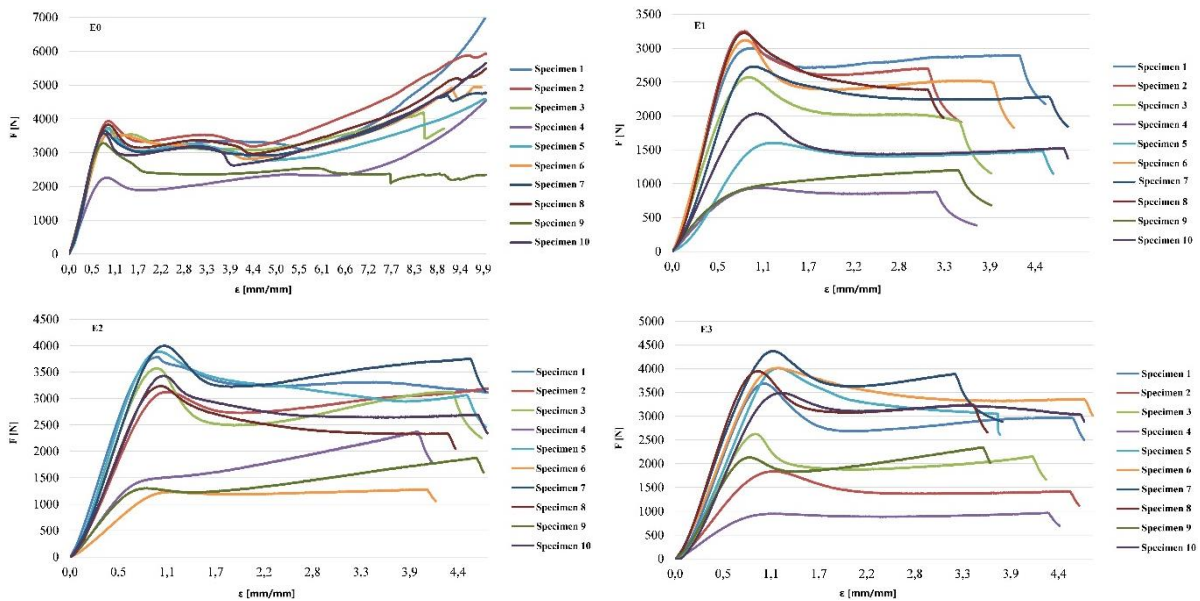


Fig. 9. Compressive behavior for E materials

The compressive behaviour of the formed composite materials is determined by the curves shown in the figure, which show both unmodified epoxy systems of type C and those modified with wheat gluten and gelatin.

From the graphs presented, the unchanged type C epoxy system shows the best mechanical properties at compression, taking into account the value of breaking strength, being approximate twice the value

of breaking strength of modified epoxy materials of the same category. In the same curves it can be seen that in the case of C0 type materials, the value of the pressing force was higher compared to the values of the pressing force for the modified materials.

For protein-modified type E epoxy composites, an increase in the degree of compression of the modified materials can be observed compared to the unmodified epoxy system.

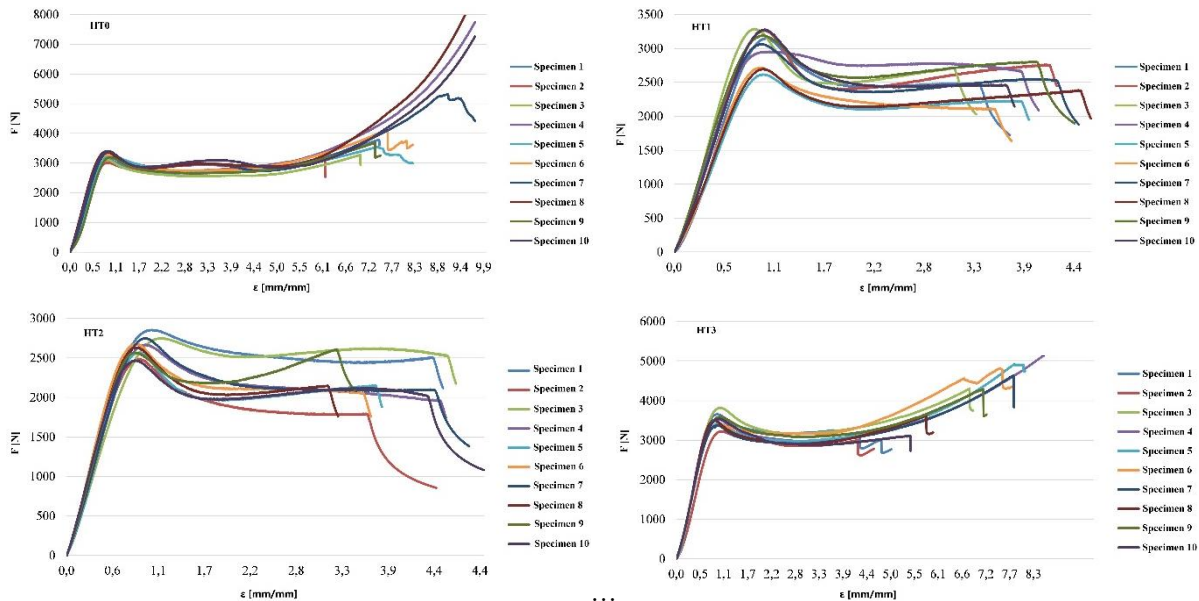


Fig. 10. Compressive behavior for HT2 materials

In the case of unmodified and modified HT2 epoxy resin modified with gluten and gelatin, subjected to compression, it can be seen from the drawn curves that the difference between the ten specimens tested is insignificant. Also, if we make a comparison between the curve for the epoxy system and the modified materials, we notice that both the force and the degree of compression are almost identical.

4. Conclusions

Following the analysis of the results, obtained after testing the materials to mechanical testing, it was possible to draw the following conclusions. The use of organic agents to change the properties of epoxy resins leads in particular to increased flexibility as well as ensuring the transport of structures in the volume of the polymer. Following the tests performed we can see that the modifying agents did not significantly change the properties of the formed material, the composite material modified with proteins had a behavior very similar to the unmodified epoxy system. The other parameters were analyzed for this category of materials, which

confirms that the concentration of the modifying agent does not significantly influence the properties of the modified materials.

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