ORGANIC MODIFIED EPOXY RESIN. TRIBOLOGIC ASPECTS

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Abstract: this article presents some results of pin-on-disk tests on modified epoxy resins compared with the tribological behavior of the epoxy resin. The tribological response of materials was studied for three regimes force, sliding speed (F,v) of pin-on-disk geometry with the pin made of studied material and steel disk. All the tests were performed under thermos-vision surveillance to point out the temperature value modifications during tests and, at the end, the wear rate was evaluated for each material. The modification of epoxy resins is an attempt to slightly change some basic properties of the polymer such as electric conductivity but without changing their most valuable properties – thermal dimensional stability, high adhesion to almost any other material and mechanical properties. One of the major disadvantages of epoxy resins is their chemical stability, which makes them almost impossible to neutralize after their life cycle. In this regard, the modification of epoxies by adding small amounts of organic or inorganic compounds could lead to an increase of their environmental acceptability.

Keywords: friction, wear, thermal field, epoxy resin.

1. INTRODUCTION

Epoxy resins are widely used in both industrial and consumer electronics because of, among other things, their chemical resistance, low shrinkage on cure, superior electrical and mechanical properties, and good adhesion to many other materials. Various types of curing agents, such as nitrogen – (amines and polyamides), oxygen – (anhydrides), and sulphur – (mercaptans) containing agents, have been reacted with epoxy resin to provide crosslinked adhesives. However, these systems do have some environmental problems that have been especially noted in recent years. One problem is that the systems usually generate dense smoke and toxic decomposition products during combustion. That is why it is necessary to handle separately the potential problems related to the structure and properties of the composite materials with particles, as well as the matrices that come into the composition of the composite materials [1–2].

To obtain optimal performance of the composite material, a broad variety of organic and inorganic modification agents are used [3]. The use of agents helps to improve the material by increasing the abrasion resistance and lowering the coefficient of thermal expansion [4]. Few studies demonstrated the feasibility of using an organic acid as a novel eco-friendly curing agent. Proteins are thermoplastic polymers of polar and non-polar amino acids that are capable of developing numerous intermolecular bonds and bearing various linkages [5]. Recently, wheat gluten has been investigated for potential use in non-food applications such as biopolymers and bio-composites. In order to improve the mechanical properties of gluten composites, two factors are usually considered: use of plasticizers and fiber length [6]. Gluten is a vegetable protein, used as a modifier for the formation of composite materials, which can be transformed into a bioplastic material by casting. It is used because of its availability, good biodegradability and viscoelastic properties. Gluten-based composite materials are used to make food packaging as it improves food storage, having the ability to act as a barrier against water, oxygen, and light, therefore reducing oxidation of food [7].

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Gelatin is a protein derived from collagen, being bio-compatible and non-toxic. It is used most often for many biomedical applications [8]. The friction coefficient behavior of proteins such as glucose, gelatin and gluten, dispersed in polymeric matrix are topical [9–14].

The main purpose of this study was to determine the modifications of epoxy resins properties induced by organic compounds. The main targeted properties are, of course, the mechanical ones but also the chemical properties are of high interest. In this regard the tribological analysis is done to complete the full characterization of materials.

2. MATERIALS AND METHODS

The study was carried out using an epoxy resin, namely Epiphen RE4020–DE4020 [15]. The epoxy system is bi-component one consisting of a resin and a hardener that mixed in exact proportions, given by the producer, lead firstly to a gel and, at the polymerization end, to a solid. The Epiphen RE–4020 (resin)–DE 4020 (hardener) system is an epoxy resin with pot-time of about 45 minutes allowing an easy and facile maneuver for casting.

Previous studies showed that amino-acids and inorganic salts can be used to obtain modified epoxy resins with slightly modified properties. The presence of organic modifying agents as starch or organic-inorganic mixtures as clay or inorganic substances as talc are solving a problem that is mentioned by many authors namely the aggregation of CNTs, fullerenes, carbon black or graphenes when these are dispersed into a polymer [16–19].

The tests that had been performed regarding the solubility of organic substances into one of the two components of an epoxy resin and showed a lower degree of solubility for the majority of tested substances excepting starch. One of ours previous studies was regarding the influence of modifying agent dispersion method over the properties of the modified polymer and it was about starch and the same epoxy system – Epiphen RE4020 – DE4020.

For this study gluten and gelatin had been used as modifying agents thinking that their dispersion inside the polymer could increase the polymer bio-compatibility on one hand and, on another hand, hopping to place into the polymer bulk some future points from where the neutralization might begin. The two proteins had been milled together in equal amounts (equal weight ratios) and from this mixture certain amounts were dispersed into the polymer such as to obtain modified polymers with 1%, 2%, 3%, 4% and 5% proteins (weight ratios). Another point of interest in this study concerns with the possibility to modify the proteins themselves prior to their dispersion into the polymer such as, at the end, to create favorable conditions for polymer nano-structuration.

As the studied epoxy system is a bi-component one and previous studies confirmed that the dispersion way is important, the present study is based on the properties analysis between one material obtained by dispersing the modifying into the resin and one corresponding material obtained by dispersing the modifying agent into the hardener prior to their mixture. In order to obtain a uniform dispersion in both cases the components of the epoxy system and the modifying agent were stirred on a magnetic stirrer for 24 hours at 70°C. After that, in the case of first materials the right amount of hardener was added while in the case of second materials the modifying agent-hardener mixture was added to the right amount of resin. The new mixtures were stirred for 15 minutes and the modified pre-polymer was casted into cylinder molds as in. The molds are actually polypropylene straws of 200 mm length and 8mm diameter and they were chose because the polypropylene is one of the few materials to which the epoxy resin does not adhere. More than that such straws are cheap and the sample extraction is very facile.

The materials are described as Eax or Ebx meaning that Ea is the material obtained by dispersing the modifying agent (the proteins mixture) into the resin while Eb represents the materials obtained by dispersing the proteins mixture into the hardener. The x takes values from 1 to 5 and represents the weight ratio of the proteins (%).

After the samples were removed from molds (two weeks after casting) they were thermally treated according with the producer’s recommendations in order to reach their best properties. The thermal
treatment consists of three stages – the first stage eight hours at 60°C, the second stage two hours at 80°C and the final stage one hour at 90°C.

The mechanical tests were performed on an Instron testing machine with 25 kN maximum loading force. The samples for the tensile tests had been extracted from the initial samples (after the thermal treatment) and they were of 160 mm length ensuring a length of 10 mm as engagement zone (at each end 30 mm were used for gripping). The test procedure was established at a speed of 55 mm/min and the stop condition was set at a 40% drop of the loading force.

The tribological tests were performed on a TRM1000 tribometer (Wazzau) with pin-on-disk configuration with the pin made of tested material and standard steel disk. There were set three regimes R1:(10;1,50), R2:(15;1,00), R3:(20;0,75) where the first position represents the force in N and the second position represents the sliding speed in m/s. The sliding distance was set for 1000 m and during the tests the thermal field was monitored with a Fluke thermo-vision camera. The wear rates had been evaluated as the loss of weight reported to the product between force and sliding distance.

3. RESULTS AND DISCUSSIONS

As it is well known for the homogenous and isotropic materials generally the values for tensile elastic modulus and compressive elastic modulus are considered equals. The results of tensile tests confirmed that the presence of proteins mixture inside the matrix had changed the tensile response of epoxy resin. As it can be observed in Fig. 1. in the described configuration the epoxy resin – denoted as E₀ – presents an initial elastic behavior (as long as the matrix remains continuous) and after that it looks as if it has another elastic behavior and we chose to determine the elastic modulus, for all the materials, on this first segment.

![Figure 1. Tensile behavior of epoxy resin up to the failure (left). The epoxy resin behavior on the first elastic segment. On the graph is mentioned the value of elastic modulus in MPa.](image)

Figure 2 and Figure 3 contain the tensile tests results for the materials obtained by modifying the epoxy resin with the smallest and the highest amounts of proteins mixture. In these cases just the segment of elastic response is presented both for the two materials with the same concentration of proteins mixture. What is to be noticed is the fact that the length of the first segment is shorter when the concentration of the modifying agent increases and also the spread of the results is higher when the concentration increases. That means that the elastic response of the materials is diminished with consequences regarding the loading during the tribological tests. The elastic response minimal limit was identified at a load of 200 N, in the case of 5% materials, and the three regimes of the tribological tests that had been done requires a maximum load of 20 N. So, the three regimes are applied on the elastic response conditions for materials. The values of elastic moduli are decreasing when the concentration of the modifying agent increases as it can be noticed from the results presented in table 1.

In the case of higher concentrations seems that the proteins mixture leads to formation of small defects of the polymer network with consequences at the level of loading transfer even the tensile tests did not emphasize any modifications regarding the maxim deformation of the material (deformation at break) in any of the cases.
Figure 2. Elastic tensile behavior for the two materials obtained by dispersion of 1% proteins mixture. (Ea1, left and Eb1, right).

Figure 3. Elastic tensile behavior for the two materials obtained by dispersion of 5% proteins mixture. (Ea5, left and Eb5, right).

Table 1. Elastic modulus values for the studied materials [GPa].

<table>
<thead>
<tr>
<th>Material</th>
<th>Elastic modulus [GPa]</th>
<th>Material</th>
<th>Elastic modulus [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0</td>
<td>2.26</td>
<td>E0</td>
<td>2.26</td>
</tr>
<tr>
<td>Ea1</td>
<td>1.96</td>
<td>Eb1</td>
<td>2.04</td>
</tr>
<tr>
<td>Ea2</td>
<td>1.84</td>
<td>Eb2</td>
<td>1.89</td>
</tr>
<tr>
<td>Ea3</td>
<td>1.75</td>
<td>Eb3</td>
<td>1.68</td>
</tr>
<tr>
<td>Ea4</td>
<td>1.66</td>
<td>Eb4</td>
<td>1.65</td>
</tr>
<tr>
<td>Ea5</td>
<td>1.64</td>
<td>Eb5</td>
<td>1.55</td>
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As per tribological tests results, they are presented in the next figures as the evolution of friction coefficient. In each of the graphic representations, on the right side, the wear rate for each material. In order to facilitate the result interpretation each graph contains the tribological response of the epoxy resin E0 for each of the three tribologic regimes.
Generally the value of friction coefficient is lower in the case of modified polymers than in the case of epoxy resin but for the first regime it is easily to notice that the transitory regime of friction (the first approximately 100m) the friction coefficient of modified polymers (in all the cases) is higher than the one of the epoxy resin. While the epoxy resin friction coefficient on steel increases during the tests for the two lowest concentrations of proteins mixture the friction coefficient seems to decrease during the tests. The Eb3 material is the only modified mixture showing a value of friction coefficient higher than the one of the epoxy resin friction coefficient. It has to be said that for each material five samples were tested and the presented results are averaged.

In the case of the second tribologic regime R2:(15;1,00) the transitory regime of the friction for the modified materials show higher values of the friction coefficient against steel. In this case only the Ea5 and Eb5 materials show lower values for the friction coefficient but these values are close to the ones of the friction coefficient of epoxy resin. For this regime the wear rate of epoxy resin reaches its lowest value while, generally, the wear rates of modified materials are different for different concentrations.

The third regime – figure 6 – indicate that the all modified materials have high friction coefficients against steel while the epoxy resin shows the lowest friction coefficient but the wear rate of epoxy resin is superior to any of the other modified materials for this R3 tribologic regime. The smallest value of the wear rate of epoxy resin is reached in the case of R2 tribologic regime but it is closed to the value reached for the R1 tribologic regime. In fact, the weight loses during tests are of order of micrograms and at this level some experimental errors could be important. The same observation is valid also for the other materials. Analyzing the presented data it is difficult to get a real conclusion.
regarding the connection between proteins concentration and their effect on frictional wear rate of the modified material.

Figure 6. Evolution of friction coefficient during tests under conditions of R3:(20;0,75) tribologic regime.

The wear rate of Ea materials seems to decrease with the proteins concentration for the first two regimes and to decrease with the proteins concentration for the third tribologic regime. For the Eb materials just for the first tribologic regime the wear rate is proportional with the proteins concentration while for the last two regimes the wear rate decreases from 1% to 3% and increases from 3% to 5% in a symmetric manner.

4. CONCLUSIONS

Based on the fact that epoxy resins are usually formed by mixing two chemical liquid compounds proteins modified epoxy resins were formed using a mixture of gelatin and gluten. The weight ratios of proteins into the polymer are from 1% to 5% with 1 increment. The materials were formed by dispersing the proteins into the resin (the main component of the epoxy system) or into the hardener of the epoxy system.

Mechanical analysis showed that the elastic modulus values are decreasing with the concentration of proteins in both cases of proteins dispersion and the decrease is almost proportional with the concentration. Since the material could be considered as homogenous and isotropic the values of the tensile elastic modulus could be considered values for the compressive elastic modulus.

The tribological analysis – pin-on-disk – with the pin made of studied material and steel disk. There were set three tribologic regimes such as the force-sliding speed product to be the same for each of the regimes. Analysis showed that there are variations in friction coefficient evolution during the tests on the same tribologic regime but also there are modifications of the behavior that are related to the tribologic regime. The wear rates were evaluated for each material and for each regime but they are not offering enough information to make a conclusion regarding the connections between this parameter and the proteins concentrations. For the lowest force the friction coefficient of materials against steel is lower than the one of the epoxy resin, for the second regime the friction coefficients are comparable while for the last all the modified materials showed higher values of friction coefficient.
The presence of proteins mixture inside the polymer matrix (epoxy resin) is not dramatically changing the properties of the polymer such as it is possible to move to the next step namely functionalizing the proteins in order to control the polymer sensitive properties such as electromagnetic properties.

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REFERENCES