

Epoxy-Toughened, Unsaturated Polyester Interpenetrating Networks

Z. G. SHAKER, R. M. BROWNE, H. A. STRETZ, P. E. CASSIDY, M. T. BLANDA

Institute for Environmental and Industrial Science and Department of Chemistry and Biochemistry, Southwest Texas State University, San Marcos, Texas 78666

Received 2 May 2000; accepted 21 May 2001

ABSTRACT: A series of translucent interpenetrating polymer networks (IPNs) made of a reactive elastomer [linear (D) and branched (T) with varying molecular weights] (Jeffamine™), a commercially available epoxy (D.E.R. 331), and an unsaturated polyester (15:85 wt %) were prepared. DSC data indicated complete cure after 8 h at 90°C. DMTA data showed a single glass-transition temperature (T_g) for all elastomer-containing IPNs, an indication of homogeneity. As expected, all IPNs showed a decrease in T_g with incorporation of elastomer, from 16 to 114°C or lower, the largest decrease being with T-5000. Izod impact strengths were increased by 28–44%, but with no apparent pattern among structure and molecular weight variations. In several cases the standard deviation of impact data increased significantly. Flexural data were measured using a three-point bend test. The highest flexural modulus obtained was that which incorporated linear D-2000 with a decrease of only 22% upon incorporation of the elastomer, whereas other compositions dropped up to 55% in flexural modulus. The strongest material obtained was that using D-2000 with a flexural strength increase of 65% upon incorporation of the elastomer. Two of the three branched elastomer components showed flexural strength increases of about 53%, but one was only equal to the base polyester resin. TGA data were recorded for all IPNs and values compared well to that of the pure polyester resin, with the exception of T-403, which showed a 20°C decrease, and D-2000 with a 10°C decrease. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2283–2286, 2002

Key words: interpenetrating polymer network; Jeffamine; polyesters; rubber-toughened plastics

INTRODUCTION

Interpenetrating polymer networks (IPNs) are a combination of two or more network polymers synthesized in juxtaposition.¹ An alternative definition is offered by Kim²: IPN is a mixture of two or more crosslinked polymers with a physically

interlocked network structure between the component polymers. IPNs are thermosets that are characterized by thermal stability and chemical resistance.

Several types of rubber-toughened materials have been prepared from unsaturated polyesters (UPE) to improve their physicomechanical properties.^{2–4} For example, polyurethanes (PU) have long been used as an elastomeric component to toughen polyesters (and vice versa). A fourfold improvement in impact strength for 80/20 (w/w) UPE/PU composition has been reported² as has a twofold increase in fracture toughness.³

Correspondence to: M. T. Blanda (mb29@swt.edu).

Contract grant sponsor: U.S. Environmental Protection Agency.

Journal of Applied Polymer Science, Vol. 84, 2283–2286 (2002)
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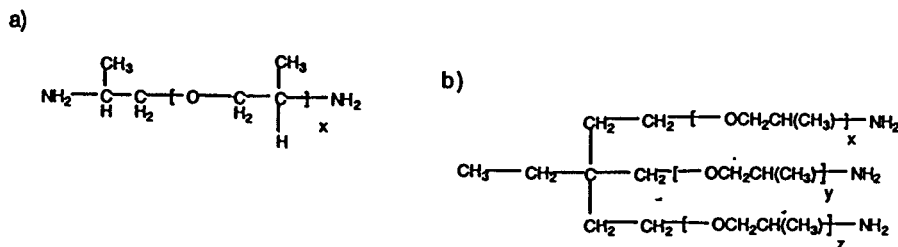


Figure 1 Typical structural formula for (a) linear (D-series) reactive, amine-terminated elastomer (D-2000, $x = 33.1$); and (b) a branched (T-series) reactive, amine-terminated elastomer (T-401, $x + y + z = 5.3$).

Based on the previous strategies, therefore, to improve the toughness, a desirable polyester system would have good stiffness and chemical resistance while retaining a higher impact resistance. The incorporated rubbery phase ideally would be a separate, dispersed component in the polymer with the UPE as the continuous phase. If achieved, the toughness of the UPE is improved without significantly sacrificing the overall mechanical properties of the material, such as stiffness or ultimate strength. An elastomer-modified unsaturated polymer would, therefore, be comprised of an unsaturated polyester and a low molecular weight elastomer. However, keeping the elastomer composition below 20% of the composition is critical with respect to phase separation^{3,5} and subsequent beneficial effects on properties. The degree of toughening is strongly dependent on the phase-separated morphology; therefore, a fine dispersion of elastomer is desired in the UPE matrix. Further, adhesion between the matrix and dispersion is a major factor in producing rubber-toughened plastic.²

The elastomer components used in these studies were the derivatives of linear and branched Jeffamines™, which are oligomers containing ether links and terminated by primary amine groups (see Fig. 1).

As shown in Figure 1, the first letter of the Jeffamine name designates whether linear (D) or branched (T) structures are present, whereas the number is an indication of molecular weight. For the purposes of this study we examined four Jeffamines™: D-2000, T-403, T-509, and T-5000. The elastomer component was made up of the reactive rubber (Jeffamines™) added to an epoxy resin (D.E.R. 331).

EXPERIMENTAL

The styrene-containing (40–65%) unsaturated polyester resin was obtained from Reichhold, Inc.

(Research Triangle Park, NC). Benzoyl peroxide was used as received from Aldrich (Milwaukee, WI). The epoxy resin used was D.E.R. bisphenol A-type liquid resin (Dow, Midland, MI) with an epoxy equivalent weight (EEW) of 182–193. Jeffamines were obtained from Huntsman Chemical (Austin, TX) and were used as received: D-2000, T-403, XJT-509, and T-5000 (MW range 400–5000). All elastomer/UPE mixtures were 15/85 (percentage w/w) in composition. Ultra 2 Yellow Label Universal Mold release (Price-Driscoll Corp.) was used in fabrication of IPN molds.

Thermal gravimetric analysis (TGA) data were collected on a Rheometric Scientific TGA at a heating rate of 20°C/min (5-mg samples). Dynamic mechanical thermal analysis (DMTA) data were collected with single cantilever bending mode at a temperature range of –150 to 250°C, 0.01%, 1 Hz, at 5°C/min. A second DMTA was reported, obtained in compression mode, 1 Hz, 0.05%, at 5°C/min. All elastomer/epoxy compositions were cured at 90°C for 8 h and allowed to sit at room temperature for 3 days. Three-point bend samples were prepared according to ASTM standard D 790-97 (3 in. long, 0.5 in. wide, and $\frac{1}{8}$ in. thick). The toughness was measured on an Izod Notch TMI Monitor/Impact instrument with samples prepared according to ASTM standard D 256-92 (2.5 in. long, 0.5 in. wide).

Preparation of Polyester Component

The UPE resin (225 g) was poured into a 600-mL beaker and 3.94 g of benzoyl peroxide (1.75%) was added. The polyester was transferred to a 500-mL round-bottom flask and was mixed/degassed for 1 h on a rotary evaporator at 35–40°C.

Preparation of Elastomer-Cured Epoxy Component

Jeffamine D-2000 (33.12 g) was poured into a 400-mL beaker to which 11.92 g of epoxy resin

Table I IPN Properties

Composition	Thermal Properties			Mechanical Properties			
	TGA (°C) ^a		T_g^c (°C)	Impact Strength (ft. lb./in.)	Flexural Strength (psi)	Flexural Modulus (psi)	Tan δ
	N ₂ ^b	Air					
PE	402	381	197	18 ± 1.8	5570 ± 1175	458 ± 38	0.133 ± 0.002
D-2000	393	389	181	25 ± 6.4	9190 ± 2500	360 ± 10	0.123 ± 0.002
T-403	382	363	165	23 ± 4.6	8510 ± 600	289 ± 20	0.131 ± 0.002
T-509	402	382	168	26 ± 2.2	5620 ± 1020	206 ± 10	0.121 ± 0.002
T-5000	404	383	83	24 ± 6.4	8590 ± 1720	324 ± 12	0.127 ± 0.005

^a Temperature of 10% weight loss.

^b Char yields ranged from 3 to 7%.

^c By DMTA.

was added. The contents were mixed well by hand until a homogeneous mixture was obtained.

Three other elastomeric compositions were prepared by blending with 11.92 g of epoxy as follows: 5.2 g of T-403, or 34.2 g of T-509, or 61.9 g of T-5000.

Preparation of IPNs: General Procedure

All IPNs were 15/85 w/w elastomer-cured epoxy/ UPE in composition and were prepared as follows: 37.5 g of the D-2000/epoxy component was poured into a 600-mL beaker containing 212.5 g of the polyester component. The solution was mixed well and transferred to a 500-mL round-bottom flask and degassed on a rotary evaporator for 3 to 3.5 h at 35°C. The degassing was critical to avoid cracking as well as to avoid bubbles in the final cast. Both sides of the mold were sprayed with mold release. The mold was set upright, the JO/ UPE mixture was poured in, and it was placed in a preheated oven (90°C) and allowed to cure for 8 h. The mold was allowed to cool in the oven before disassembling. DSC data indicated a full cure was achieved.

RESULTS AND DISCUSSION

The best notched Izod toughness values were obtained for T-509-containing IPN, a 45% increase compared to that of the base polyester resin. The lower standard deviation ($\pm 8\%$) is, perhaps, indicative of an overall more homogeneous system than that of other compositions (Table I). These impact data, more than any other types of data, show that the T-509 material gives the most reli-

able composition with regard to homogeneity and consistency/reproducibility.

The increase in toughness compares well with the range of toughness values provided by the literature,^{2,3} and though it is tempting to draw a comparison with the literature values, the type of elastomer used and the method of toughness measurement used make such comparison limited.

All IPNs showed a single T_g with a peak width comparable to that of the pure polyester, indicating good compatibility of the IPN components. All blends showed a lower T_g from the base PE, as anticipated, by some 15–30°C for most. However, the T-5000 composition lowered T_g by 104°C from that of the base resin, an indication that this high molecular weight additive was extremely effective in lowering T_g . However, it is important to note that other properties for the T-5000 are not that dissimilar from other compositions. So, if only a lower T_g is desired, this component would be an attractive option.

Flexural results (Table I) showed T-509 to be lowered by 22% in modulus when compared to that of the pure polyester, although its flexural strength compared well with that of the pure polyester resin. This material had the highest flexural modulus of any other composition, all others being up to 55% lower than that of the base PE.

TGA data (Table I) for all IPNs compared well with the UPE thermal stability value in air and nitrogen. The notable exception was that of T-403, which was lower in thermal stability by 20°C under nitrogen. T-403 was lower by 10°C in air, which is barely significant. All stability data by TGA in air were essentially identical (382–

389°C), with the exception again of T-403 at 363°C. Clearly, T-403 has a structure that detracts from thermal stability.

CONCLUSIONS

A series of translucent, compatible IPNs were prepared using an elastomeric amine-cured epoxy as the toughening component in an unsaturated polyester. The best toughness results were for that of T-509 IPN (MW 3000, tribranched Jeffamine™). A 45% toughness increase for T-509 was recorded through the notched Izod test with the lowest standard deviation. This perhaps is a reflection of a more compatible IPN with better homogeneous distribution of the rubber component, which improves the overall toughness of the material. T_g values had a single peak with narrow width by DMTA, which compared well with the unsaturated polyester neat peak showing good compatibility of IPNs. The highest modulus (flexural) material obtained was that of the linear D-2000, which was also the strongest material in flexure.

The authors appreciate Richard Thomas for technical assistance with DMTA data; Dr. Ed Neih of Huntsman Chemical Company for guidance and materials; Aicha Dekar for sample preparation; and Drs. Joseph Koo, Sreenivasulu Venumbaka, and John W. Fitch III for their consultation, advice, and support. Special thanks go to Dr. Venumbaka for his work on this paper and presentation of data. Gratitude is also due to the Waste Minimization and Management Research Center at Southwest Texas State University for providing funding via a grant from the U.S. Environmental Protection Agency.

REFERENCES

1. Klempner, D.; Sperling, L. H.; Utracki, L. A. *Interpenetrating Polymer Networks*, Division of Polymeric Materials: Science and Engineering, ACS, 202nd National Meeting of the American Chemical Society, New York, NY, August 25–30, 1999.
2. Kim, S. C. *Trans Mater Res Soc Jpn* 1994, 15A, 215.
3. Kim, D. S.; Cho, K.; An, J. H.; Park, C. E. *J Mater Sci* 1994, 29, 1854.
4. Ma, C. C. M.; Gong, Y. G.; Chen, C. H. *Ann Tech Conf Soc Plast Eng* 1992, 1, 1484.
5. McGarry, F. J.; Subramanian, R. J. *Adv Mater* 1996, 252, 133.