

THE MECHANICAL PROPERTIES OF ORGANIC MODIFIED EPOXY RESIN

Georgel MIHU, Claudia Veronica UNGUREANU, Vasile BRIA, Marina BUNEA, Rodica CHIHAI (PEȚU)

"Dunarea de Jos" University of Galati, Cross-Border Faculty, Romania Research and Development Centre for Thermoset Matrix Composites, Romania e-mail: claudia.ungureanu@ugal.ro, rodica.petu@yahoo.com

ABSTRACT

Epoxy resins have been presenting a lot of scientific and technical interests and organic modified epoxy resins have recently receiving a great deal of attention. For obtaining the composite materials with good mechanical proprieties, a large variety of organic modification agents were used. For this study gluten and gelatin had been used as modifying agents thinking that their dispersion inside the polymer could increase the polymer biocompatibility. Equal amounts of the proteins were milled together and the obtained compound was used to form 1 to 5% weight ratios organic agents modified epoxy materials. To highlight the effect of these proteins in epoxy matrix mechanical tests as three-point bending and compression were performed.

KEYWORDS: mechanical properties, gluten, epoxy resin, gelatin

1. Introduction

Composites have been found to be the most promising and discerning material available in this century. The composite material has a variety of advantages, such as: excessive energy to weight ratio, convenient availability, ease and hassles free fabrication methods and improvised thermal and mechanical properties. Some unique composite materials have higher stiffness and higher-pressure rate, which is associated with metals, the strength of the composite material additionally, depends on the geometry and shape [1].

Epoxy resins are the most widely used thermosetting matrices due to their good mechanical strength, low shrinkage, excellent manufacturability, effective electrical insulation, and stable thermal properties [2]. In addition, these systems do have some environmental problems. An environmental problem of epoxy resins is that all the curing agents are toxic before the cure. Even for cured epoxy resins that seem safe, toxicity cannot be totally avoided because of the possibility of incomplete consumption of curing agents and subsequently the hazards introduced by the residue curing agents. [3]. A new approach in the development of an eco-friendly curing agent for epoxy resins in the industry is of great importance. Among frequently used curing agents for epoxy resins, especially organic and inorganic compounds, are of prime significance in practical applications [4]. In addition, the modifying agents are small particles dispersed in the matrix material, which can be easily obtained and incorporated in the material [4-6]. Also, the organic modification agents help to improve the material by increasing the abrasion resistance and lowering the coefficient of thermal expansion [7]. Recently amino acids have been used to cure epoxy resins, which take the advantages of the reduced toxicity and environmental friendliness [8].

Protein polymers are natural macromolecules derived from plants and animals which makes them an easily obtainable, renewable resource [9]. The gelatin, a natural biopolymer, has properties like biocompatibility and water solubility, low immunogenicity, plasticity, adhesiveness, promotion of cell adhesion, growth, and cost economy, as well as the ability to form transparent gels under specific conditions. Also, gelatin has a large variety of applications, including food industry, pharmaceutical formulations and other technical products. [10-13]. Wheat gluten is an important source of proteins. Being a by-product of the starch industry, it is widely available, cheap, and fully biodegradable. Among other possible uses, wheat gluten has been extensively tested to produce renewable thermoplastic materials [14-15]. Two factors such as, use



plasticizers and fiber length, are usually considered for improving the mechanical properties of gluten composites [16]. Materials obtained from gluten are considered a promising source with which to produce sustainable packaging as it improves food storage. These materials have the capacity to act as a barrier against water, oxygen, and light, therefore reducing oxidation of food [17].

The objective of this study was to determine the modifications of epoxy resins properties induced by organic modification agents. Also, besides mechanical properties, chemical properties presented high potential to be investigated.

2. Materials and methods

The experiments were carried out using the Epiphen system consisting of RE4020 (resin) and DE4020 (hardener), with 100:30 ratio, due to its properties before and after polymerization [18]. Wheat gluten and gelatin were purchased from Sigma-Aldrich and were used as received.

In order to improve the mechanical response of the final polymer equal amounts of the proteins had been mixing with the resin, such as finally their weight ratios into the formed polymers to be 1%, 2%, 3%, 4% and 5%.

For organic modified polymers, two alternatives were used: firstly, disperse the powders into the resin (the main component – liquid – of an epoxy resin) and then to add the hardener (the second component of the epoxy system) and the second it was dispersing the powder inside the hardener volume and then forming the material. Taking into account the fact that, in the absence of chemical interaction, the physical interaction is probably leading to dispersion of some aggregates (powder particles surrounded by resin or hardener molecules) inside a liquid phase which for sure will differently respond after resinhardener blending. The composite materials modified with organic agents were mixed mechanically at 300 rotation/min for 15 minutes, at 70 °C, for 24 hours. After that, the right amount of hardener was added and the new mixtures were stirred for 15 minutes to ensure the homogeneity. Then, the pre-polymers mixtures were casted into cylindrical polypropylene tubes, with 8 mm diameter and 200 mm length. The obtained materials are notated as *Eax* and *Ebx*, where Ea represents the material obtained by mixing the organic agents with the resin and Eb meaning the materials obtained by mixing the wheat gluten and gelatin mixture with the hardener. The x represents the weight ratio of the proteins (%) and takes values from 1 to 5.

After the polymerization (24 h) the samples were extracted from molds and three thermal treatments were applied (8 hours at 60 °C, 2 hours at

80 °C and 1 hour at 90 °C, to ensure a higher value of glass transition of the polymer).

The mechanical tests were performed on an *Instron* testing machine and the conditions for testing was 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 compression test. Samples extraction for the mechanical analysis was performed after the thermal treatment. They have been of 160 mm length ensuring a length of 10 mm as engagement zone.

3. Results and discussion

As it has been previously reported in the literature, amino-acids, inorganic and organic compounds can be used to obtain modified epoxy materials with slightly modified properties [19-21].

The results of mechanical tests showed that the presence of wheat gluten and gelatin mixture inside the matrix had a modification in the compressive and bending response of epoxy resin. The configuration of the epoxy resin-denoted as *E0*, is illustrated in Figure 1. All the curves are the average of five tests performed for each material.

Figures 2 and 3 illustrate the compressive tests results for the polymers obtained by modifying the epoxy resin with the smallest and the highest, amounts of wheat gluten and gelatin mixture.

It can be observed that the compressive behaviour, is characteristic of thermosetting polymers with an area of elasticity below 0.1 mm, which is followed by a compaction area and the force is almost unchanged. Also, the cracking of the specimens was followed by the final tearing of materials.

The compressive modulus of unmodified epoxy (E0) reached the highest value while all the organic modified materials showed lower values of the parameter, possibly due to the formation of small defects of the polymer network due to high concentrations of the proteins mixture. By way of consequences, the level of loading transfer in, the compressive tests did not present any modifications regarding the maxim deformation of the material.

One usual way to get superior properties of polymers is to modify them by placing another phase, for instance a nano-sized one, into the polymer volume [22]. Amit *et al.* [23] showed that these materials should provide unique mechanical and thermal properties combined with low specific weight and high wear resistance in order to ensure the safety and economic efficiency.

The behaviour of modified materials with organic agents is almost identical to that of unmodified materials. The significant parameters obtained by the three-point bending testes were found to have similar behaviour (Fig.4 and Fig.5).



THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI FASCICLE IX. METALLURGY AND MATERIALS SCIENCE N°. 3 - 2020, ISSN 2668-4748; e-ISSN 2668-4756 Article DOI: <u>https://doi.org/10.35219/mms.2020.3.02</u>



Fig. 1. Compressive behaviour of epoxy resin (left). Bending modules of epoxy resin (right)



Fig. 2. Compressive behaviour for the materials with 1% proteins mixture



Fig. 3. Compressive behaviour for the materials with 5% proteins mixture



Fig. 4. Bending modules for the materials with 1% proteins mixture



Fig. 5. Bending modules for the materials with 5% proteins mixture

Following these tests, the materials practically did not break during the test, demonstrating their elasticity.

For this category of materials, the others, elastic parameters analysed confirmed that the concentration of the modifying agent does not significantly influence the behaviour of the modified materials.

In addition, with the increase of solution of modifying agent concentration the elasticity limit measured during a three-point bending tests of the materials correspondingly decreased. Analysing the bending elastic modulus, it might be noticed that the proteins mixtures ratio has a considerable importance, because with increasing its ratio, the bending elastic modulus decreases.

4. Conclusions

For this study wheat gluten and gelatin had been used as modifying agents. The materials were formed by dispersing the mixture of gelatin and gluten into the resin or into the hardener and the weight ratios of organic compounds into the polymer are from 1% to 5%.

The mechanical analysis presented that the elastic modulus values are decreasing, almost

proportionally, with respect to the concentration of both proteins mixtures dispersion cases.

The presence of organic mixture (wheat gluten and gelatin) inside the epoxy resin is not considerably modifying the properties of the polymer. Therefore, it is possible to continue to the next step regarding the functional analysis of the proteins in order to control the polymer sensitive properties. In addition, the modification of epoxy resin with small amounts of organic compounds could lead to an increase of their environmental acceptability.

Acknowledgements

The work of Georgel Mihu was supported by the project ANTREPRENORDOC, in the framework of Human Resources Development Operational Programme 2014-2020, financed from the European Social Fund under the contract number 36355/23.05.2019 HRD OP /380/6/13 – SMIS Code: 123847.

This work has been funded by the European Social Fund through the Sectoral Operational Programme Human Capital 2014-2020, through the Financial Agreement with the title "Burse pentru educația antreprenorială în rândul doctoranzilor și



cercetătorilor postdoctorat (Be Antreprenor!)" (in English: "Scholarships for entrepreneurial education among doctoral students and postdoctoral researchers (Be Entrepreneur!)", Contract no. 51680/09.07.2019 - SMIS code: 124539.

References

[1]. Guduru R. K. R., Shaik S. H., Tuniki H. P., Domeika, A., Development of mono leaf spring with composite material and investigating its mechanical properties, Materials Today: Proceedings, https://doi:10.1016/j.matpr.2020.02.289, 2020.

[2]. Shen Y., Cong Y., Zhang B., Lang Q., Influence on properties of epoxy nanocomposites with nanoparticles modified by surfactants with different molecular structures: liquid crystal, rigid and flexible segment structures, Materials Research Express, https://doi:10.1088/2053-1591/ab38c9, 2019.

[3]. Yi L., Fei X., Kyoung-sik M., Wong C.P., Novel Curing Agent for Lead-Free Electronics: Amino Acid, Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 44, 1020–1027, 2006.

[4]. Chihai R., Ungureanu C., Cojan A, Bîrsan I. G., Cîrciumaru A., Organic modified epoxy resin. Tribologic aspects, The 10th International Conference BALTTRIB'2019, https://doi.org/10.15544/balttrib.2019.03, 2019.

[5]. Xu H., Feng Z., Chen J., Zhou H., Tribological behavior of the polyamide composite coating filled with different fillers under dry sliding, J. of Applied Polymer Science, 104, p. 2554-2560, 2007.

[6]. Samyn P., Kalacska G., Keresztes R., Zsidai L., De Baets P., *Design of a tribotester for evaluation of polymer components under static and dynamic sliding conditions*, Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology 221 pp 661-674, 2007.

[7]. DeFrates K., Markiewicz T., Gallo P., Rack A., Weyhmiller A., Jarmusik B., Hu X., Protein Polymer-Based Nanoparticles: Fabrication and Medical Applications, International Journal of Molecular Sciences, 19(6), 1717, https://doi:10.3390/ijms19061717, 2018.

[8]. Bălan I., Bosoancă R., Căpățină A., Graur I., Bria V., Ungureanu C., A study regarding friction behaviour of lysine and isoleucine modified epoxy matrix, IOP Conf. Series: Materials Science and Engineering 174.012023 doi:10.1088/1757-899X/174/1/012023, 2017.

[9]. Djagny K. B., Wang Z., Xu S., Gelatin: a valuable protein for food and pharmaceutical industries: review, Crit. Rev. Food Sci. Nutr. 41 (6), 481e492, 2001. [10]. Rapisarda M., Valenti G., Carbone D. C., Rizzarelli P., Recca G., La Carta S., Fincchiaro S., Strength, fracture and compression properties of gelatins by a new 3D printed tool, Journal of Food Engineering, 220, p. 38-48. https://doi:10.1016/j.jfoodeng.2017.05.016, 2018.

[11]. Li X., Jiang G., Yang L., Peng S., *Study of gelatin as biodegradable shale hydration inhibitor*, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 539, p. 192-200., https://doi:10.1016/j.colsurfa.2017.12.020, 2018.

[12]. Fabra M. J., Lopez-Rubio A., Lagaron J. M., Effect of the film-processing conditions, relative humidity and ageing on wheat gluten films coated with electrospun polyhydryalkanoate, Food Hydrocolloids, 44, p. 292-299, 2015.

[13]. Tom Keenan, Gelatin, *Polymer Science: A Comprehensive Reference Volume* 10, Pages 237-247, 2012.

[14]. Ciapponi R., Turri S., Levi M., Mechanical Reinforcement by Microalgal Biofiller in Novel Thermoplastic Biocompounds from Plasticized Gluten, Materials, 12(9), 1476. doi:10.3390/ma12091476, 2019.

[15]. Jin F.-L., Li X., Park S.-J., Synthesis and application of epoxy resins: A review, Journal of Industrial and Engineering Chemistry, 29, p. 1-11, doi:10.1016/j.jiec.2015.03.026, 2015.

[16]. Vo Hong N., Van Puyvelde P., Van Vuure A., Verpoest I., Preparation of biocomposites based on gluten resin and unidirectional flax fibers, Conference: ECCM15 - 15th European Conference on Composite Materials, 2012.

[17]. Gällstedt M., Mattozzi A., Johansson E., Hedenqvist M. S., Transport and tensile properties of compression-molded wheat gluten films, Biomacromolecules 5, p. 2020-2028, 2004.

[18]. ***, http://www.polydis.ro/wpcontent/uploads/2014/08/Epiphen-4020.pdf.

[19]. Bîrsan I. G., Andrei G., Ungureanu V., Roman I., Cîrciumaru A., Wear behavior of fabric reinforced epoxy based composites, Proceeding of the International Conference BALTTRIB'2009, p. 158-163, 2009.

[20]. Bîrsan I. G., Andrei G., Bria V., Postolache I., Cîrciumaru A., *Tribological behavior of clay/epoxy reinforced epoxy composites*, Proceeding of the International Conference BALTTRIB'2009, p. 154-169, 2009.

[21]. Bîrsan I. G., Cîrciumaru A., Bria V., Ungureanu V., Tribological and Electrical Properties of Filled Epoxy Reinforced Composites, Tribology in industry, 31, 1-2, p. 33-36, 2009.

[22]. Bart J. C. J., Additives in Polymers. Industrial Analysis and Applications, John Wiley & Sons, 2005.

[23]. Amit C., Muhammad S. I., Fabrication and characterization of TiO2–epoxy nanocomposite, Materials Science and Engineering A 487, p. 574-585, 2008.