Toughening of Epoxy Resin Using Synthesized Polyurethane Prepolymer Based on Hydroxyl-Terminated Polyesters

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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 a relatively low toughness. One approach to improve epoxy resin toughness includes the addition of either a rigid phase or a rubbery phase. A more recent approach to toughen brittle polymers is through interpenetrating network (IPN) grafting. It has been found that the mechanical properties of polymer materials with an IPN structure are fairly superior to those of ordinary polymers. Therefore, the present work deals with epoxy resin toughening using a polyurethane (PU) prepolymer as modifier via IPN grafting. For this purpose, a PU prepolymer based on hydroxyl-terminated polyester has been synthesized and used as a modifier at different concentrations. First, the PU-based hydroxyl-terminated polyester has been characterized. Next, an IPN (Epoxy–PU) has been prepared and characterized using Fourier transform infrared (FTIR) spectroscopy, thin-layer chromatography (TLC), and scanning electron microscopy (SEM) prior to mechanical testing in terms of impact strength and toughness. In this study, a Desmophen 1200-based PU prepolymer was used as a modifier at different concentrations within the epoxy resin. The results also showed that, further to the IPN formation, the epoxy and the PU prepolymer reacted chemically (via grafting). Compared to virgin resin, the effect on the mechanical properties was minor. The impact strength varies from 3–9 J/m and K_c from 0.9–1.2 MPa m$^{1/2}$. Furthermore, the incorporation of a chain extender with the PU prepolymer as a modifier into the mixture caused a drastic improvement in toughness. The impact strength increases continuously and reaches a maximum value (seven-fold that of virgin resin) at a modifier critical concentration (40 phr). K_c reaches 2.5 MPa m$^{1/2}$ compared to 0.9 MPa m$^{1/2}$ of the virgin resin. Finally, the SEM analysis results suggested that internal cavitation of the modifier particles followed by localized plastics shear yielding is probably the prevailing toughening mechanism for the epoxy resin considered in the present study. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2603–2618, 1998

Key words: toughening, epoxy, IPN, PU prepolymer, grafting

INTRODUCTION

The first and still the most important commercial epoxy resins are reaction products of bisphenol A and epichlorohydrin. The reaction giving the diglycidyl ether of bisphenol A and a higher molecular species is as follows:

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 rearrangement polymerization type of reaction.[1] The type of epoxy group and its location within the molecule will influence the reactivity of this later. Steric factors will also affect reactivity so that compact molecules containing a number of epoxy groups may not, under normal conditions, undergo complete reaction.[2]

Epoxy resins are 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 approach to improve epoxy resin toughness includes the addition of a rigid phase (sillica, kaolin, glass beads, and $CaCO_3$ fillers). Generally, fillers have been widely 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 both the volume fraction as well as particle size and shape of the filler.[6–7] The increase in fracture energy of a brittle material due to the addition of a brittle second phase was explained by Lange as arising from interactions between the moving crack front and the second dispersed phase.[8] This evidence for the interactions came from fractographic studies, which showed that as a moving crack front interacts with heterogenities present in the brittle matrix, tails or steps are formed close to the inclusion due to the connection of the 2 arms of the crack front resulting from different fracture phases.

Other approaches to toughen epoxy resins is through resinous modifiers. 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),

and 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 particles. The mechanism involves internal cavitation of the rubber particles and the subsequent formation of shear bands. Sankaran and Chanda[15] proved that toluene diisocyanate (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 (combination of rubber particles and fillers) in toughening epoxy resins, thus supporting previous findings.[18]

Hydroxyl-terminated aliphatic polyesters are widely used in the reaction with the polyurethane resins, and some of these commercial materials are suitably reactive with the epoxy resins to improve the toughness.[2,19] In addition, it was found that hydroxyl aliphatic polyester improved fracture toughness more than amine- or acid-terminated polyester due to effective molecular weight buildup by a chain extension reaction. Hydroxyl-terminated polyesters may be considered as a special case of polyols. Recently, it has been proved that some types of polyols may greatly improve the impact strength as well as the fracture toughness of epoxy resin.[20]

Polyurethane (PU) resins are a unique family of materials that possess some of the properties of plastics and of rubbers. There are several methods available for the preparation of PUs, but the most widely used one is the reaction of di- or polyfunctional hydroxyl compounds, such as hydroxyl-terminated polyesters or polyethers with di- or polyfunctional isocyanate.[1,21]

A great deal of literature has been devoted to the toughening of epoxy resins via PU incorpora-

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 1 (Eurdur 460)	Imidazoline polyamine (Eurdur 460)	Shering France Company
Crosslinking agent 2 (TMP)	Trimethylolpropane (TMP)	PUR-Chim France
Chain extender	1.4 Butanediol (1,4-BD)	Eastman Kodak (USA)
Toluene diisocyanate (TDI)	TDI 80 : 20 mixture of 2.4 and 2.6 isomers; NCO = 33%	—

tion as a second phase in a specific matrix to form a grafted or ungrafted interpenetrating polymer network (IPN). It has been found that the mechanical properties of polymer materials with an IPN structure are fairly superior to those of ordinary polymers, namely, the maximum tensile strength. Such improvement is generally attributed to an increase in crosslinking density within IPNs.[22–26]

Therefore, and within this framework, the main objective of the present work is an attempt to toughen the epoxy resin using a PU prepolymer as a modifier via IPN grafting.

For this purpose, a PU prepolymer has been synthesized based on hydroxyl-terminated polyester resins and used as a modifier for epoxy resin at different concentrations. The effect of a chain extender is also investigated.

EXPERIMENTAL

Materials

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

Sample Preparation

Before being used, hydroxyl-terminated polyester (Desmophen 1200), crosslinking agent [Trimethylolpropane (TMP)], chain extender [1,4-butanediol (1,4-BD)], TDI, 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.

PU Prepolymer Synthesis

Based on the results obtained previously,[20] hydroxyl-terminated polyester (Desmophen 1200) was selected. Then, 2 approaches were followed for PU prepolymer synthesis.

Effect of TDI (80 : 20)-to-Desmophen Ratio. A range of ratios has been used (1 : 1, 1 : 2, 2 : 1); based on the results obtained, only the 2 : 1 ratio was selected. It is to be mentioned that the 2 : 1 ratio is in accordance with works reported in the literature.[23]

Effect of Temperature. The effect of temperature on PU synthesis may significantly affect the final prepolymer structure. Taking this into consideration, PU synthesis was carried out at the following 3 different temperatures: 45, 70, and 100°C. Two equivalents of TDI were poured into a reaction kettle, connected with a dry nitrogen input, a thermometer, dropping funnel, and a mechanical

Table II   Chemical Structure of the Reagents Used

Ingredient	Chemical Structure
Epoxy: DGEBA–GY-260	
Curing agent: Eurdur 460	R—NH_2
Chain extender: 1-4 butanediol (1,4-BD)	
Crosslinking agent: Trimethylol propane (TMP)	
Hydroxyl-terminated polyester (Desmophen)	HO—[〰〰]—OH

stirrer. Then, 1 equivalent of Desmophen was added drop by drop to the TDI via the dropping funnel. Once Desmophen addition completed, the dropping funnel was replaced by a reflux condenser, and the temperature was varied, as mentioned above (that is, 45, 70, and 100°C in a water bath). The reaction ended when the NCO content, which was determined by the di-n-butylamine titration method (ASTM D 1638), reached a constant value, that is, assymptot on the curve, representing the unreacted isocyanate versus time.

Epoxy–PU Preparation

The preparation of IPN (epoxy–PU) was carried out by adding specific amounts of PU prepolymer (5, 10, 20, 30, 40, and 50 phr) to a constant amount of epoxy resin into the reaction kettle. The temperature was maintained at 70°C under dry N_2. The reaction was controlled every 10 mm using Fourier transform infrared (FTIR) spectroscopy. The reaction ended when a constant ratio of the absorption peak of the —NCO group (2270 cm^{-1}) to that of epoxide group (920 cm^{-1}) was reached. Finally, 65 phr of the curing agent (Eur-

dur 460) was added to the mixture. After mechanical agitation and degassing under vacuum for 30 s, the mixture was cast into an aluminium mold at 80°C in an oven for 2 h. Then it was further heated to 120°C and kept at this temperature for 6 h. Upon removal from the mold, samples were kept in a dessicator for a minimum period of 3 days.

Epoxy–PU Preparation With a Chain Extender (1,4-BD) and a Second Crosslinking Agent (TMP)

To prepare the above system, the following 2 cases were considered.

1. In addition to the previously used curing agent (Eurdur 460), and based on the literature,[23] the effect of the ratio (4 : 1) of TMP to 1,4-BD was considered.
2. Ingredient addition has been carried out in two different ways, as follows: (1) epoxy–(TMP : 1,4-BD)–PU–curing agent; and (2) epoxy–(TMP : 1,4-BD)–curing agent–PU.

The same procedure for sample preparation, as above, was followed. It has to be mentioned that

procedure (2) was abandoned because curing took place before PU addition.

Testing

Fourier Transform Infrared Spectroscopy

FTIR spectroscopy was used in this study for 2 main reasons. The first was the identification of new chemical groups formations; the second related to the —NCO-to-OH ratio monitoring.

Infrared (IR) analysis was performed using a Philips analytical PU 9800 FTIR spectrometer. The following 2 methods were used: the PU prepolymer in liquid form is analyzed following the conventional way, while the remaining preparations in solid form are either ground and then put into KBr discs, or finely sliced and then analyzed.

Thin-Layer Chromatography

Thin-layer chromatography (TLC) is one of the most powerful analytical separation techniques available nowadays. It is based on conventional chromatography techniques. The real usefulness of the technique in the analysis of polymers is the ability to separate and isolate almost every component within a complex mixture. Once the method has been developed for a given system, the results can be obtained rapidly, accurately, and at a very low cost. Silica gel is the most widely used coating materials in this technique.[27,28]

In TLC, substances are identified primarily on the basis of their mobility in a suitable solvent, but a reference compound should be compared with unknown substances. Further indications to identify a given substance are supplied by the reactions of the unknown substance with the paper. Depending on the system, when 2 spots of the same substance are present, reactions such as oxydation, hydrogenation, acetylation, and halogenation can be used for identification. In order to make the spots visible, revealing agents, such as Ninhydrine, are used.[28]

It has been reported in the literature[28] that in the case of PU synthesized from liquid components, several reactions are possible. Such reactions may lead to the formation of additional components to the prepolymer (PU), thereby affecting the overall properties of the final product. Therefore, TLC is used to detect the formation of such additional components; however, for the purpose of the present study, the test (TLC) has required a revealing agent (Ninhydrine) and the following

3 different eluants: chloroform–methanol, used to identify 2.4 TDI; ether–methanol, used to detect any alcohol in the mixture; and diisopropyl ether–formic acid–water, used to detect traces of organic acids.

Fracture Studies

Izod Impact Energy. Izod impact tests were performed according to ASTM procedure D256 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:

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

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[29]:

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

where P is the critical load for crack propagation (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 (mm), which was prepared at room temperature using a razor blade and measured using

an optical microscope (0.9–1.5 mm); t is the specimen thickness (4 mm); $f(x)$ 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

PU Prepolymer Synthesis

Synthesis

Based on previous results,[20] Desmophen 1200 was selected for the synthesis of the PU prepolymer. The following 2 variables have been considered: the TDI-to-Desmophen ratio and the effect of temperature on the reaction.

TDI-to-Desmophen Ratio. It has to be mentioned that the TDI used contains a ratio of 80/20 of 2,4 and 2,6 isomers, respectively. Several ratios of TDI to Desmophen, 1 : 1, 2 : 1, and 1 : 2, have been prepared. However, only the results related to the 2 : 1 ratio are presented. The selection was based on the fact that rapid curing takes place when using the 1 : 1 and 1 : 2 ratios.

Temperature Effect on the Reaction. Figure 1 represents the variation of unreacted isocyanate (%) as a function of time at different temperatures (45, 70, and 100°C). This indicates the rate of reaction of TDI with Desmophen 1200. It is clearly seen that the isocyanate content decreases with time. Concerning the reaction at 45°C, the decay is almost linear with a small slope, indicating a relatively slow reaction with a big amount of unreacted NCO group 40% after 120 min. At a higher temperature ($T = 100°C$), the reaction rate was very fast. A rapid decrease in the NCO content is observed after 30 min, followed by a solidification of the product. At a moderate temperature and based on the literature,[22–24] 70°C

was chosen. The reaction rate follows 2 linear paths: The first one decreases moderately until 75 min, then a steady state is reached with approximately 3% of unreacted isocyanate. It has to be mentioned that at $T = 70°C$, and even at longer times (75–120 min), the obtained resin remained in a liquid form (prepolymer). Similar results have been reported in the literature.[14,26,30,31] It has to be mentioned that the quantitative determination (using dibutylamine titration according to ASTM D 1638) of the unreacted —NCO group in the synthesized PU prepolymer is important. This serves as a mean to monitor the product quality as well as the crosslinking reactions. It can be observed that the unreacted NCO content decreases during the reaction and becomes constant at various times, depending on the temperature used.

Since both —NCO groups present in the TDI molecule have different reactivities (because of their position in the molecule), and because the polyol may contain primary and secondary OH groups, it is possible to conceive that the following series of reactions can occur simultaneously.[32–33]

Primary and/or secondary hydroxyl groups can react with monomeric paraisocyanate, monomeric orthoisocyanate, polymeric paraisocyanate, or polymeric orthoisocyanate. All these reactions lead to the formation of the urethane prepolymer, which itself may react with the above-based isocyanate monomer or polymers, leading to allophonates. The term *monomeric* represents the most

Figure 1 Temperature effect on the reaction rate in PU synthesis.

reactive isocyanate group in the diisocyanate molecule (position 4). The term *Polymeric* refers to the remaining free isocyanate (position 2) after polymerization.

It has to be mentioned that upon adding an excess of TDI to Desmophen (hydroxyl-terminated polyester), the reaction occurs very readily to yield PU prepolymer with isocyanate terminated, as illustrated in Scheme 1.

Isocyanate-Terminated PU
The obtained PU prepolymer with fairly high reactive terminal isocyanate groups may react with NH groups belonging to the same molecular chain and/or with isocyanate groups belonging to adjacent urethane molecular chains to produce allophonate crosslinks, as shown in Scheme 2.

FTIR Spectroscopy

The above reactions are confirmed by FTIR spectroscopy and are shown in Figure 2(a). Figures 2(a) and (b) represent the IR spectra of synthesized PU prepolymer and a typical IR spectra[32] of a PU prepolymer based on polyester, respectively, for comparative purposes. When comparing the 2 spectra, a similar trend is observed, although a slight difference exists and might be attributed to the nature of ingredients involved in the synthesis of PU. A hidden doublet appearing, that is, a partially resolved peak at 3340–3420 cm^{-1}, is a characteristic of NH vibration belonging to urethane linkages. Both position and broadness of the peak (NH) are determined by strong intermolecular hydrogen-bonding interactions.

Furthermore, new peaks are detected in the PU prepolymer [Fig. 2(a)]. Since an excess of TDI has been used, it can be observed in the region of 1620–1595 cm^{-1}, a characteristic doublet associated with the absorption of TDI (aromatic ring

Scheme 2

modes). All the remaining peaks support the formation of new chemical bonds, particularly, the band at 1700 cm^{-1} associated with the carbonyl (COO) stretching mode of the urethane groups. The complex shape of the peaks observed in the

Scheme 1

Scheme 3

Figure 2 Infrared absorption spectrum of (a) synthesized PU (Desmophen 1200–TDI) and (b) a typical polyester-based PU

carboxyl region does not mean that more carboxyl species have been formed, but, in addition to this intermolecular hydrogen bonding, interactions have taken place, as shown in Scheme 3.

Thin-Layer Chromatography

Based on a comparison of experimental R_fs and theoretical ones, TLC results (Table III) led to the detection of the following chemicals: NCO (TDI),

as expected; 1,4-BD; adipic acid; and diethylene glycol (unexpected).

TLC results (Table III), together with those of FTIR spectroscopy and titration, further confirm the presence of NCO belonging to TDI; whereas 1,4-BD, adipic acid, and diethylene glycol are thought to be traces remaining after polyol synthesis. The presence of such species may significantly affect the quality of the PU

Table III   Frontal Ratio (R_F) of Species Existing or Resulting from the Synthesis of PU Prepolymer

Existing and/or Resulting Species	Eluant (Vol)	Experimental R_f	Theoretical R_f[a]
2.4 TDI	CHCl$_3$–MeOH (12 : 1)	0.27	0.27
1,4-Butane diol	Ether–MeOH (9 : 1)	0.65–0.68	0.67
Adipic acid	Isopropylether–formic acid–water (90 : 7 : 3)	0.60–0.63	0.62
Diethylene glycol	Ether–MeOH (9 : 1)	0.44	0.44

The R_f expresses the relative rate of movement of the solute and the solvent.
[a] Gasparic and Churacek.[28]

prepolymer as well as the properties of the modified epoxy.

MODIFICATION OF EPOXY WITH PU PREPOLYMER

FTIR Spectroscopy

Figure 3(a) illustrates the IR absorption spectrum of the pure (as-received) epoxy resin (GY260) for further comparison. Figure 3(b) represents the spectra of the reaction mixture epoxy–hardner (referred to as virgin resin). According to these spectra, there is evidence that epoxy reacts chemically with the hardner. The presence of an absorption peak at $\sim$ 3500 cm^{-1} is due to —OH stretching vibrations of the pure epoxy [Fig. 3(a)]. On adding the hardner, an increase in the OH peak intensity is observed [Fig. 3(b)]. It has to be mentioned that, initially, in the virgin resin (containing the hardner), the amount of epoxy resin is less than in the pure resin (without hardner) for steochiometric reasons; therefore, less OH groups are present, and, consequently, the OH intensity peak at 3500 cm^{-1} should be lower. The observed equal percentage of transmission when comparing spectra (a) and (b) comes from the fact that additional OH groups are formed. Such phenomenon might be related to the following factors: (1) the existence of OH groups inherent to the pure epoxy, (2) the reaction of each Eurdur polyfunc-

tional amine primary group with epoxy groups, and (3) the creation of hydrogen bonding between epoxy OH groups and the product obtained at stage (2).

An illustration of the above-mentioned reactions (2) is shown in Scheme 4.

In the case of the modification of the epoxy resin using the synthesized PU prepolymer, the epoxy group does not contribute in the PU grafting reaction. This is shown in Figure 4, which represents a superposition of the starting [curve (a)] and the ending [curve (b)] spectra of the PU–epoxy reaction. Only a slight change in the epoxy intensity peak is observed. This is thought to be due to the reaction of epoxy group with the NH$_2$ of the hardner. Moreover, the ratio of the intensity of the isocyanate peak (2270 cm^{-1}) to that of the epoxy (920 cm^{-1}) can be used as an indication of the degree of grafting between the isocyanate and the pendant hydroxyl groups within the epoxy resin. Figure 4 also shows that the intensity peaks ratio is high at the beginning of the grafting reaction; then as the reaction proceeds, it decreases until the pendant hydroxyl groups in the epoxy has completely reacted with isocyanate groups in the PU prepolymer, thus confirming that PU is grafted to the epoxy resin. Similar results have been reported previously.[22–24] The remaining isocyanate and epoxy groups in the system were further polymerized simultaneously to form graft IPNs.

Figure 5 represents the superposition of the starting [curve (a)] and ending [curve (b)] spectra of epoxy–PU reaction with a 4 : 1 ratio of the chain extender (1.4 BD) to a second crosslinking agent (TMP). A comparative study of the 2 curves reveals that the NCO peak, normally present at 2270 cm^{-1} in the PU prepolymer, has totally disappeared. This means that all isocyanates have been consumed. The following alternatives should be considered: the PU prepolymer isocyanate re-

Scheme 4

Figure 3 Infrared spectrum of (a) pure epoxy and (b) virgin epoxy.

acts with all OH groups belonging to the second crosslinking agent (TMP), to the chain extender (1,4-BD), to the epoxy, and to the first crosslinking agent (Eurdur). In addition, in such reactions, hydrogen bonding takes place. This is illustrated in Scheme 5.

However, despite the fact the OH group has undergone complete reaction, an increase in the IR intensity peak has been observed. This might be due to the reaction between the Eurdur NH and the epoxy, leading to OH formation. Furthermore, the remaining NH is detected in the same wavelength as OH stretching, resulting in a fairly broader peak.

It has also been observed that the peaks at $2500-500$ cm^{-1} (present in Fig. 4) tend to disappear, resulting in an end product with high crosslinking density, considerable entanglement, and expected improved mechanical properties.

The above observations lead to the conclusion that a complex graft polymer network has been formed.

Mechanical Properties

Figure 6 [curve (b)] represents the impact strength of the modified epoxy resin versus PU content. A sudden rise in impact strength is ob-

Figure 4 IR spectrum of epoxy–PU: (a) Start of the reaction; (b) end of the reaction.

served prior to levelling off. This might be related to the grafting reaction between the isocyanate terminated PU and the epoxy OH group and the reaction of this latter and the Eurdur amine group. In fact, 5 phr bring about a two-fold increase in the impact strength. This can be considered as a critical concentration beyond which no significant change is observed. Such a relatively low improvement in impact strength can be explained by the fact that the chain length remains constant; that is, the distance between crosslinks does not change.

Indeed, when the scission of PU chains takes place, the loading is supported by the epoxy resin network alone, even with grafting, particularly in the crack tip zone, which is characterized by a large plastic deformation. At this stage, an explanation connected to the interpenetration degree might exist. If the interpenetration between the 2 networks occurs at the molecular level, the early PU fracture does not improve the toughness. In this case, the modified epoxy network can be considered as unmodified with lower entanglement density.

Figure 7 [curve (b)] represents the K_c of epoxy resin versus PU content. A similar behavior to that of the impact strength [Fig. 6, curve (b)] has been observed. PU modified epoxy resin does not

Figure 5   IR spectrum of epoxy–PU (with 1,4-BD–TMP): (a) Start of the reaction; (b) end of the reaction.

seem to significantly affect the pure resin toughness.

In addition to the above arguments, the slight improvement observed in toughness (IS and K_c), as seen in Figures 6 [curve (b)] and 7 [curve (b)] might be related to the presence of a small amount of 1,4-BD according to TLC results (Table III). It has to be mentioned that 1,4-BD is known to be generally used as a chain extender. This latter is known to improve epoxy chain flexibility as well as its toughness.[2]

Figure 6 [curve (a)] represents the effect of PU content (with 4 : 1 ratio of 1,4 BD-to-TMP) on the

impact strength of epoxy resin cured with Eurdur. Upon addition of the PU prepolymer, the IS increases significantly until it reaches a maximum value of 22 J/m at a critical PU concentration (40 phr). This is probably due to the high crosslinking density obtained, on the one hand, and, on the other hand, to the fact that the chain length has been modified with the introduction of the chain extender; that is, the distance between knots increases, resulting in higher flexibility. This latter contributes to the improvement in toughness. These results are in accordance with IR spectra (Fig. 5) and the chemical reactions that

a/

b)

or → HO—CH2—CH2—CH2—CH2—OH

or → CH3—CH2—C(CH2OH)—CH2OH (with CH2OH above and CH2OH below)

or → R——NH2

c)

Scheme 5

led to a high crosslinking density, as discussed previously. This drastic improvement might be the result of the obtained complex graft IPN.[22–26,34]

Figure 7 [curve (a)] illustrates the critical stress intensity factor (K_c) versus PU content. K_c

Figure 6   Effect of PU content on the IS of the epoxy-based formulations.

increases significantly until it reaches a maximum value of 2.5 MPa m$^{1/2}$ compared to 0.9 MPa m$^{1/2}$ of the unmodified epoxy prior to levelling off. This confirms the IS results [Fig. 6, curve (a)], as well as previous findings.[35] The above arguments, distance between knots, flexibility, crosslinking

Figure 7   Effect of PU content on the critical stress intensity factor, K_c, on epoxy-based formulations.

Figure 8 SEM of fractured surfaces of epoxy–PU at (a) 40 phr (×400); (b) is a magnification of (a) (×1000).

density, and grafting can be used to explain this improvement in toughness. Another observation is that grafting seems to stabilize the morphology, to reduce phase separation, as indicated by the relative continuous increase in impact strength and K_c (Figs. 6 and 7).

Fractography

Figure 8 is an SEM micrograph of fractured surface of PU modified epoxy. Figure 8(b) is a magnification of Figure 8(a). A plastic deformation can be observed as well as the presence of elongated cavities. It seems that the PU phase has detached from the epoxy matrix. This is probably due to a poor adhesion between the 2 phases or to some sort of phase separation.[36]

Figure 9(a) and (b) are micrographs of fractured surfaces of 1,4-BD–TMP–PU-modified ep-

oxy samples. A homogeneous surface is clearly observed [Fig. 9(a)] with nondistinct phases (epoxy–PU). The white regions are indicative of plastic deformation. Figure 9(b) is a magnification of the previous fractured surface [Fig. 9(a)]. It reveals the presence of some cavities. These latters have been magnified and presented in Figure 9(c) and (d). Large and deep cavities (20–25 μm) are generally characteristic of rubber-modified epoxy resins [Fig. 9(c)]. These cavities represent the initial position of the rubber particles, which were pulled out or broken during the fracture process. In fact, these cavities are not empty but filled with the PU phase [Fig. 9(d)] and are firmly attached to the epoxy matrix, resulting in a good adhesion and a strong interface between the 2 phases. A mechanism, proposed by Kinloch et al.[37] and reported by Pearson and Yee[14] and which seems to fit relatively well with the results of the present study, suggests that the fracture resistance increases, arising from a great extent of energy-dissipating deformation occuring in the material in the vicinity of the crack tip. The resulting deformation processes are (1) cavitation in the rubber or at the particles–matrix interface, and (2) multiple, but localized, plastic shear yielding in the matrix, initiated by the rubber particles.

Indeed, this cavitation of the rubber particles is also strikingly apparent in the SEM micrographs, Figures 8(a) and 9(b)–(d), where the rubber particles appear as partially filled holes following the cavitation mechanism. The cavitated particles, in turn, relieve the plane strain constraints and thereby facilitate shear yielding. The most probable mechanism is based on internal cavitation of the rubber particles, followed by localized plastic shear yielding.

Such results explain the increase in the epoxy resin toughness. A further observation relates to the fact that most of the rubbery domains appear as circular cavities in the matrix; such a phenomenon can be explained assuming that, during the fracture process the particles break into 2 parts that remain bonded to the original sites. After failure, the split particles retract due to the vanishing of the triaxial tensile stress, and the surface particles lie below the fracture plan. This phenomenon has already been observed with rubber-modified epoxy systems.[13] An important finding as far as the present project is concerned relates to the fact that the PU behaves as a rubber in modifying epoxy resins.

Figure 9 SEM micrographs of fractured surfaces of epoxy–PU–(1,4-BD–TMP): (a) ×400; (b) is a magnification of (a) (×2000); (c) and (d) are magnifications of (b).

Another probable explanation may be related to the multiphase nature of IPN, which corresponds sometimes to a microstructure of well-dispersed PU particles [Fig. 9(b)]; hence, the stress concentration occuring in the epoxy network, after PU fracture, may reinforce toughening mechanisms. The simplest alternative approach is therefore to assume that the complete loss of phase continuity, with respect to the PU phase, is probably the reason behind the maximum IS and K_c values of 1,4-BD–TMP–PU-modified epoxy, as shown in Figures 6 and 7.[10,13,35]

CONCLUSIONS

The results obtained in the present study lead to the following conclusions. A PU prepolymer based on Desmophen 1200 was synthesised and used as a modifier at different concentrations within the epoxy resin. Further, to the IPN formation, the epoxy and the PU prepolymer reacted chemically (via grafting). Compared to virgin resin, the effect on the mechanical properties was minor. The impact strength varies from 3–9 J/m and K_c from 0.9–1.2 MPa m$^{1/2}$.

The incorporation of a chain extender with the PU prepolymer as modifiers into the mixture caused a drastic improvement in toughness. The impact strength increases continuously and reaches a maximum value (seven-fold that of virgin resin) at a modifier critical concentration (40 phr). K_c reaches 2.5 MPa m$^{1/2}$ compared to 0.9 MPa m$^{1/2}$ of the virgin resin.

The SEM analysis results suggest that internal cavitation of the modifier particles, followed by

localized plastic shear yielding, is probably the prevailing toughening mechanism for the epoxy resin being considered.

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