A study regarding friction behaviour of lysine and isoleucine modified epoxy matrix

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Abstract. The aim of this study is to point out the effect of L-lysine and L-isoleucine used as modifying agents for epoxy resins. The amino acids are largely used to turn the usual polymers in bio-compatible materials but they effect also other significant proprieties of formed materials. The general study developed in Polymer Composite Laboratory is focused on analysis of 14 amino acids used as modifying agents but the two above mentioned showed a special behaviour namely they re-crystalized during the polymerization of the matrix. The coefficient of friction was obtained through the calculation of friction torque measured with a loaded cell sensor. As far as we know, there is no report on the friction proprieties of amino acids modified epoxy resins.

1. Introduction

Epoxy resins have long been receiving a lot of scientific and technical interests and are a family of thermosetting materials widely used as adhesives, coatings and matrices in polymer composites because of the low viscosity of the formulations [1]. Epoxy resins possess excellent thermal stability, moisture resistance, chemical stability, superior electrical and mechanical properties [2]. Diglycidylether of bisphenol A (known as DGEBA) is the most common epoxy monomer. These resins are synthesized via the addition of epichlorohydrine and bisphenol A so oligomers with a relatively narrow distribution of polymerization degrees are obtained [3].

Because of the high adhesive strength and low cost, epoxy-type resins have been primary matrix resins of the adhesives, and various types of curing agents, such as nitrogen - (amines and polyamides), oxygen- (anhydrides), and sulphur – (mercaptans) containing agents, have been used for 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. Another environmental problem of epoxy resins is that all the curing agents are toxic before curing. The curing agents, such as aromatic and aliphatic amines, which are most commonly employed for epoxy curing, are known to be toxic, and to reduce the toxicity, adduct types of amines are sometimes employed. Recently was demonstrated the feasibility of using an amino acid as a novel ecofriendly curing agent. Therefore, the development of environmentally friendly epoxy systems is a great importance for designing green and biocompatible materials in many applications. L-lysine is one of the essential amino acids used in a wide range of applications. In this study an amino acid was used for the preparation of polymeric materials.
The more important epoxy hardeners are the amines and their derivatives, because are less reactive but with higher mechanical properties than those of aliphatic amines. However, these aromatic amines can be also toxic and there is a need for biobased and nonharmful amine hardeners. Unfortunately, there are very few biobased amines; some have been prepared such as isosorbide diamine but through complex chemistries. More simple is the hydrolysis and decarboxylation of amino acids which can lead to diamines, mostly aliphatic diamines. One example is lysine, which can be an interesting platform chemical and which can be converted into a number of industrial monomers, including 1,5-diaminopentan. Li at al., [4] reported that lysine was used as a novel curing agent for a cycloaliphatic-type epoxy. Also, the reaction between L-lysine amino acid and bisphenol A epoxies was not been widely investigated yet. Yong Lv et al. [5] studied the curing kinetics of a diglycidyl ether of bisphenol A with a methanol etherified amino resin [2].

There are many studies concerning the problem of turning polymers into bio-compatible materials and many attempts were developed by using amino acids as agents to ensure the bio-compatibility. The selection of amino acids is due to their availability with high optical purity and lower cost [6, 7, 8].

The fundamental understanding of synergy in tribological performance [9] among various functional fillers is essential for successful applications [10]. The tribological behaviour of epoxy matrix can be significantly improved by addition of suitable filler materials as lysine and isoleucine. Besides the type, the shape and size of the materials added also influence the tribological properties [11].

The aim of this study is to point out the effect of L-lysine and L-isoleucine used as modifying agents for epoxy resins and to explore their role in the friction of the composite. We studied the influence of test speed and applied force values on the friction behavior of three epoxy systems with certain ratio of L-lysine and L-isoleucine as modifying agents. To highlight the effect of these aminoacids in epoxy matrix it is mandatory to perform some mechanical tests as three-point bending and compression to establish where such modified polymers might be used as.

2. Experimental procedure

2.1. Materials

Three epoxy systems were chosen mostly because of their different bisphenol A content namely Epiphen RE4020-DE 4020 78% bisphenol A diglycidyl ether (Bostik), Epoxy Resin C 75% bisphenol A diglycidyl ether (R&G GmbH Waldenbuch), and Epoxy Resin HT-2 50% bisphenol A diglycidyl ether (R&G GmbH Waldenbuch). All these epoxy systems are bicomponent, namely consist of a resin and a hardener mixed in exact proportions given by producer. All the systems are slow resins with a gel time between 20 and 45 minutes time which allows the manoeuvres required by moulding.

All these systems were modified by mixing the main component (the resin) with various amounts of amino acids such as finally their weight ratios into the formed materials to be 1%, 3%, and 5%. L-lysine and L-isoleucine obtained from Sigma-Aldrich were the chosen filler.

2.2. Fabrication of the samples

L-isoleucine was used as received. L-lysine is not miscible with epoxy resin, it cannot be incorporated into epoxy as such. For this reason, L-Lysine was dispersed in methanol (1%, 3% and 5% of epoxy resin). Thereafter, the epoxy resin was added. Methanol was evaporated at 50°C on a magnetic heating stirrer and curing agent for each resin was added. For each pair of substances and for each concentration first of all the mixtures were homogenised by mechanical stirring at 300 rotation/min for 15 minutes. After the mixtures were uniformed the right amount of hardener was stirred for ten minutes to ensure the homogeneity. The pre-polymer mixtures were moulded in cylindrical moulds 8 mm diameter and 200 mm height. After curing, three thermal treatments were applied: 8 hours at 60°C, 2 hours at 80°C and 1 hour at 90°C.
The codifications for the materials used in this study are shown in Table 1.

### Table 1. Materials codification.

| C         | Epiphen (E)                        | HT2                        |
|-----------|------------------------------------|----------------------------|
| C1i-1% L-isoleucine | E1i-1% L-isoleucine in E | HT1i-1% L-isoleucine in HT |
| C3i-3% L-isoleucine in C | E3i-3% L-isoleucine in E | HT3i-3% L-isoleucine in HT |
| C5i-5% L-isoleucine in C | E5i-5% L-isoleucine in E | HT5i-5% L-isoleucine in HT |
| C1l-1% L-lysine in C    | E1l-1% L-lysine in E            | HT1l-1% L-lysine in HT     |
| C3l-3% L-lysine in C    | E3l-3% L-lysine in E            | HT3l-3% L-lysine in HT     |
| C5l-5% L-lysine in C    | E5l-5% L-lysine in E            | HT5l-5% L-lysine in HT     |
| HT1i-1% L-isoleucine in HT | HT1i-1% L-isoleucine in HT     | HT1l-1% L-lysine in HT     |
| HT3i-3% L-isoleucine in HT | HT3l-3% L-lysine in HT     | HT3l-3% L-lysine in HT     |
| HT5i-5% L-isoleucine in HT | HT5l-5% L-lysine in HT     | HT5l-5% L-lysine in HT     |

### 2.3 Details on the friction tests

Coefficient of friction of lysine and isoleucine modified epoxy matrix was measured using pin-on-disc tribometer TRM 1000 (Wazau®, Germany) in the Polymer Composites Laboratory of Dunărea de Jos University of Galați.

All friction tests were carried out in dry condition for pin on disc geometry, the pin having a flat contact surface (figure 1).

![Testing device WAZAU Tribometer TRM 1000 pin-on-disc module.](image)

Cylindrical samples (Ø 8×2.5 mm) were manufactured from the produced materials. The counterbody consisted of a steel disc with 100 mm diameter). All tests were performed in laboratory environment (20 ± 2°C).

The friction tests were carried out under three different regimes, such as:
- R1 – 1 m/s sliding speed and 10 N normal load,
- R2 - 1.5 m/s sliding speed and 15 N normal load,
- R3 – 2 m/s sliding speed and 20 N normal load.

The sliding distance was constant for all studied regimes, namely 1000 m.

For each material three tests were carried out for each regime and the presented results are average values of the three tests.

### 3. Results and discussion

The evolutions of the coefficient of friction during sliding for L-isoleucine and L-lysine in C, E and H epoxy resins against steel disk are shown in Figures 2, 3 and 4. In each representation three curves are shown, which correspond to the three different regimes: R1, R2 and R3.

It is well known that during sliding there are two regions: the running-in region regime (where surfaces adapt to each other and coefficient of friction changes significantly during the first period of sliding, increasing with the sliding distance) and the steady-state region (coefficient of friction remains approximately constant during the whole test).
A typical behaviour of the coefficient of friction with the sliding distance for a sliding test can be observed for all the studied cases. After a very short period (approximately 20 m sliding distance) corresponding to the running-in the coefficient of friction enters in steady-state conditions and remains approximately constant during the whole test [12, 13].

Figure 2 presents the evolution of coefficient of friction for C epoxy system with L-isoleucine and L-lysine for all concentrations with applied force and sliding speeds, respectively. For C1i material, at 1 and 1.5 m/s sliding speed, the coefficient of friction decreases compared to 2 m/s sliding speed. The best graphical representation is for C1i, C3i and C5i for all applied forces. Concerning the C3l material the best coefficient of friction value is for 10N applied force.

![Figure 2](image_url)

**Figure 2.** Evolution of the coefficient of friction with the sliding distance for L-isoleucine (a-C1i, c-C3i, e-C5i) and L-lysine (b-C1l, d-C3l, f-C5l) in C epoxy resin for all concentrations.

From figure 2 can be observed that during the running-in period the values recorded for the three studied regimes are different. The lowest coefficient of friction values for the running-in period are observed for regime R1. The coefficient of friction value increased with the increasing the normal load. The same behaviour was reported by Cui s.a. [14] in their study about epoxy composites reinforced by carbon nanotubes for higher normal load 40-120 N. The increase of the coefficient of friction with the increasing normal load was explained based on the adhesion phenomenon (due to higher loads the material is subjected to plastic deformation).
Some other authors observed a decrease of the coefficient of friction with the increase of the applied normal load [15].

Figure 3 presents the variation of coefficient of friction for E epoxy system with L-isoleucine and L-lysine for all concentrations with applied force and sliding speeds, respectively. In the case of E epoxy system it is clear that the sliding speed influence is rather low excepting E3l material where 1.5 m/s sliding speed leads to a reduction of coefficient of friction value.

Figure 3. Evolution of the coefficient of friction with the sliding distance for L-isoleucine (a-E1i, c-E3i, e-E5i) and L-lysine (b-E1l, d-E3l, f-E5l) in E epoxy resin for all concentrations.

Figure 4 presents the variation of coefficient of friction for HT epoxy system with L-isoleucine and L-lysine for all concentrations with applied force and sliding speeds, respectively. In figure 4, for all composite tested and within the applied force, it is shown that the values of coefficient of friction are very much influenced by applied force.

It can be seen from figure 4 that the coefficient of friction has higher oscillation HT epoxy system as compared to the other two types of resins studied (figures 2 and 3). It can be observed that these oscillations are slightly more pronounced in the case of R1 and R2 regimes.

It is well known that the sliding speed is another parameter that has a great influence on the evolution of the coefficient of friction. It can be seen that in almost of the studied cases the coefficient of friction is increasing with the increasing sliding speed. A higher sliding speed is leading to softening of the epoxy resin (due to the physical and/or chemical interactions) in the contact zone and these as a consequence some particles may be detached from the material (abrasive wear).
Conclusions
From the results of this research, the following conclusions can be made:

1. Coefficient of friction is very much affected by sliding distance and applied force.
2. In the range of applied force studied in this research, the coefficient of friction values for C1l and C3l materials at 10N applied force remains constant. The same remark for C5i at all applied forces.
3. The sliding speed has stronger affect the E1l and E3l materials.
4. HT3l material proved worst in terms of coefficient of friction values for 20N applied force.
5. Finally it was concluded that it is mandatory to perform some mechanical tests for a better understanding of the effect of these aminoacids in epoxy matrix.

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