Epoxy/Castor Oil Graft Interpenetrating Polymer Networks

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ABSTRACT: Full-interpenetrating polymer networks (IPNs) were prepared from epoxy and castor oil-based polyurethane (PU), by the sequential mode of synthesis and were characterized by different techniques: swelling test, scanning electron microscopy (SEM), thermomechanical analysis (TMA), thermogravimetric analysis (TGA), tensile test, and instrumented impact test. 2,4-Toluene diisocyanate (TDI) was used as a curing agent for castor oil, at a NO/OH ratio = 1.50. Diglycidyl ether of bisphenol A (DGEBA) was cured and crosslinked using 2,4,6-tris(dimethylaminomethyl)phenol (TDMP) at 1.5%, by weight, of epoxy resin. The homogeneous morphology of IPN samples of PU compositions up to 40%, by weight, revealed by SEM may be attributed to some extent to grafting of the PU phase onto the epoxy matrix, which results from the reaction between NCO groups in the PU phase with OH groups in the epoxy matrix. This has some synergistic effect on the thermal resistance and tensile properties of IPNs compared to those of the pure components, such as illustrated by the data from TGA and tensile tests. However, the grafting structure appears not to enhance their impact resistance, which probably requires the formation of rubbery particles of suitable size. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1649–1659, 1998

Key words: graft interpenetrating polymer network; epoxy; castor oil; morphology; toughness

INTRODUCTION

Epoxy resins, which are associated with high modulus and strength, have been employed in high-performance structural composites. However, such resins suffer from low fracture strength and brittle behavior.[1] Therefore, applications are often limited by the low mechanical properties. To meet required end-use performance, epoxy resins must be modified with either thermoplastics,[2] conventional rubbers, or elastomers.[3] For example, the introduction of a reactive carboxyl-terminated butadiene acrylo-nitrile copolymer (CTBN) into epoxy has been commercialized to improve the toughness of the resin.[4–7] Only recently, interpenetrating polymer networks (IPNs) using a rubbery polyurethane (PU) phase have been considered for such applications.[8–11] IPNs are polymer alloys consisting of two or more polymers in a network form, held together by permanent entanglements with only occasional covalent bonds between the chains of the two different types of polymers. One of these polymers is synthesized and/or crosslinked in the immediate presence of the others.[7] IPNs can be prepared either sequentially or simultaneously. IPNs generally possess improved physical properties in comparison to normal polyblends of their components.

One of the natural polyols most useful for the synthesis of the PU phase in IPNs is castor oil due to its three reactive hydroxyl groups.[12–18] In our

previous work,[19,20] PUs prepared from castor oil showed high impact properties and a large synergistic effect in the mechanical properties of IPNs obtained from methyl methacrylate and castor oil. In this work, IPNs were prepared from epoxy resin and castor oil following a sequential method of synthesis, and their morphology and thermal and mechanical properties were determined.

EXPERIMENTAL

Materials

Diglycidyl ether of biphenol A (DGEBA), 2,4,6-tris(dimethylaminomethyl)phenol (TDMP), castor oil, and 2,4-toluene diisocyanate (TDI) were supplied by Aldrich Chemical, Inc (Milwaukee, WI). Castor oil and DGEBA were dried under a vacuum prior to use. The equivalent weight per hydroxyl group of castor oil is 373.2 g and that of TDI per NCO group is 87.0 g. These two values were used to calculate the NCO/OH ratio for the synthesis of the PU phase.

IPN Synthesis

A weighed amount of castor oil was placed in a round-bottomed flask, heated until 60°C, and thoroughly mixed with a predetermined amount of TDI, which corresponds to a fixed NCO/OH ratio of 1.50. The reaction system was stirred vigorously with a Teflon-coated magnetic stir bar, under a dry nitrogen atmosphere, for about 45 min to form a urethane prepolymer. Then, a predetermined amount of the epoxy precursor (DGEBA), corresponding to a given IPN composition, was added to the system which was stirred for a while before adding 1.5%, by weight, of TDMP (based on the amount of DGEBA). The mixture was degassed under a vacuum for some minutes and then poured and pressed into different preheated molds made from Teflon, according to the tensile dumbbell shape or impact disk shape. The filled molds were heated until 120°C and then the IPN samples were cured at that temperature for 6 h to allow completion of the polymerization in both phases. After curing, the molds were allowed to cool and the specimens were separated. IPN samples with different PU compositions were prepared.

Measurements

Swelling Test

A specimen of known weight of pure castor oil-based PU, cured epoxy, or graft IPN of 30% PU was cut from the corresponding samples and swollen in the dimethylformamide (DMF) solvent. The degree of swelling was measured by increase in the specimen weight after immersion for 15 days at room temperature.

Scanning Electron Microscopy (SEM)

Electron micrographs were taken on a JEOL JSMT100 scanning electron microscope operated at 25 kV. Samples were frozen under liquid nitrogen, then fractured and mounted on a stub. They were coated with gold (100 A) using a Edwards S150A sputter coater. Photographs were taken on Polaroid 52 film at a magnification of 5000×.

Thermomechanical Analysis (TMA)

The glass transition temperatures of cured epoxy, castor oil-based PU, and IPN samples were determined by TMA. This technique is based on the principle that there is an abrupt change in the coefficient of expansion of the sample when it passes through the softening temperature or T_g under constant heating. This manifests itself as that temperature at which the regression line before the break intersects that after the break. TMA was performed using a Mettler TA-4000 with a TMA 40 measuring cell linked to a TA 11 processor. Approximate sample dimensions were 3 mm thick in the direction of measurement and 6 mm in diameter. Measurements were carried out in the range of −60 to 200°C at 15°C min^{-1}, and a constant probe force of 0.02 N was applied to the sample.

Thermogravimetric Analysis (TGA)

TGA thermograms were obtained on a Universal V1.6I TA Instruments equipment, under a nitrogen atmosphere at a heating rate of 10°C min^{-1}, and scanned from 25 to 550°C. The samples were cut in the shape of thin discs. The samples ranged between 8 and 12 mg in weight and were placed in platinum sample pans under a continuous nitrogen flow of 200 mL min^{-1}.

Tensile Test

Tensile tests were performed on an Instron tensile tester, Model 4206, at room temperature. The samples were cast in a dumbbell shape, 10 mm in width, 3.0 mm in thickness, and 25 mm in gauge length. The ASTM D638 procedure was followed

using a crosshead velocity of 5 mm min^{-1}. The ultimate tensile strength, elongation at break, Young's modulus, and tensile toughness (integration of the area under the stress–strain curve) were instantaneously determined using a computer.

Impact Test

Impact testing was performed using a Rheometrics drop weight tester (RDT-5000). A high-speed dart weighing 3.73 kg was employed. A probe with a hemispherical end, 12.7 mm in diameter, was used. A force-sensing load cell in the dart had a full range of 1134 kg. The impact test specimens were cast in a disk shape, 37.0 mm in diameter and 3.0 mm thick. The disk specimens were held in place on an annular stainless-steel ring with an internal diameter of 25.2 mm (1 in.). The impact drop velocity was set at 7.6 m s^{-1}. The impact force-displacement trace was recorded to determine the impact energy of the specimens.
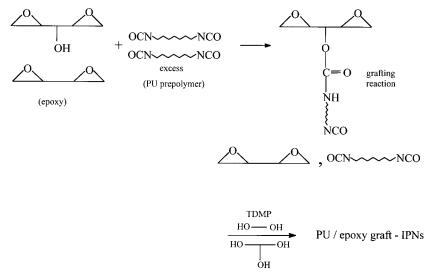
RESULTS AND DISCUSSION

Swelling Degree

The swelling test provided the swelling degree of 0.75 (or 75%), 0.33, and 0.42 for PU, cured expoxy and the IPN sample, respectively. It is known that the swelling degree is a direct measure of the crosslink density of a network. The relatively low swelling degree of cured epoxy may be attributed mainly to the small amount of the crosslink agent (TDMP) used. This low crosslink density, consequently, explains the fact that the tensile strength and the modulus of cured epoxy have relatively low values, as presented in Figures 5 and 7, respectively. However, the low crosslink density of the cured epoxy could have facilitated the molecular entanglement between the two networks forming an IPN system.[21]

Morphology and Graft IPN Mechanism

It has been shown[3,7,22] that the morphology of IPN systems, at a given composition, is controlled by the chemical miscibility of the two components, interfacial tension, and crosslink densities. This last factor is, in turn, ultimately related to the percent of crosslinker used as well as the method of synthesis. Usually, IPN materials have a two-phase morphology where the size of the

phase domains decreases with increasing crosslink density. In the case of the studied epoxy/castor oil-based IPNs, it was experimentally observed that mixtures of uncured epoxy resin with castor oil in the low concentration range of the latter are completely miscible, at the working temperature, forming clear solutions. This miscibility may be attributed to strong intermolecular interactions established between molecules of the two uncured components via their hydroxyl groups or the epoxide groups of the epoxy. Similar strong interactions were also observed in the uncured epoxy/n-butyl acrylate system.[21] Such a good miscibility between the two uncured components should eventually have a positive effect on the interpenetration (or entanglement) between their resulting cured networks. Indeed, the SEM micrographs obtained from epoxy/castor oil-based IPN samples of compositions of 80/20, 70/30, and 60/40 in weight of epoxy/PU (figures not shown) likely indicate one continuous phase morphology without manifest dispersed microdomains. However, this apparent homogeneous morphology should be regarded as a consequence of another much more important cause, that is, the chemical process of grafting between epoxy and PU. The grafting reactions are believed to occur in the following way (Fig. 1) according to ref. 23: As the epoxy resin is mixed with the PU prepolymer phase, the excess of NCO groups in the PU phase could react with the OH groups in the epoxy resin to create the grafting and then TDMP performs the curing of the epoxy resin according to the general mechanism.[1] The amino group of TDMP then approaches one of the carbon atoms of the epoxide rings and attaches itself to create an alkoxide ion, and this ion allows the chain-reaction process to continue. TDMP is an aromatic substituted derivative of trimethylamine. The former has an increased reactivity and yields a stronger cured epoxy with respect to the latter due to the accelerating action of the phenolic hydroxyl and the presence of the aromatic ring.[1] In a recent work, Hsieh and Han[8] used infrared analysis to check the grafting reaction between PU and epoxy. This method was based on the fact that the intensity of the IR absorption of the epoxide group (920 cm^{-1}) should not change during the grafting reaction while that of the isocyanate group (2270 cm^{-1}) would change. Thus, the intensity ratio of those two absorption peaks was successfully used as an indication of the progress of grafting. Effectively, this intensity ratio de-

Figure 1 Scheme of the grafting process between epoxy and PU prepolymer, according to ref. 23.

creased until a minimum value corresponding to the end of the grafting reaction.

There is another distinctiveness of castor oil being used as a polyol for the formation of the PU network: the presence of the third OH group on each molecule. This hydroxyl group may remain unreacted during the first stage of the PU formation. Therefore, it could later participate in the curing process of DGEBA by exactly the same mechanism as that played by the pendant OH group of the latter[1] for the opening of the epoxide ring. Consequently, the grafting reaction could occur in two ways.[24]
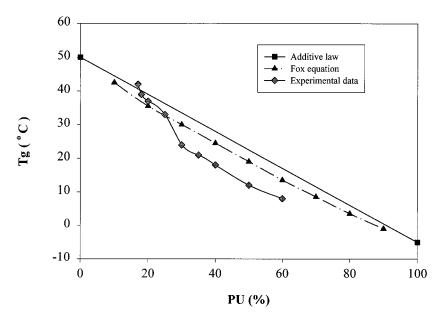
Overall, the observed morphology of epoxy/castor oil graft IPNs results from two successive processes: the grafting of epoxy on the PU network and then the interpenetration of the remaining cured epoxy network and the former. The effect of one or the other process on the morphology of the resulting IPN may become dominant depending upon the experimental conditions of the synthesis, in particular, the PU percent, the chemical compositions of both constituents (the NCO/OH ratio of PU, as well as the TDMP/DGEBA ratio in the case of epoxy), the timing in the sequential method of synthesis, and the curing temperatures. All these factors would affect the sequence of the gelation of the two networks and possibly the phase separation of the mixture. This sequence is very important in determining the morphology of the sample.[21]

Glass Transition Temperatures

The glass transition temperatures (T_g) of epoxy/castor oil graft IPNs were measured by TMA and are reported in Figure 2 as a function of the PU percent. The value of T_g was taken at the intercept between the regression line and the inflectional tangent line from the curve of the linear expansion coefficient as a function of temperature. Only one T_g was observed for each graft IPN sample. There might be a second T_g belonging to a second minor phase but it could not be detected because of a short gap between the two glass transition temperatures of the pure components. This apparent one-phase behavior, which may be essentially regarded as a consequence of the grafting of epoxy on the PU prepolymer, is in good agreement with the homogeneous morphology revealed by the SEM micrographs, as discussed above. If the studied graft IPNs are considered as miscible polymer blends, their T_g values can be predicted by the Fox equation[25,26]:

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \qquad (1)$$

where T_{gi} is the glass transition temperature of the pure blend component and W_i is its weight fraction. The broken line in Figure 2 represents the calculated T_g according to the Fox equation. However, there is a negative deviation between the experimental and calculated T_g's when the
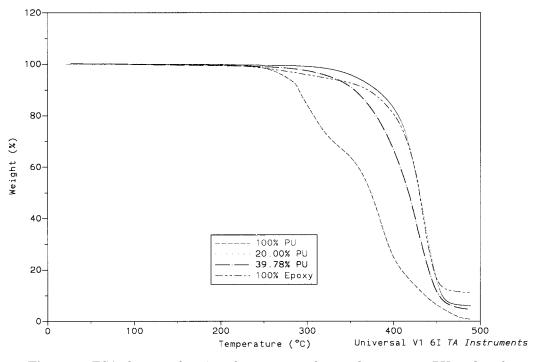
Figure 2   Glass transition temperature, T_g, of graft IPNs as a function of PU composition: (solid line) experimental data; (broken line) Fox equation.

PU percent increased significantly above 25%. This could be explained by the fact that the increasing amount the PU prepolymer, with its corresponding excess of NCO groups, might have increased the grafting degree between the two components and, at the same time, created a diluting effect which might have slowed down the curing rate of the epoxy and eventually reduced its maximum conversion.[21] As a consequence, the graft IPNs with higher PU percent should be preferentially dominated by the rubbery character of PU, which lowered their T_g with respect to the calculated values. On the reverse side, when the PU content decreased below 30%, there is an abrupt increase of T_g. The narrow composition window between 25 and 30% PU may correspond to a phase-inversion area where the morphology of the IPN samples consisted of a dual-phase continuity[26] with the graft epoxy/PU phase being in equilibrium with that of the ungrafted epoxy network. For the samples containing less than 25% PU, their properties become more and more dominated by the rigid character of the epoxy network which provided higher values of T_g than those calculated by the Fox equation.

Thermal Degradation Pattern

The integral results from the TGA are shown in Figure 3, while the differential thermogravimet-ric data (DTG) are reported in Figure 4, for the cured epoxy, pure PU, and two graft IPN samples. The data presented in Figure 4 were deduced from Figure 3 by means of the derivation of the weight loss percent with respect to temperature, where the peaks in each trace correspond to the inflection points of its TGA curve. Each peak represents the temperature where the degradation rate is maximum for each degradation stage in the whole process. It is found that the degradation of cured epoxy is a two-stage process: a relatively short stage with a very small percent of weight loss beginning at about 250°C, attributed to the breaking of unreacted TDMP molecules or other impurity traces apart from the cured epoxy, followed by a much higher thermal-resistant stage, characteristic of cured epoxy, starting at about 350°C. This major stage is attributed to the thermal degradation of the cured epoxy network. Meanwhile, the thermal degradation pattern of castor oil/TDI-based PU is clearly inferior to that of cured epoxy. It consists of a two-stage degradation: an early stage starting at around 250°C with a maximum rate at about 290°C, assigned to the urethane bond breaking. This stage corresponds to about a 30% weight loss, which is approximately the amount of TDI incorporated into the PU sample. The second stage begins at around 350°C, assigned to the thermal degradation of the
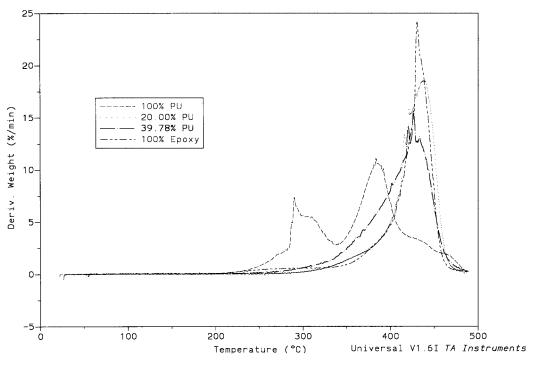
Figure 3 TGA plots as a function of temperature for cured epoxy, pure PU, and graft IPNs of 80/20 and 60/40 in epoxy/PU, respectively.

castor oil molecules where the maximum rate is at 375°C. The overall superiority in the thermal degradation pattern of cured epoxy compared to that of PU, particularly during the first degradation stage, is likely related to the much higher chemical stability of both DGEBA and TDMP molecules with respect to the castor oil and TDI molecules. DGEBA contains many aromatic rings while castor oil consists of only aliphatic elements.

With regard to the degradation pattern of the epoxy/PU graft IPN sample of 80/20 composition, it behaves nearly like a single-step degradation which starts at a temperature even higher than that of cured epoxy. This synergistically improved heat resistance of the IPN sample with respect to the cured epoxy is probably attributed to the following factor, as already discussed above: a good interpenetration between the two networks added to some extent by the grafting between them. A possible alternate explanation about this synergistic thermal effect is that one polymer absorbs free radicals generated by the other polymer; as a consequence, both polymers create a mutual protection against the thermal degradation process.

The degradation curve of the IPN sample of 60/40 of epoxy/PU is, as expected, of a lower temperature range than that of the cured epoxy, but it remains well above that of pure PU, because of the presence of epoxy as the major phase in the whole sample.

Tensile Properties

It has been known that the mechanical properties of polymer materials with IPNs are superior to those of ordinary polymers.[27,28] In particular, the maximum tensile strength of IPNs is much higher than that of the constituent polymers due to an increase of the crosslinking density in IPNs.[21,29] In the cases of graft IPNs prepared from the DGEBA epoxy resin and poly(butylene adipate) or polyoxypropylene,[8] the maximum tensile strength occurred at PU/epoxy ratios between 19/81 and 27/73. In some cases, the maximum values are much higher than those obtained for systems without a grafting reaction. This improvement in tensile strength could probably result from the increased degree of interpenetration as a consequence of the graft structure.[8] In this work, the tensile strength, elongation

Figure 4 DTG plots as a function of temperature for cured epoxy, pure PU, and graft IPNs of 80/20 and 60/40 in epoxy/PU, respectively.

at break, and Young's modulus of graft IPNs from epoxy/castor oil are illustrated on Figures 5–7, respectively, as functions of PU percent. Similarly to the results cited above,[8] the tensile strengths of graft IPNs are quite superior to that of cured epoxy and they pass through a maximum at around 20% PU, then drastically drop beyond 30% PU. Meanwhile, the elongations at break also seem to reach a minimum value at around 20% PU before beginning to increase with higher PU percents. The
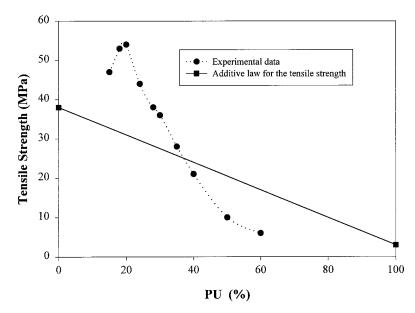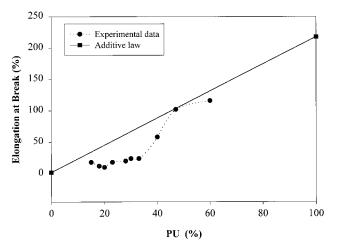

Figure 5 Tensile strength of graft IPNs as a function of PU composition.

Figure 6   Elongation at break of graft IPNs as a function of PU composition.

Young's modulus of graft IPNs is much lower than that of pure cured epoxy, and again it undergoes a steep drop for PU compositions higher than 30%. According to the glass transition temperature pattern presented in Figure 2, it is suggested that a dual-phase continuity could exist between the 20 and 30% PU composition range. The effect of the composition on the modulus in such dual-phase systems was treated by Davies:[26,30,31]

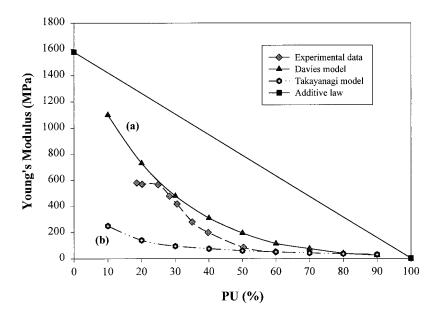$$E^{1/5} = v_1 E_1^{1/5} + v_2 E_2^{1/5} \qquad (2)$$

where E, E_1, and E_2 are the composite modulus and the moduli of phase 1 and phase 2, respectively, and v_1 and v_2 represent the volume fractions of phases 1 and 2, respectively. The calculated E is represented as curve (a) in Figure 7. There is good agreement with the experimental data within the composition range of 20–30% PU, while a discrepancy between the calculated and experimental moduli in other composition areas may be attributed to the effect of some degree of grafting between the two components of the IPN systems, which caused a drop in their modulus. For the purpose of comparison, the Takayanagi series model corresponds to the case in which the softer component (PU) is continuous and the stiffer component (epoxy) is dispersed[26,32]

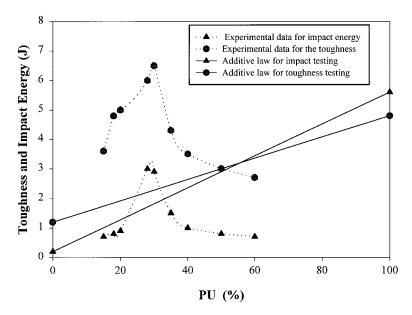$$E = \{(\theta_1/E_1) + [(1 - \theta_1)/E_2]\}^{-1} \qquad (3)$$

where θ_1 is a function of the volume fraction of the PU phase. The calculated E using eq. (3) is shown by curve (b) in Figure 7. As expected, a very large deviation from the experimental data is observed up to 50% PU. This lends support to the above observation that the studied IPNs might not contain rigid microdomains dispersed in a rubbery continuous phase.

Toughness and Impact Energy

The tensile (ductile) toughness, or energy to break, of graft IPNs was obtained from the inte-

Figure 7   Young's modulus of graft IPNs as a function of PU composition: (a) Davies model; (b) Takayanagi series model.

Figure 8 Tensile (or ductile) toughness (●) and impact energy (▲) of graft IPNs as a function of PU composition.

gration under their tensile stress–strain curves until the break point. The results are presented in Figure 8 as a function of PU percent. The ductile toughness increases with increasing PU percent and reaches a maximum value at around 30% PU, then steeply falls with higher PU compositions. This large toughening effect is likely due to a dissolution of the PU phase into the epoxy network resulting from some grafting degree within the mentioned concentration range. The usual methods for toughening thermosetting resins (i.e., epoxy) are in many aspects similar to that applied for thermoplastics (i.e., polystyrene)[33] consisting of incorporating dispersed rubber particles into the continuous resin phase, provided that the rubber content is kept below the critical level for the system, usually about 15–20%. However, this critical level seems to be shifted to about 25–30% for the epoxy/castor oil graft IPNs, which is similar to that observed for similar systems.[8,9] This difference may be first attributed to the contribution of some grafting degree which makes the IPN morphology much more homogeneous, and, second, the castor oil-based PU prepared using TDI behaves like a hard rubbery material with a T_g about −4°C. The key property of rubber-toughened materials is their enhanced ability to reach relatively high strains before fracture.[34] They absorb considerably more energy in a tensile test because of their higher extension to

break, which can be achieved only as a result of yielding in the matrix. The rubber particles play a second part, since they must conform to the deformation in the material surrounding them. Nevertheless, their role is a vital one because they mainly accelerate, yielding by acting as stress concentrators, initiating deformation in the matrix. In the case of graft IPN systems, even though the rubbery PU particles did not form because of the grafting process, the PU phase which probably existed as a dual-phase continuity with the epoxy network continued to act in the same manner as that of stress concentrators. This is in agreement with the observation that the rubber particle size has no significant effect on the toughness of the epoxy resins.[34,35] This likely explains the large synergistic effect on the tensile toughness of epoxy/castor oil-grafted IPNs, within the 25–30% PU composition range.

The impact strength of plastic materials is usually characterized by the total impact energy, U_t, which in the case of instrumented impact testing is measured by the area under the force-displacement curve.[19] Data on the total impact energy of graft IPNs are reported together with those of tensile toughness in Figure 8. In contrast to the tensile toughness, the total impact energies are below the values calculated from the additive law, except those corresponding to a narrow composition window of 25–30% PU, where the total im-

pact energy is a little higher than the calculated value. This composition window also corresponds to an abrupt change in the glass transition temperature as found in Figure 2, where the dual-phase continuity is believed to determine the morphology of the graft IPNs. It is then reasonable to suggest that the dual-phase continuity should have a strong positive effect on the tensile properties of graft IPNs, but not much on their impact strength. According to the data on the Izod impact tests performed on the graft IPNs based on epoxy/polyoxypropylene or poly(butylene adipate),[8,9] the grafting structure combined with the good miscibility, which led to a homogeneous morphology of the IPNs, enhanced only their impact strength but not their fracture energy since the latter seemed to increase with the rubber particle formation. In addition, these effects are compounded as they depend upon many factors such as the miscibility between the epoxy and polyol used, the molecular weight of the polyol, and the degree of grafting.

CONCLUSIONS

Graft IPNs prepared from DGEBA cured with 1.5% TDMP and castor oil cured with TDI at NCO/OH = 1.50, following a sequential method, exhibited a homogeneous morphology within the composition range up to 30% by weight of the PU phase. This resulted from a high compatibility between the epoxy resin and castor oil, leading to a good interpenetration between the two networks and some degree of grafting between the two phases. As a consequence, graft IPNs of 20% PU provided better heat resistance than that of cured epoxy as well as large synergistic effects on the tensile properties. The tensile toughness of graft IPNs was found to be greatly superior to those predicted by the additive law. This toughening may be attributed to the formation of a dual-phase continuity between the epoxy network and the graft epoxy/PU. However, their impact energy obtained from instrumented impact testing did not show much enhancement except for a narrow PU composition gap between 25 and 30%. The impact-resistance enhancement might require some formation of rubber particles of suitable dimensions.

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