Dispersion Pathway on Increasing Toughness of Epoxy Resins

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A B S T R A C T

Epoxies resins (ER) are considered as one of the most important classes of thermosetting polymers and are extensively used in various applications. But they are very brittle, with poor resistance to crack propagation and have low impact strength. In the present work, a series of hydroxyl terminated polybutadiene (HTPB) was directly dispersed in the epoxy resin. Then, the dispersed phase was cross-linked by divinylbenzene (DVB) that was previously added to HTPB. Different content of DVB and HTPB are evaluated for effecting on the most of physico-chemical properties of the epoxy resin. The FTIR analysis evidenced the occurrence of a chemical reaction between HTPB and DVB and also ER which was led to improved compatibility. The DMTA analysis of samples indicated different T_g for HTPB/DVB and ER in the mixture and explaining the phase separation between rubber and matrix phases. On adding DVB the stress-at-break increased accompanied by an increase in the elongation-at-break value. Maximum impact strength is obtained by adding 20 phr of DVB and 5 phr HTPB. Finally, SEM analysis showed that modified rubber particles’ diameter is about 5 µm (corresponding to maximum of toughness).

INTRODUCTION

Epoxies resins (ER) are thermosetting polymers for many applications with required high modulus and strength, low creep, and good performance at elevated temperatures. However, their brittleness, low toughness, and poor impact resistance result in their limitation of applications.

Much research about ER toughening has been reported. One of the most successful methods of increasing the toughness of ER is to incorporate some dispersed particles as second phase into the cross-linked...
polymer [1]. The impact strength of epoxy resin can be increased by 1-3 times when the rubbery material in the system be lower than 10 wt%. According to this procedure, the filler can be rigid particles such as SiO2 or glass spheres or reactive rubbery particles or both rigid and rubbery materials [2-16]. Another approach for toughening thermosets is to incorporate some liquid crystalline polymers [17]. Synthetic rubbers containing methylol, hydroxyl, carboxyl, anhydride or thiol groups potentially react with epoxy resins. Barcia et al. [18] used hydroxyl terminated polybutadiene (HTPB) as surface modifier in carbon fiber (CF) reinforced, epoxy matrix composites. The surfaces of CFs were grafted with HTPB, and the latter formed a flexible interface between CF and epoxy matrix, which improved the mechanical behaviour of the system.

The main objective of the present work is to evaluate the effect of cross-linked HTPB (CHTPB) with divinylbenzene (DVB) content on impact strength of diglycidyl ether of bisphenol-A (DGEBA) epoxy resin. In this work, a series of HTPB/DVB-toughened epoxy resins, with different levels of HTPB were evaluated for affecting on the most of physico-chemical properties of an epoxy resin. It is aimed to improve the toughness of DGEBA epoxy resin using 1-methylimidazole as a curing agent. The chemical reactions that possibly take place during the modification of the epoxy resin were monitored using a Fourier transform infrared (FT-IR), while glass transition temperature (Tg) was measured using a dynamic-mechanical thermal analyzer (DMTA). The mechanical behaviour of modified epoxy resins was evaluated in terms of the Izod IS, the critical stress intensity factor (KIC) at different modifier concentrations. The fractured surfaces were studied using a scanning electron microscope (SEM) to elucidate the mechanisms of deformation and toughening as well as other morphological features. Finally, stress-strain curves of the modified epoxy resin were evaluated in terms of studying the tensile properties.

**EXPERIMENTAL**

**Materials**

A liquid epoxy resin system based on DGEBA, (Araldite GY 6010, Jana Co.), used in all experiments and it was dried at 80°C under vacuum for 1 h before use throughout this work. A liquid 1-methylimidazole, from Fluka was supplied as curing agent of ER and used throughout this work.

The elastomer employed was a liquid HTPB with Mn = 2900 containing terminal allylic OH groups and having equivalent weight of hydroxyl equal to 1280 g/eq was supplied from the market and used as the epoxy modifier. Divinylbenzene (DVB) from Merck as cross-linker of HTPB and azobisisobutyronitrile (AIBN) from Merck as initiator of cross-linking reactions were employed in all experiments.

**Sample Preparation**

Rubber and DVB were first mixed together with AIBN. Next, the mixture was added to ER at different weight ratio of ER/HTPB. The mixture was heated for 60 h at approximately 50-60°C, while stirring under N2 atmosphere. Then, the mixture was cooled to 40°C and the curing agent of ER was then added dropwise prior to hand mixing. Next, the resin mixture was vacuumized about 30 min, poured into a silicon mould. Prepared samples, at first, remained at room temperature for 2 h and then were cured for 24 h at 60°C and then post-cured at 120°C for 3 h [19].

**Apparatus**

Differential scanning calorimetry [DSC] was carried out on a STA 625 analyzer (Polymer Labs, Poole, UK) under N2 at atmosphere a heating rate of 10°C/min to analysis resin curing. The glass transition temperature (Tg) and tan δ of cured and modified DGEBA resins with various DVB contents were evaluated at a heating rate of 10°C/min and a bending mode using a PL dynamic-mechanical thermal analyzer (DMTA) (Polymer Labs Co., UK). Izod impact strength (IS) was evaluated according to ASTM D 256 using a standard notched and un-notched specimen. Tests were performed on a Zwick Model 5102 impact tester type machine equipped with a hammer (Zwick Co., Germany). The fracture toughness was measured in terms of KIC. Fracture toughness values were determined with un-notched specimens in three-point bending with a span of 50 mm (ASTM D 790). These tests were performed with an Instron model 6025 (Instron Co., England) at a crosshead speed of 2mm/min and a 1 kN load cell at room temperature. KIC was determined according
to ASTM E 399, with the following relationship [1]:

\[
K_{IC} = \frac{3PSa^{1/2}Y}{2tw^2}
\]

where, \(K_{IC}\), \(P\), \(S\), \(a\), \(t\), \(w\), and \(Y\) are the critical load for crack propagation (N), the length of the span (mm), the specimen length (mm), the specimen thickness (mm), the specimen width (mm), and the geometrical factor given by the following equation, respectively:

\[
Y = 1.93 - 3.07(a/w) + 14.53(a/w)^2 - 25.11(a/w)^3 + 25.80 (a/w)^4
\]

Fractured surfaces of samples of epoxy resin modified with different HTPB/DVB contents examined using a SEM (Cambridge 5360, 20KV).

**RESULTS AND DISCUSSION**

As series of FT IR spectra has been obtained to evidence the occurrence of any chemical interaction between ER, HTPB, and DVB in the first step of their reaction. Initially, the cross-linking reaction between C=C double bonds of DVB and HTPB (radical polymerization), was run in the presence of ER at reaction temperature about 50-60°C for 60 h. In this step, a prepolymer of HTPB/DVB was formed, where DVB and HTPB were bound through C-C linkages. The FTIR spectra of the products formed in this step exhibited an absorption band at 1700-2000 cm\(^{-1}\), indicating the formation of the benzene substitution and elimination of absorption bands at 1640 and 1697 cm\(^{-1}\) indicating the HTPB cross-linking by DVB. The FTIR spectrum for HTPB/DVB mixture showed the typical absorption band of C=C of benzene thus, confirms the above results [19].

Curing step of the ER in absence and presence of rubber particles was studied by using DSC technique (Figure 1). It was found that the curing temperature and heat flow through curing process did not change. Thus rubber particles have not influenced on curing of ER.

The glass transition temperature (T\(_g\)) was obtained from DMTA thermograms of epoxy resin versus HTPB/DVB ratios. Addition of HTPB/DVB causes a very slight decrease in the [19] which is attributed to an increase in the dissolved rubber content within the epoxy matrix. But the main amount of HTPB/DVB system reduces as a separated phase therefore, it indicates a glass transition temperature separately at approximately -60°C. The T\(_g\) of pure ER appears at approximately 160°C.

In addition, using DMTA, the changes of mechanical loss tangent (tan \(\delta\)) relative to DVB content is measured (Figure 2). When the DVB concentration is increased to 20 phr, the tan \(\delta\) is slowly increased, but above that tan \(\delta\) decreases intensively. Thus the maximum of tan \(\delta\) is given at 20 phr DVB concentration which at this concentration, maximum toughness is expected.

Figure 3, represents the Izod IS of the notched and un-notched epoxy modified samples as a function of DVB and HTPB contents. The impact strength of these materials increased as the DVB and HTPB contents were increased upt0 20 and 5 phr, respectively. But IS
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... the Izod IS of both notched and un-notched specimens exhibited a bell-shaped curve with a maximum at 20 and 5 phr of DVB and HTPB content, respectively.

Notched samples showed lower values than the un-notched ones. The main reason behind this behaviour was that notches act as stress concentrators, which leads to a decrease in the IS. Furthermore, the sensitivity of a material to notches is also affected by the fact that fracture is a process that involves both crack initiation and propagation. In notched specimens, an apparent crack is already initiated, so the amount of energy absorbed is dependent primarily on the energy which propagates the crack. However, in un-notched specimens, the energy for initiating a crack is added to the required energy for its propagation [11].

For notched and un-notched specimens, the IS reached maximum values of 0.71 and 6.66 kJ/m², respectively, at 20 phr before decreasing with increases of DVB content. This corresponds to a two-fold increase in IS caused by the addition of just 20 phr DVB and 5 phr HTPB compared to the neat resin. This also shows the beneficial effect of using DVB and HTPB. In fact, at 20 phr DVB content the cross-linking of HTPB by DVB caused Liquid rubber changes in to solid state (cured rubber) that have maximum damping (Figure 2).

A similar trend was observed for Izod IS, and the maximum was reached at 20 and 5 phr of DVB and HTPB, respectively. This result proves the observation of Izod IS and its results.

The difference between results of these two tests might be attributed to the fact that the tests were done...
under different conditions. The $K_{IC}$ was realized at a relatively low speed (Figure 4), whereas the impact was done at a high speed (Figure 3). In other words, when the sample is tested at a high speed (impact) the molecules have not had time to relax or respond to this type of loading and consequently, only a small amount of filler could be tolerated, whereas a higher filler loading could be tolerated when molecules were tested at a slow speed. Maximum Izod IS is reached at 5 phr HTPB. This maybe relate to the size of the formed rubber particles in resin.

In order to correlate the mechanical properties of the modified epoxy resin to morphology, particularly, the correlation between particle size of the elastomeric phase and impact strength results, the fracture surfaces of rubber-modified epoxy networks were analyzed by SEM. The SEM micrographs of some of the HTPB/DVB modified ER presented in Figure 5. They show the large difference in rubber particle sizes that exist in these materials. The micrographs of ER modified with HTPB/DVB shows distinct separated particles of rubber, indicating a heterogeneous system. This heterogeneous morphology resulted opaque samples. The observed holes in the micrographs are related to the rubber particles.

Materials that show maximum impact strength have an average particle diameter in the range of 2-5 μm. Two factors responsible for the size variation of elastomeric particles are:

1. the DVB concentration as shown in Figures 5a and b;
2. the HTPB concentration as shown in Figures 5a and c. With increasing DVB and HTPB concentrations, the rubber particles size were increased and therefore, Izod IS and $K_{IC}$ were decreased.

CONCLUSION

The HTPB/DVB system has a potential as a toughening agent for ER, although the procedure used in this work may impose a limitation to the amounts of HTPB and DVB. This limitation is dependent on the compatibility between HTPB/DVB system and ER, which is affected by their employed ratio.

Based on the results obtained and discussed previously the following conclusions may be drawn; the value of rubber/DVB content have no influence on the cure temperature of these systems, addition of HTPB/DVB causes a very slight decrease in the glass
transition temperature, Izod IS of both notched and un-notched specimens exhibited a bell-shaped curve with a maximum. The same behaviour is observed for $K_{IC}$ results, and SEM analysis indicates the ER modified with HTPB/DVB shows distinct separated particles of rubber, indicating a heterogeneous system.

REFERENCES