Toughening of Epoxy Resin Using Hydroxyl-Terminated Polyesters

H. HARANI, S. FELLAHI, M. BAKAR

Plastics and Rubber Engineering Department, Institut Algérien du Pétrole (IAP), Boumerdes–35000, Algeria

ABSTRACT: Epoxy resins are increasingly finding applications in the field of structural engineering. A wide variety of epoxy resins are available, and some of them are characterized by relatively low toughness. Several approaches to improve epoxy resin toughness include the addition of fillers, rubber particles, thermoplastics, or their hybrids, as well as interpenetrating networks and flexibilizers, such as polyols. It seems that this last approach did not receive much attention. So in an attempt to fill this gap, the present work deals with the use of hydroxyl-terminated polyester resins as toughening agents for epoxy resin. For this purpose, the modifier, that is, a hydroxyl-terminated polyester resin (commercially referred to as Desmophen), which is a polyol, has been used at different concentrations. The prepared modified structure has been characterized using Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) prior to mechanical testing in terms of impact strength and toughness. Two types of Desmophen (800 and 1200) have been used as modifiers. The obtained results showed that hydroxyl-terminated polyester improves the epoxy toughness. In fact, the impact strength increases with Desmophen content and reaches a maximum value of 7.65 J/m at 10 phr for Desmophen 800 and 9.36 J/m at 7.5 phr for Desmophen 1200, respectively. At a critical concentration (7.5 phr), Desmophen 1200 (with higher molecular weight, longer chains, and lower branching) leads to better results. Concerning K_c, the effect of Desmophen 800 is almost negligible; whereas a drastic effect is observed with Desmophen 1200 as K_c reaches a maximum of 2.41 MPa $m^{1/2}$, compared to 0.9 MPa $m^{1/2}$ of the unmodified epoxy prior to decreasing. This is attributed to the intensive hydrogen bonding between epoxy and Desmophen 1200, as revealed by FTIR spectroscopy. Finally, the SEM analysis results suggested that the possible toughening mechanism for the epoxy resin being considered, which might prevail, is through localized plastic shear yielding induced by the presence of the Desmophen particles. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 29–38, 1999

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INTRODUCTION

Epoxy resins are increasingly being used in structural applications. The success of epoxy resins use

Correspondence to: S. Fellahi.
Present address: M. Bakar, Politechnika Radomska, 26-600 Radom, Poland.

is based on several attributes. Epoxy resin systems do not lead to volatile formation upon curing; in fact, once cured, they become highly chemical and corrosion-resistant. They are also known to exhibit low shrinkage during cure. Such factors are important for almost any application.

Epoxy resins are known to possess more than one 1,2 epoxy group per molecule. This structure is reactive to many substances, thus leading to chain extension and/or crosslinking through a rearrange-

ment polymerization reaction type.[1] Steric factors, as well as the type of epoxy group and its location within the molecule, will influence the reactivity of this later. Compact molecules containing a number of epoxy groups may not, under normal conditions, undergo complete reaction.[2] Consequently, epoxy exhibits a relatively lower curing shrinkage than any other type of thermosetting resins. Whereas the nonepoxy part of the molecule may be either aliphatic, cycloaliphatic or highly aromatic hydrocarbon.[1,2]

The first and still the most important commercial epoxy resins are reaction products of bisphenol A and epichlorohydrin, leading to the diglycidyl ether of bisphenol A (DGEBA). It is also commonly used as thermosetting matrices for glass, carbon, and aramid fiber-reinforced composites used in structural and isolation applications. However, some unsolved problems, encountered with some types of epoxy resins during application, such as relatively poor toughness still remain. Several attempts have been made to alleviate this problem.

One way to improve the toughness of epoxy resins includes the addition of a rigid phase (sillica, kaolin, glass beads, and $CaCO_3$ fillers). Fillers are generally used in the plastic industry to lower the cost while increasing the final product rigidity. Several studies have demonstrated that the fracture energy of brittle polymers may be significantly improved with the incorporation of solid particles. In fact, it has been reported that in the case of filled polymers, fracture energy can attain a maximum at a specific volume fraction of added particles which, however, may also decrease the elongation at break and the impact resistance.[3–5] The degree of toughness enhancement was found to depend upon the volume fraction, as well as the particle size and the shape of the filler.[6,7] The increase in fracture energy of a brittle material due to the addition of a rigid second phase was explained by Lange as arising from interactions between the moving crack front and the second dispersed phase.[8]

Other approaches to toughen epoxy resins is through resinous modifiers. The number of modifiers that have been evaluated in relation with epoxy resins is considerable. In fact, with compatible resins, the epoxy may interact through active hydrogens to produce a variety of heteropolymers.

The addition of a thermoplastic to toughen epoxy resins is a rather new technology. Venderbrosch et al.[9] used Polyphenylene ether PPE, Pearson and Yee[10] used Polyphenylene Oxide PPO, and Hofflin et al.[11] used polyetheresters to toughen epoxy resins.

The use of rubber particles as a second phase to the epoxy resins to increase the toughness of the brittle matrix has been considered extensively.[12] Yee and Pearson[13] concluded that rubber particles acting as stress concentrators enhance shear localization. In another article,[14] the same authors report that smaller particles are more efficient in producing a toughening effect than larger one. The mechanism involves internal cavitation of the rubber particles and the subsequent formation of shear bands. In another study, Sankaran and Chanda[15] proved that toluene di-Isocyanate TDI acts as a coupling agent between the epoxy resin and the rubber, leading to improved mechanical properties. Beaumont and coworkers[16] have proposed another toughening mechanism, which emphasizes the role of deformation and fracture of the rubber particles. The rubber particles are considered to bridge the crack as it propagates. The increase in toughness of a multiphase polymer may be identified with the amount of elastic stored energy in the rubber particles during stretching, which is dissipated irreversibly when the particles break.

A more recent work[17] illustrates the benefits of hybrids structures (filler and rubber simultaneously) in toughening epoxy resins, thus supporting previous findings.[18]

A great deal of litterature has been devoted to the toughening of epoxy resins via polyurethane incorporation as a second phase in a specific matrix to form an interpenetrating polymer network.[19–22] In this case, the mechanical properties are found to be fairly superior to those of ordinary polymers, namely, through maximum tensile strength. Such improvement is generally attributed to an increase in crosslinking density within interpenetrating networks.

Because of the lack of studies on the toughening effect of polyols, the present work is an attempt to toughen the epoxy resin using hydroxyl-terminated polyester resins as modifiers.

For this purpose, 2 hydroxyl-terminated polyester resins (commercially referred to as Desmophen), which are polyols, have been used at different concentrations as modifiers for epoxy resin.

EXPERIMENTAL

Materials

The materials used are listed in Table I. Their chemical structures are displayed in Table II.

Table I   Materials Used

Designation	Description	Supplier
Epoxy	Diglycidyl ether of bisphenol A: GY-260; MW = 381	Shering France Company
Hydroxyl-terminated polyester (Desmophen 1200)	Slightly branched polyester with 5% OH	Bayer
Hydroxyl-terminated polyester (Desmophen 800)	Branched polyester with 7.5% OH	Bayer
Crosslinking agent (Eurdur 460)	Imidazoline polyamine (Eurdur 460)	Shering France Company

Sample Preparation

Before being used, hydroxyl-terminated polyester (Desmophen 1200 and Desmophen 800) and epoxy were continuously stirred in a flask and degassed under vacuum of 0.1 mm Hg overnight at 60°C. The curing agent (Eurdur 460) was not submitted to this treatment.

Preparation of the Epoxy–Curing Agent

A general purpose recipe based on the literature[2] has been used to prepare the epoxy–curing agent system (100 : 65 phr) at 68°C. This was done for comparative purposes.

Preparation of the Epoxy–Hydroxyl-Terminated Polyester (Desmophen)

To prepare the hydroxyl-terminated-polyester-modified epoxy, an appropriate amount of Desmo-phen was added to the epoxy. These ingredients were continuously mixed for 20 min by means of a mechanical stirrer. The temperature was maintained at 68°C in a water bath. Then the mixture was allowed to cool. After that, the curing agent (Eurdur 460) was added while mixing and degassing under vacuum for 30 s to remove any trapped air or moisture that may have condensed on the flask. The mixture was poured into an aluminum mold (covered with Teflon film for easy removal) with well-defined geometry. Curing was carried out at room temperature for 24 h, followed by a post-curing for 3 h at 120°C in an oven. Upon removal from the mold, samples were kept in a dessicator for at least 3 days before testing. It has to be mentioned that 2 types of hydroxyl-terminated polyester (Desmophen 1200 and 800) were used at different concentrations, while epoxy resin and curing agent amounts were kept con-

Table II   Chemical Structure of the Ingredients Used

Ingredient	Chemical Structure
Epoxy: DGEBA–GY-260	
Curing agent: Eurdur 460	$R-NH_2$
Hydroxyl-terminated polyester (Desmophen)	$HO-[\sim\!\sim\!\sim]-OH$

stant. Desmophen 1200 has long molecular chains with limited ramifications and contains 5% OH groups. Desmophen 800 has shorter molecular chains but more branching with 7.5% OH groups.

Testing

Infrared Spectroscopy

For characterization purposes of the prepared formulations in terms of chemical reactions, new chemical groups and the NCO-to-OH ratio Fourier transform infrared (FTIR) spectroscopy was used. The infrared (IR) spectroscopy was used in this study for 2 main reasons as follows: the first one was the identification of new chemical groups formation; the second related to the —NCO-to-OH ratio monitoring.

IR analysis was performed using a Philips analytical PU 9800 FTIR spectrometer. The preparations in solid form were either ground and then put into KBr disc or finely sliced and then analyzed.

Fracture Studies

Izod Impact Energy. Izod impact tests were performed according to ASTM-D 256 at room temperature using a TMT No. 43-1 impact tester type machine equipped with a hammer. The Izod type test uses a standard notched (1 mm) specimen, held as a vertical cantilever beam broken by a single swing of a pendulum, and measures the energy to failure. The specimen is struck by the blow of the hammer on the notch side. The Izod impact strength (IS) is given as follows:

$$IS = E/w \text{(J/m)} \qquad (1)$$

where E is the energy to break a specimen (J), and w is the width of a specimen (m).

IS values reported herein represent the average of a minimum of 6 tests. Samples were prepared by casting the different preparations into rectangular-shaped, $65 \times 15 \times 4$ mm aluminium molds. The notch was prepared manually using a razor blade and measured using an optical microscope.

Critical Stress Intensity Factor. The critical stress intensity factor (or fracture toughness, K_c) was determined using a fracture mechanic technique. In this study, K_c value was measured by single-edge-notched (SEN) specimen under a three-point bending (3PB) mode. These tests were performed using an INSTRON tensile machine type 1195 at a crosshead speed of 5 mm/min and at room temperature. K_c was determined according to ASTM E399-78, using the following relationship[23]:

$$K_c = \frac{3PS(a)^{1/2}f(x)}{2tw^2} \qquad (2)$$

where P is the critical load for crack propagtion (in Newton); S is the distance between the spans (50 mm); w is the specimen width (15 mm); L is the specimen length (135 mm); a is the precrack length (0.9–1.5 mm), which was prepared at room temperature using a razor blade and measured using an optical microscope; t is the specimen thickness (4 mm); and $f(x)$ is a geometric factor. For $3PB$ specimens, $f(x)^{10}$ is given by

$$f(x) = 1.93 - 3.07x + 14.53x^2 - 25.11x^3$$
$$+ 25.80x^4 \quad (3)$$

where $x = a/w$.

Scanning Electron Microscopy Analysis

Scanning electron microscopy (SEM; CAMEBAX MICRO BEM) was used to analyze the fractured surfaces as related to the type and content of the modifier. Fractured surfaces were coated with a thin layer of gold palladium alloy prior to SEM observation.

RESULTS AND DISCUSSION

IR Spectroscopy

Virgin epoxy was modified using 2 types of polyols (Desmophen 800 and Desmophen 1200). The change in the epoxy structure, if any, was recorded by IR spectroscopy.

A whole series of IR spectra have been obtained to revealing the presence or absence of any chemical interaction between epoxy resin and polyol. They are presented in Figure 1(a)–(d). Figure 1(a) illustrates the IR absorption spectrum of the pure (as-received) epoxy resin (GY260) for further comparison, while Figure 1(b)–(d) represent the spectra of the reaction mixtures, that is, epoxy–Eurdur [referred to as virgin epoxy; Fig. 1(b)], epoxy–Desmophen 1200–Eurdur [Fig. 1(c)], and

Figure 1   Infrared spectrum: (a) pure epoxy; (b) virgin epoxy; (c) epoxy–Desmophen 1200–Eurdur (7.5 phr); (d) epoxy–Desmophen 800–Eurdur (10 phr).

epoxy–Desmophen 800–Eurdur [Fig. 1(d)]. According to these spectra, there is evidence that epoxy reacts chemically with the hardener.

The presence of an absorption peak at $\sim$ 3500 cm^{-1} is due to —OH stretching vibrations of the pure epoxy [Fig. 1(a)]. On adding the hardener, an increase in the OH peak intensity has resulted [Fig. 1(b)]. It has to be mentioned that, initially, in formulation (b) containing the hardener, the amount of epoxy resin is less than in formulation

(a), that is, pure epoxy, for steochiometric reasons; therefore, less OH groups are present and, consequently, the OH intensity peak at 3500 cm^{-1} should be lower. But an equal percentage of transmission is observed when comparing spectra (a) and (b) of Figure 1. This equality comes from the fact that additional OH groups are formed during the reaction between the resin and the hardener. Such phenomenon might also be related to the following factors: (1) the existence of

Figure 1   (*Continued from the previous page*)

OH groups inherent to the pure epoxy, (2) the reaction of each Eurdur polyfunctional amine primary group with epoxy groups, and (3) the creation of hydrogen bonding between epoxy OH groups and the product obtained at stage (3). An illustration of the above-mentioned reactions (b) is shown in Scheme 1.

The OH stretching peak appearing at $\sim$ 3500 cm^{-1} and resulting from the above reaction becomes more important [Fig. 1(c) and (d)] due to the creation of hydrogen bonding between all OH groups present in the mixture. This is illustrated in Scheme 2.

Figure 1(b) and (c) provide further information relating to the reduction of the epoxy intensity peak at 920 cm^{-1}; such behavior is, in fact, evidence as to the effective contribution of the epoxy ring in the reaction.[2]

This is considered true for either Desmophen types at different content percentages. A comparative study of all spectra revealed that the same by-products were obtained.

Scheme 1.

Mechanical Properties

Figure 2 represents the impact strength (IS) of the epoxy modified using either types of Desmophen (800 and 1200) versus Desmophen content.

In both cases, the impact strength increases with Desmophen content and reaches a maximum value of 7.65 J/m at 10 phr for Desmophen 800 and 9.36 J/m at 7.5 phr for Desmophen 1200, respectively, and then decreases with increasing Desmophen content. This decrease could be attributed to some phase separation.[24] It was also observed that Desmophen 1200 leads to much better impact properties compared to Desmophen 800. This improvement in impact strength could be attributed to an increased degree of entanglement between the epoxy resin and the polyols, as well as the flexibility effect of Desmophen, as reported in the literature.[2,22]

Figure 3 represents the critical stress intensity factor (K_c) versus Desmophen content for both types (Desmophen 800 and 1200). As far as Desmophen 800 is concerned, K_c is not affected if not reduced, whereas a drastic effect is observed with Desmophen 1200: K_c reaches a maximum value of 2.41 MPa m$^{1/2}$ compared to 0.9 MPa m$^{1/2}$ of the unmodified epoxy prior to decreasing. This result is similar with that reported in the case of impact strength and can be attributed to the fact that Desmophen at a critical concentration acts as an effective impact modifier. Either the chain length and the branching degree of these polyols might be the reason behind the toughness improvement in the case of Desmophen 1200, while for Desmophen 800, the effect is nil. Furthermore, a rela-

Scheme 2.

Figure 2   Effect of Desmophen content on the impact strength (IS) of the epoxy-based formulations.

tively higher crosslinking density is obtained when using Desmophen 1200. This might be related to relatively more intense hydrogen bonding interactions in the case of Desmophen 1200, as shown on the IR spectra (Fig. 1). This is supported by the fact that Desmophen 1200 has longer chain, but less branching will have a greater chance that all its OH groups will form

Figure 3   Effect of Desmophen content on the critical stress intensity factor (K_c) of the epoxy-based formulations.

Figure 4   SEM micrograph of the fractured surface of pure epoxy.

hydrogen bonding. On the other hand, Desmophen 800, even with higher OH content initially (7.5%) compared to Desmophen 1200 (5%), will have less chance for all its OH groups form hydrogen bonding totally. This is due to the fact that Desmophen 800 has short chains and is more branched; thus, some of its OH groups are hidden and inaccessible for such interactions. Such a result further reinforces the difference in effects between the 2 polyols, hereby confirming what has been reported in the literature.[2]

An important result of this study is the tremendous increase in the toughening of epoxy resin just by using a hydroxyl-terminated polyester. It was found that the Desmophen (1200)-modified epoxy has an impact strength ranging from 3–9 J/m and a K_c from 0.9–2.5 MPa m$^{1/2}$, meaning that IS and K_c were improved three-fold compared to the virgin epoxy.

Fractography

The scanning electron micrographs of fractured surfaces of both unmodified and modified epoxy resin are shown in Figures 4–6. Concerning the unmodified epoxy resin samples (Fig. 4), the crack propagation occurs in a brittle, unstable manner. The presence of fine lines emanating mainly from the crack initiation region is evidenced. These lines extend approximately along the crack propagation direction and are associated with the point of arrest of the crack front.[22]

The fractured surfaces of Desmophen 1200-modified epoxy are shown in Figures 5(a)–(c) for various Desmophen content 5, 7.5 and 15 phr,

respectively. Figures 5(a) and (c) show a heterogeneous structure going along with relatively low impact strength and K_c, while at 7.5 phr, the structure is more homogeneous [Fig. 5(b)], corresponding to the maximum impact strength and K_c

(a)

(b)

(c)

Figure 5   SEM micrographs of fractured surfaces of epoxy–Desmophen 1200: (a) 5 phr, (b) 7.5 phr and (c) 15 phr Desmophen.

(a)

(b)

(c)

Figure 6 SEM micrographs of fractured surfaces of epoxy–Desmophen 800: (a) 5 phr, (b) 10 phr, and (c) 20 phr Desmophen.

(Figs. 2 and 3). The presence of very fine particles firmly attached to the matrix, probably those of Desmophen, with some whitening seems to be the

reason behind this increase in toughness. This means that Desmophen 1200 plays the role of an effective impact modifier at 7.5 phr. It seems that some interactions between the 2 phases have taken place through hydrogen bonding, leading to better a interface, resulting in an increased toughness. Based on SEM observations, the possible toughening mechanism that might prevail is through localized plastic shear yielding induced by the presence of the Desmophen paricles.

While the epoxy modified with Desmophen 800, as shown in figure 6(a)–(c) exhibits a heterogeneous morphology with loose, tiny, round, and irregular-shaped domains distributed in the matrix. This might be attributed to its relatively lower incompatibility with the epoxy, confirming the IR results; that is, less hydrogen bonding due to the fact that some OH groups did not participate in the reaction. This result goes along with the obtained low toughness (Fig. 2), although a surprising result was observed with a relatively improved impact strength obtained at 10 phr of Desmophen 800. This can be due to the nature of the testing procedures; that is, the impact test is done at high speed, while the K_c is obtained at lower speed. Similar results have been reported.[25]

Concerning the difference in the effect of Desmophen 800 and 1200, this might be due to the structure of both polyols. Desmophen 1200, having a higher molecular weight, thus longer molecular chains with minor ramifications, will have more chance for better interactions with the resin and higher crosslinking density, resulting in better mechanical properties. Desmophen 800, with a lower molecular weight and short chains, is more branched and more compact, thus, less flexible and with less of a chance than Desmophen 1200 that all its OH groups interact.

CONCLUSIONS

The results obtained in the present study lead to the following conclusions. Hydroxyl-terminated polyester, a polyol, improves the epoxy toughness. Polyol type (M_w and branching) and concentration are 2 parameters that significantly affect the mechanical properties of epoxy resins, namely, the impact strength and critical stress intensity factor. In fact, at a critical concentration (7.5 phr), Desmophen 1200 (with higher molecular weight, longer chains, and lower branching) leads to fairly good results. The impact strength and the K_c increase from 3 J/m and 0.9 MPa m$^{1/2}$ for the

virgin epoxy to 9 J/m and 2.4 MPa m$^{1/2}$ for the modified epoxy, respectively.

The SEM analysis results suggest that localized plastic shear yielding is probably the prevailing toughening mechanism for epoxy resin.

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