

Toughening of Epoxy Resins by Hydroxy-Terminated, Silicon-Modified Polyurethane Oligomers

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ABSTRACT: Epoxy resins are among the most versatile engineering structural materials. A wide variety of epoxy resins are commercially available, but most are brittle. Several approaches have been used to improve the toughness of epoxy resins, including the addition of fillers, rubber particles, thermoplastics, and their hybrids, as well as interpenetrating polymer networks (IPNs) of acrylic, polyurethane, and flexibilizers such as polyols. This last approach has not received much attention; none of them have been able to suitably increase resin toughness without sacrificing tensile properties. Therefore, in an attempt to fill this gap, we experimented with newly synthesized hydroxy-terminated silicon-modified polyurethane (SiMPU) oligomers as toughening agents for epoxy resins. SiMPU oligomers were synthesized from dimethyl dichlorosilane, poly(ethylene glycol) (weight-average molecular weight ~ 200), and toluene 2,4-diisocyanate and characterized with IR, $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$, and gel permeation chromatography. The synthe-

sized SiMPU oligomers, with different concentrations, formed IPNs within the epoxy resins (diglycidyl ether of bisphenol A). The resultant IPN products were cured with diaminodiphenyl sulfone, diaminodiphenyl ether, and a Ciba-Geigy hardener under various curing conditions. Various mechanical properties, including the lap-shear, peel, and impact strength, were evaluated. The results showed that 15 phr SiMPU led to better impact strength of epoxy resins than the others without the deterioration of the tensile properties. The impact strength increased continuously and reached a maximum value (five times greater than that of the virgin resin) at a critical modifier concentration (20 phr). The critical stress intensity factor reached $3.0 \text{ MPa m}^{1/2}$ (it was only $0.95 \text{ MPa m}^{1/2}$ for the virgin resin). © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1497–1506, 2003

Key words: toughness; polyurethanes; NMR; gel permeation chromatography (GPC); curing of polymers

INTRODUCTION

Cured epoxy resins are known to exhibit good engineering properties, such as high stiffness, strong creep resistance, and chemical resistance. Like most thermoset plastics, however, they are intrinsically brittle.

For the alleviation of this problem, epoxy resins are frequently modified by being dissolved in a small proportion (10–20%) of a liquid rubber containing reactive end groups such as carboxy-terminated acrylonitrile copolymer (CTBN)¹ and amine-terminated butadiene acrylonitrile copolymer (ATBN).² Although CTBN and ATBN oligomers are very efficient for improving the fracture properties of epoxy resins without sacrificing modulus and strength, the presence of high-level unsaturation in their structures provides sites for degradation reactions.

To avoid deterioration in the inherent stiffness and strength and a reduction in the glass-transition temperature of the resin, some engineering plastics, such as poly(ether sulfone) (PES)³ and poly(ether imide),^{4,5}

have been used to produce systems containing rigid, ductile particles dispersed in the epoxy matrix.

Kim and Robertson⁶ studied the toughening of an aromatic amine cured diglycidyl ether of bisphenol A (DGEBA) epoxy with particles of crystalline polymers, such as poly(vinylidene fluoride) (PVDF), poly(butylene terephthalate) (PBT), and nylon 6. The authors reported that nylon 6 and PVDF toughened epoxy resins to an extent similar to that of CTBN. The fracture toughness, however, was increased twofold by the inclusion of PBT over that achieved with nylon 6 and PVDF.

Kubotera and Yee⁷ reported that both poly(ether ether ketone) (PEEK) and PBT could form crystals in the form of triblock copolymers with amorphous PES. The most effective modifier for increasing toughness appeared to be the triblock PEEK–PES–PEEK system, which gave an almost single-phase structure.

Banthia et al.⁸ used various carboxyl-terminated elastomeric acrylate oligomers to toughen a DGEBA resin. They found that acrylate oligomers exhibited extremely good miscibility with conventional epoxy resins, and cured castings exhibited enhancements in impact strength comparable to those of traditionally toughened epoxy systems.

A different approach was taken by Toughsaent et al.⁹ They synthesized two polymers, one of which

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formed a network by simultaneous independent reactions in the same container. Intercrosslinking reactions were eliminated by the combination of free-radical (acrylate) and condensation (epoxy) polymerization. The mechanical properties of the resultant system increased when the extent of molecular mixing was minimized and heterophase semi-interpenetrating polymer networks (semi-IPNs) were produced. Similar observations were reported by Sperling and Sarge¹⁰ in their work concerning the production of heterogeneous interpenetrating polymer networks (IPNs) of poly(methyl methacrylate) within a poly(dimethyl siloxane) elastomer.

Recently, epoxy resin acrylated polyurethane semi-IPNs¹¹ were synthesized that were compatible and sufficiently flexible. A great deal of literature has been devoted to the toughening of epoxy resins via polyurethane incorporation as a second phase in a specific matrix to form a grafted or ungrafted IPN. The mechanical properties of polymer materials with an IPN structure are fairly superior to those of ordinarily polymers with respect to tensile strength. Such an improvement is generally attributed to an increase in the crosslinking density within IPNs with this approach.¹²⁻¹⁴

Siloxane elastomers¹⁵ have also been used as attractive alternatives to traditional toughening systems. For example, the addition of room temperature vulcanized (RTV) silicone rubber in amounts up to two times that of the unmodified resin has been reported. Although some of these oligomers are quite expensive, these oligomers are immiscible in the resin systems and migrate to the outside. To resolve this problem, Yorkgitis et al.¹⁶ chemically modified epoxy resins with functionally terminated poly(dimethyl siloxane), poly(dimethyl-*co*-methyltrifluoropropyl siloxane), and poly(dimethyl-*co*-diphenyl siloxane) oligomers.

More recently, other workers¹⁷ reported the rubber modification of bifunctional and tetrafunctional epoxy matrices by means of a block copolymer of poly(dimethyl siloxane) and poly(oxyethylene) elastomer or an anhydride-grafted polybutene. Such modifications improved the impact strength but failed for tetrafunctional epoxy resin systems.

Within this framework, the main objective of this work was to toughen epoxy resins with a silicon-modified polyurethane (SiMPU) oligomer as a modifier via IPN grafting.

For this purpose, SiMPU oligomers were synthesized from dimethyl dichlorosilane, poly(ethylene glycol) (PEG; weight-average molecular weight \sim 200), and toluene 2,4-diisocyanate (TDI), were characterized with IR, NMR, and gel permeation chromatography (GPC), and were used as modifiers for epoxy resins at different concentrations. The various mechanical properties, such as the lap-shear strength, peel

strength, and impact strength, of the resultant systems were also evaluated.

EXPERIMENTAL

Materials

Solvent

Tetrahydrofuran (S. D. Fine Chemical, India) was purified via refluxing with sodium metal and a catalytic amount of benzophenone followed by distillation.

Reagent

Dimethyl dichlorosilane (Fluka, Switzerland) and TDI (Fluka) were used as they usually are. PEG 200 was purified with anhydrous calcium chloride (CaCl₂) and vacuum-distilled. Diaminodiphenyl sulfone (DADPS; Fluka), diaminodiphenyl ether (DADPE; Fluka), and a Ciba-Geigy two-pack hardener (H-957) (India) were used as received. Bisphenol A/epichlorohydrin (DGEBA) was synthesized with a standard procedure.¹⁸ The epoxy equivalent of the standard epoxy resin was 0.51.

Synthesis of the hydroxy-terminated SiMPU oligomer

In a three-necked, 250-mL reaction flask fitted with a condenser, a thermometer, and a pressure-equalizing dropping funnel and nitrogen gas inlet, 10 mmol of dimethyl dichlorosilane was dissolved in 15% (v/w) tetrahydrofuran, and 0.05 mmol of tributyl amine was added as an acid acceptor. At -5°C , a 20-mmol equivalent of PEG (weight-average molecular weight \sim 200) was dropwise added with vigorous stirring. After 5 h, the reaction mixture was brought to room temperature. Under these conditions, 8 mmol of TDI was added, and the temperature was gradually raised to 65°C . After half an hour, excess solvent was distilled off, and a colorless, viscous mass was formed. This product was washed with water and toluene, further dissolved in acetone, and reprecipitated with petroleum ether (boiling range = $40-60^{\circ}\text{C}$; yield = 92%).

Characterization of the hydroxy-terminated SiMPU oligomer

The viscosity measurements were performed with a 0.5% (w/v) polymer solution in dimethylformamide (DMF) at 30°C with an Ubbelohde suspended-level viscometer. The elemental analysis was performed with a Carlo Erba 1108 elemental analyzer (Switzerland). The IR spectrum of the oligomer (SiMPU) was recorded with a PerkinElmer 883 spectrophotometer with KBr discs (USA). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra of the oligomer (SiMPU) were recorded with a Bruker 200-MHz FT-NMR spectrometer (Switzerland) with

CDCl_3 and dimethyl sulfoxide- d_6 as solvents. The molecular weight of SiMPU was determined by GPC.

Thin-layer chromatography (TLC)

TLC is an important tool for the separation and isolation of desired components from a reaction mixture. Silica gel is most widely used as the stationary phase.

In this technique, each component is separated and identified with respect to the reference (usually a reactant) according to its polarity matching that of the eluent.

Preparation of the epoxy–SiMPU adducts

Specific amounts of SiMPU oligomers (5, 10, 15, 20, 30, and 40 phr) were added to a constant amount of an epoxy resin in a reaction kettle for the preparation of the IPNs (SiMPU–epoxy). The temperature was maintained at 80°C. The reaction was carried out under this condition for 6, 8, 10, or 12 h.

Characterization of the SiMPU–epoxy adducts

The epoxy content of these polymers was determined by the pyridinium chloride method:¹⁸

$$\text{Epoxy equivalent} = W / [(A - B) N \times 1000]$$

where W is the weight of the sample (g), A is the amount of NaOH for the blank (mL), B is the amount of NaOH for the sample (mL), and N is the normality of NaOH.

IR spectroscopy studies

The extent of the reaction between the epoxy resin and SiMPU oligomer of the various formulations was studied with a PerkinElmer 883 IR spectrophotometer with KBr discs.

Mechanical test processes

Lap shear test

Three adherent interfaces—metal/metal (Al–Al), teak wood/metal (W–Al), and teak wood/teak wood (W–W)—were used for lap-shear and other adhesive tests. The overlapping zone was 322.58 mm² (25.4 mm × 12.7 mm) for each case. The thickness of the adhesive layer within the overlapping area was 0.03 mm. The polymers were cured with different curing agents—DADPS, DADPE, and H-957—under different conditions, and their lap-shear strength was measured according to the standard procedure.¹⁹

Before the application of adhesive materials onto the adherent surfaces, the surfaces were prepared.

Aluminum specimens were prepared with the chromic/sulfuric acid cleaning method,²⁰ and they were rubbed with 200-mesh copper-metal brushes to increase the surface area. The wood specimens were washed with toluene and petroleum ether for the removal of grease and organic oily materials and were dried at 100°C.

Peel test

The peel test involved the stripping of a flexible rigid member of an assembly that was bonded with an adhesive to another member, which could be flexible or rigid. The polymer samples were tested with the 180°C peel test.²¹ In this test, two aluminum specimens (25.4 mm × 304.8 mm × 3 mm) were bonded for the 152.4-mm length of the specimens. Two ends of the unbounded aluminum sheets were bent sharply (90°) and properly aligned to hold the specimen by the jaws of the tensile testing machine. The 180° peel adhesion was measured in terms of the force necessary to strip off the metal substrate at an 180° angle from the metal substrate at the peel rate of 50 mm/min.

Impact strength

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

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

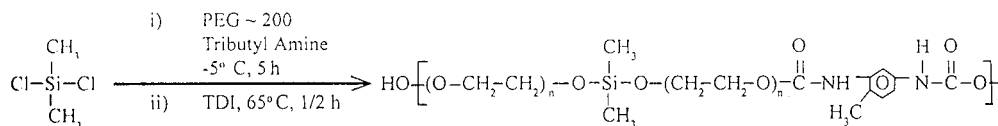
where E is the energy to break of a specimen (J) and w is the width of a specimen (m).

Critical stress intensity factor (K_c)

K_c (or the fracture toughness) was determined with a fracture mechanical technique. In this study, K_c was measured with a single-edge-notched specimen under a three-point-bending mode. These tests were performed with an Instron 1195 tensile machine (USA) at a crosshead speed of 5 mm/min and room temperature. K_c was determined according to ASTM E 399-78 with the following relationship:²²

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

where P is the critical load or crack propagation (N); S is the distance between the spans (50 mm); w is the



Scheme 1

specimen width (15 mm); L is the specimen length (135 mm); a is the precrack length (mm), which was prepared at room temperature with a razor blade and measured with an optical microscope (1–1.5 mm); and t is the specimen thickness (4 mm). $f(x)$ is given by

$$f(x) = 1.93 - 3.07x + 14.53x^2 - 25.11x^3 + 25.8x^4$$

where x is a/w .

RESULTS AND DISCUSSION

Synthesis of hydroxy-terminated SiMPU

Dimethyl dichlorosilane was reacted with 2 equiv of PEG at -5°C in the presence of tributyl amine as an acid acceptor formed hydroxy-terminated compound (Scheme 1), which was characterized by IR and TLC. With TLC, only one component was found from the reaction mixture on the TLC plat at different regions in comparison with the starting materials, and this implied that only one product was formed. The hydroxyl value of the intermediate was half that of the initial PEG, and this supported the complete reaction between PEG and dimethyl dichlorosilane.

After the completion of the first step, the reaction temperature was brought to room temperature, 0.8 equiv of TDI was added, and the temperature was gradually raised to 65°C . The yield of the product was more than 90%; this supported the idea that the reaction between dimethyl dichlorosilane and PEG took place properly. The inherent viscosity of this oligomer in a 0.5% DMF solution was 0.12 (dL/g), and this indicated good flow properties of the oligomers.

Elemental analysis

The percentages of carbon, hydrogen, and nitrogen obtained from elemental analyses were 55, 8.12 and 4.55, respectively. These results agreed well with the values calculated on the basis of the structure of the respective product, as shown in Scheme 1.

IR spectrum analysis

An IR spectrum of SiMPU is shown in Figure 1. The peak at 3434 cm^{-1} may be assigned to the hydroxyl group, and the peak at 2926 cm^{-1} is due to C—H stretching. The peak at 1700 cm^{-1} is due to the C=O stretching of a urethane linkage.²³ Another peak at 936 cm^{-1} is due to the Si—O stretching of an aliphatic

ether of the glycol part of SiMPU. This IR spectrum of the oligomer supports the idea that the silicone part was connected to the urethane chain and was also hydroxy-terminated.

$^1\text{H-NMR}$ analysis

The $^1\text{H-NMR}$ spectrum of the oligomer is shown in Figure 2. The peak at 9.496 ppm is due to the labile proton of the urethane linkage nitrogen atom.²³ A singlet peak due to the methyl proton of the tolyl group can be seen at 6.23 ppm. Around 6.76 and 7.13 ppm, there are two peaks due to the proton adjacent to the methyl group of the tolyl ring and to the proton ortho to the one of the urethane linkage, respectively. At nearly 8.00 ppm, there is a peak due to another aromatic proton of the tolyl moiety. A labile proton hydroxyl group can be seen at 5.6 ppm. The methylene proton of the glycol moiety can be seen at 3.5 ppm. The peak at 4.67 is for the adjacent proton of the urethane linkage. A triplet peak for the methylene proton of the Si—O—CH₂ group is located at 4.1 ppm. A methyl proton of the silicone moiety is close to 0.4

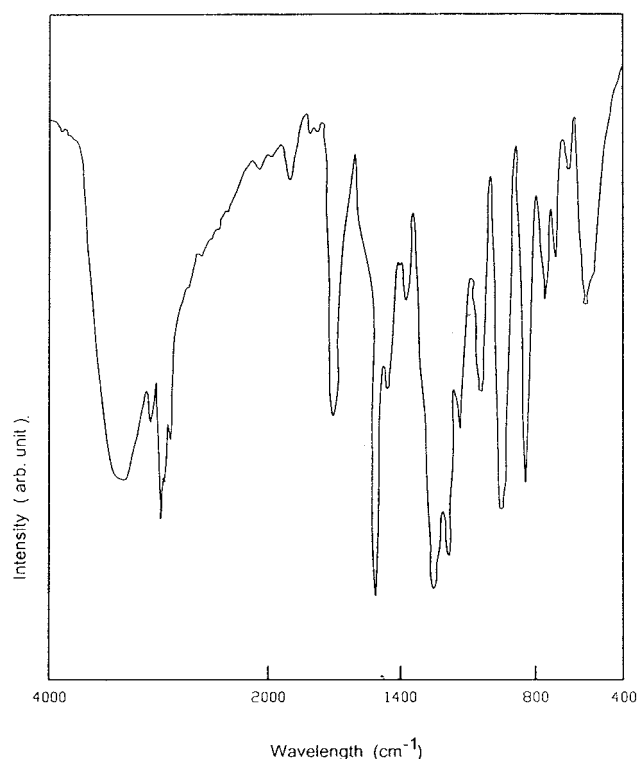


Figure 1 IR spectrum of SiMPU.

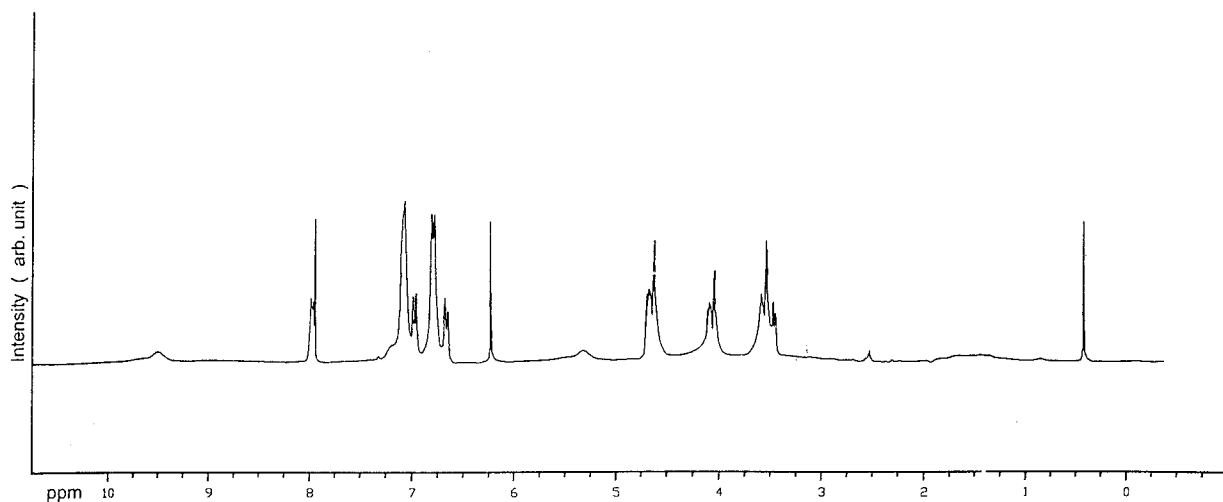


Figure 2 $^1\text{H-NMR}$ spectrum of SiMPU.

ppm. The $^1\text{H-NMR}$ results strongly support the structure of the oligomer.

$^{13}\text{C-NMR}$ analysis

The $^{13}\text{C-NMR}$ spectrum of the oligomer is shown in Figure 3. The peak at 158.33 ppm is due to the carbonyl carbon of the urethane linkage. The peaks at 120 and 127 ppm are due to the methyl-linked carbon and urethane-linked aromatic carbon atom of the tolyl moiety, respectively. A methyl carbon of the tolyl group is located at 143 ppm.²⁴ Another carbon between two urethane linkages of the aromatic ring is located at 147 ppm. Two other carbons of the aromatic ring that are chemically not very different from each other are located at 114 ppm. At nearly 68.8 ppm,

there is a peak for the ether-linked carbon atom of the aliphatic chain. A methylene carbon atom of Si-O-CH_2 can be seen at 44.5 ppm. A peak at 83 ppm is due to the adjacent carbon atom of the $-\text{N}-(\text{C}=\text{O})\text{O}$ group. A methyl carbon atom linked to a silicon atom is located at 5 ppm.

GPC study

The molecular weight and molecular weight distribution of the oligomer were measured with GPC analysis performed with a water liquid chromatography filter with a Waters 410 differential refractometer (Switzerland) with Styragel at a flow rate of 1 mL/min of the oligomer.

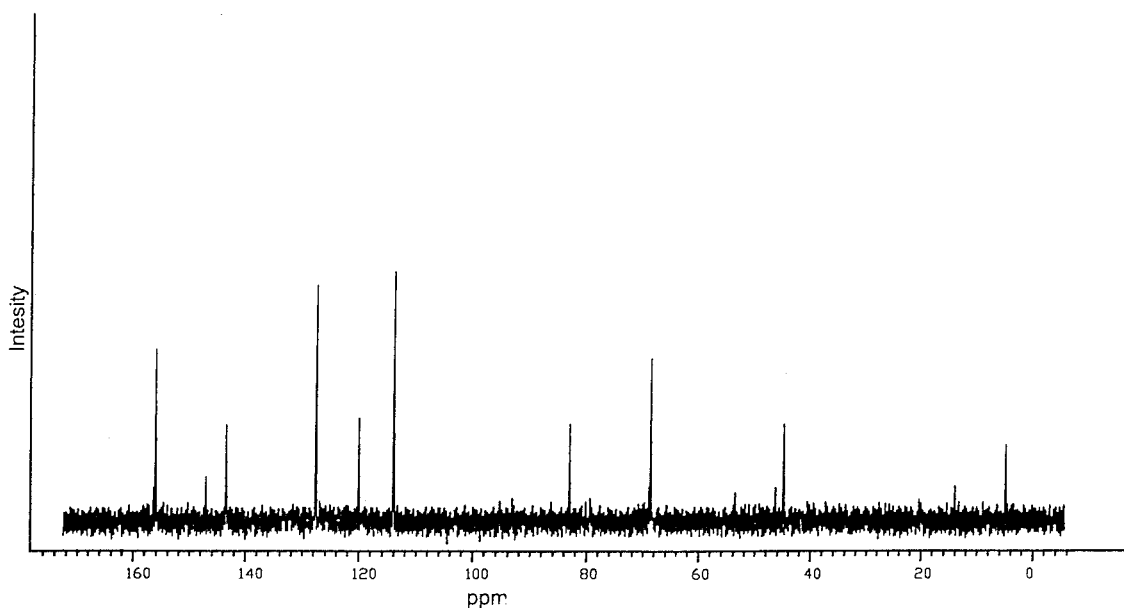


Figure 3 $^{13}\text{C-NMR}$ spectrum of SiMPU.

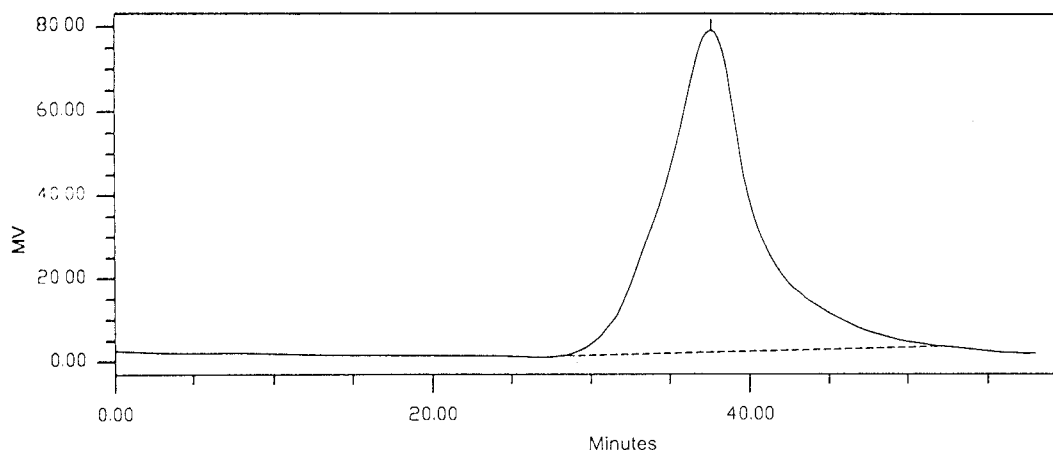


Figure 4 GPC diagram of SiMPU.

The curve of the GPC analysis is shown in Figure 4. The number-average molecular weight of the oligomer was 2860, and the polydispersity was 3.3. This cure was performed in the single mode and implied that one kind of product was formed during the polymerization reaction.

Modification of epoxy with SiMPU

The results of the epoxy content of the virgin resin and various SiMPU-epoxy adduct systems are presented in Table I. The virgin resin content was 0.519 g equiv (epoxy per 100 g of resin), whereas the epoxy content of the various SiMPU-epoxy adduct system was less than that of the virgin one. The epoxy content in set VII was 0.342 epoxy equiv, whereas the SiMPU content was 40 phr. These data support a grafting reaction of urethane oligomers onto epoxy resins through the formation of new ether linkages between the epoxy and hydroxyl groups of SiMPU oligomers.

IR spectroscopy

The IR spectra of the virgin epoxy resin and SiMPU-epoxy adduct system are shown in Figure 5. For the

virgin epoxy resin, the peak at 914 cm^{-1} for epoxy group stretching is very high intense, whereas for the SiMPU-epoxy adduct system, it becomes less intense.

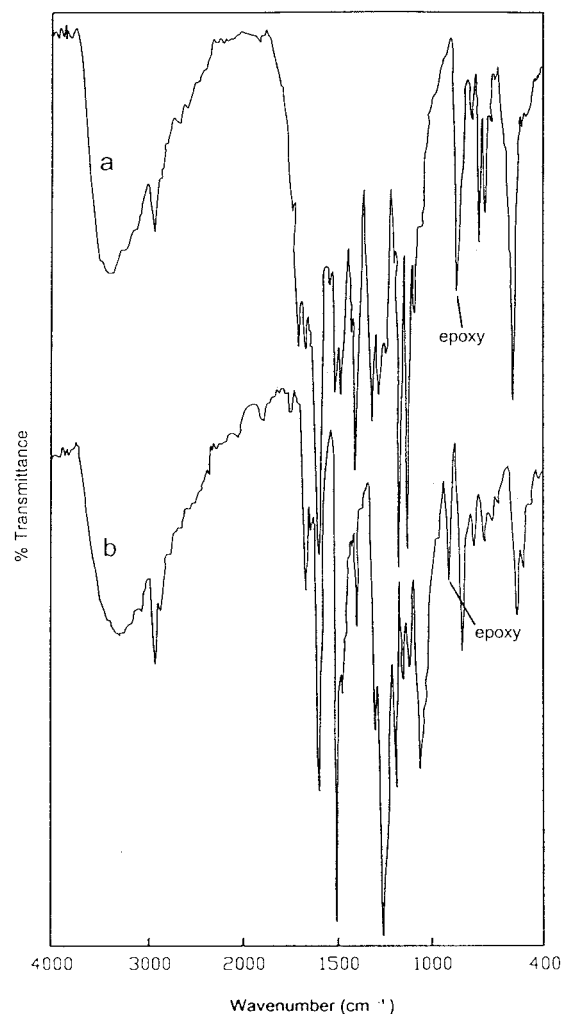


Figure 5 IR spectra of the epoxy-SiMPU adduct: (a) the initial state of the reaction and (b) the final state of the reaction.

TABLE I
Epoxy Content of Epoxy-SiMPU Adduct Systems

Resin code	Epoxy resin (parts)	SiMPU (phr)	Epoxy content (g equiv) after various reaction times		
			6 h	9 h	12 h
Set I	100	0.0	0.519	0.519	0.510
Set II	100	5.0	0.519	0.511	0.50
Set III	100	10.0	0.512	0.50	0.48
Set IV	100	15.0	0.510	0.49	0.40
Set V	100	20.0	0.49	0.46	0.36
Set VI	100	30.0	0.47	0.462	0.35
Set VII	100	40.0	0.46	0.455	0.342

TABLE II
Curing Temperatures and Conditions Used for the New Epoxy Resin

Resin code	Resin mixture (parts)	DADPE (phr)	DADPS (phr)	Curing temperature (°C)	Curing time (h)
Set I	100	15	—	175	3
	100	—	17	195	4
Set II	100	15	—	175	3
	100	—	17	195	4
Set III	100	15	—	175	3
	100	—	17	195	4
Set IV	100	15	—	175	3
	100	—	17	195	4
Set V	100	15	—	175	3
	100	—	17	195	4
Set VI	100	15	—	175	3
	100	—	17	195	4
Set VII	100	15	—	175	3
	100	—	17	195	4

The intensity ratio of these two systems ($I_{\text{virgin}}/I_{\text{epoxy-SiMPU}}$) was greater than 1, and this supported the reaction between the hydroxy group of SiMPU and the epoxy resin.

Curing characteristics of the resins

The epoxy resins were cured with the two-pack commercial hardener (H-957) at 150°C for 4 h under a pressure of 100 psi. The curing schedule is shown in Table II, with DADPS and DADPE used as curing agents. At first, the formulated resin (resins and curing agent) was recorded with differential scanning calorimetry (DSC) in an air atmosphere at a heating rate of

10°C/min (Fig. 6). The figure shows a characteristic exotherm at a particular temperature region (~175–195°C) that disappeared in the DSC curves of the preheated formulated resin within the same temperature region. The curing temperature and amount of the curing agent employed for DADPS were somewhat higher than those used for DADPE because of the lower reactivity of the former than that of the latter and other diamines on account of the electron-withdrawing characteristic of the $-\text{SO}_2-$ group.²⁵ According to the DSC study, the curing temperature for DADPS was 195°C, whereas that for DADPE was 175°C (Fig. 6).

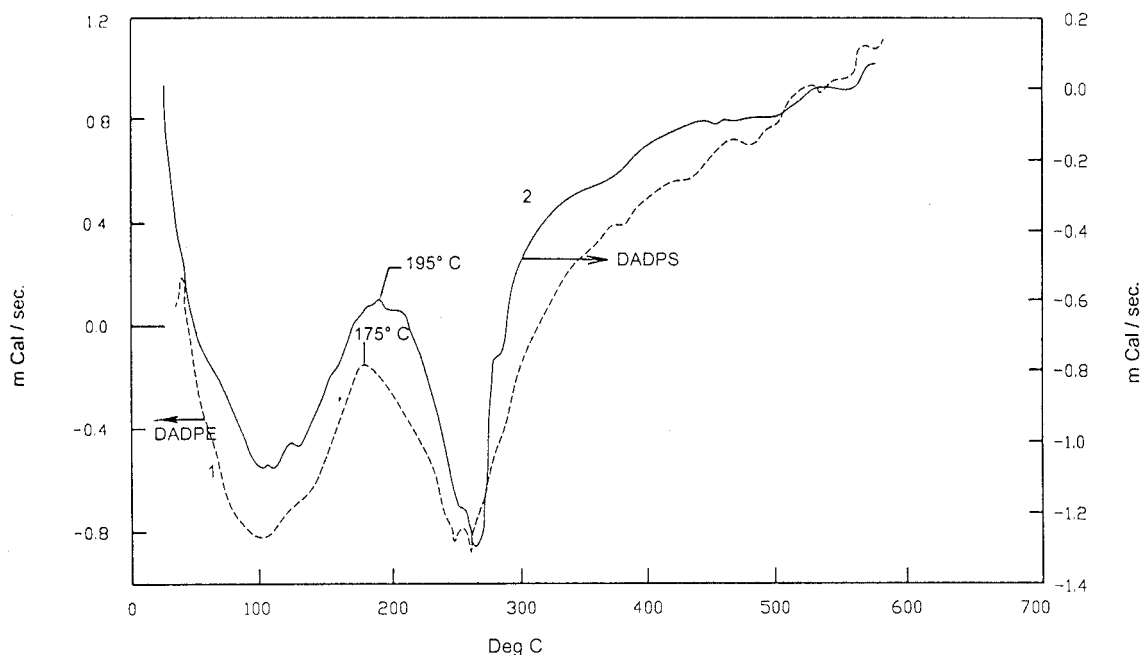


Figure 6 DSC thermogram of epoxy-SiMPU with DADPE and DADPS.

TABLE III
Results of the Lap-Shear Test of the Virgin Resin and Modified Resins with Different Hardeners

Resin system	Curing agent (phr)			Lap-shear strength (N/m ²) × 10 ⁻⁶ on different adherents		
	DADPS	DADPE	H-957	W-W	W-Al	Al-Al
Set I	17	—	—	18.76	18.67	19.01
	—	15	—	17.90	17.32	18.93
	—	—	30	20.87	21.03	21.73
Set II	17	—	—	18.60	18.71	18.95
	—	15	—	17.88	17.21	18.63
	—	—	30	20.90	21.12	21.75
Set III	17	—	—	18.89	18.69	18.86
	—	15	—	17.78	17.43	19.21
	—	—	30	20.84	21.17	21.67
Set IV	17	—	—	18.91	18.70	19.11
	—	15	—	17.87	17.50	18.87
	—	—	30	20.93	20.92	21.70
Set V	17	—	—	18.26	18.17	18.15
	—	15	—	17.50	17.02	16.92
	—	—	30	20.07	20.63	20.93
Set VI	17	—	—	17.76	17.67	17.87
	—	15	—	17.00	16.82	16.32
	—	—	30	19.57	20.03	20.03
Set VII	17	—	—	14.76	14.67	15.57
	—	15	—	13.90	15.32	15.45
	—	—	30	15.87	16.23	17.63

Mechanical properties

Lap-shear test

The results of the lap-shear strength of the adhesive systems were compared with those of the bisphenol A standard epoxy resin on the Al-Al, W-W, and W-Al surfaces. The results are shown in Table III within the limit of the standard deviation ($\pm 0.5\%$). The adhesive strengths of the various resin systems were measured with the two-pack commercial hardener (H-957), DADPS, and DADPE under appropriate curing conditions. In all cases, adhesive failure took place at the metal-adhesive interfaces.

For sets V–VII, the lap-shear strength of the resin systems was less than that of the virgin resin system (set I). In other cases, it was almost comparable to that of the virgin system.

These results indicated that the incorporation of up to 15 phr SiMPU into the virgin resin led to virtually no loss of tensile properties, but more than 15 phr SiMPU reduced the tensile properties of the epoxy resin; this was not desirable. Therefore, up to 15 phr SiMPU was acceptable for the epoxy formulations.

Peel strength

Peel tests were performed for various amounts of the SiMPU resin and the standard epoxy resin. The resin systems were cured with the two-pack hardener H-957 at 150°C for 4 h. The results of the peel tests are

shown in Table IV. The peel strength of the set IV resin system was higher than that of other systems and even better than that of the virgin resin system (set I). The results indicated that the peel strength increased by 25% with 15 phr SiMPU with respect to that of the

TABLE IV
Results of the Peel Test of the Virgin Epoxy Resin and Modified Epoxy Resin on Al-Al Interfaces

Resin code	Curing agents (phr)			Peel fracture energy (kJ/m ²)
	DADPS	DADPE	H-957	
Set I	17	—	—	7.82
	—	15	—	7.11
	—	—	30	9.07
Set II	17	—	—	7.90
	—	15	—	7.32
	—	—	30	9.63
Set III	17	—	—	8.01
	—	15	—	7.89
	—	—	30	10.15
Set IV	17	—	—	8.90
	—	15	—	8.13
	—	—	30	11.28
Set V	17	—	—	7.61
	—	15	—	7.39
	—	—	30	10.34
Set VI	17	—	—	7.21
	—	15	—	7.19
	—	—	30	10.15
Set VII	17	—	—	7.01
	—	15	—	7.09
	—	—	30	9.15

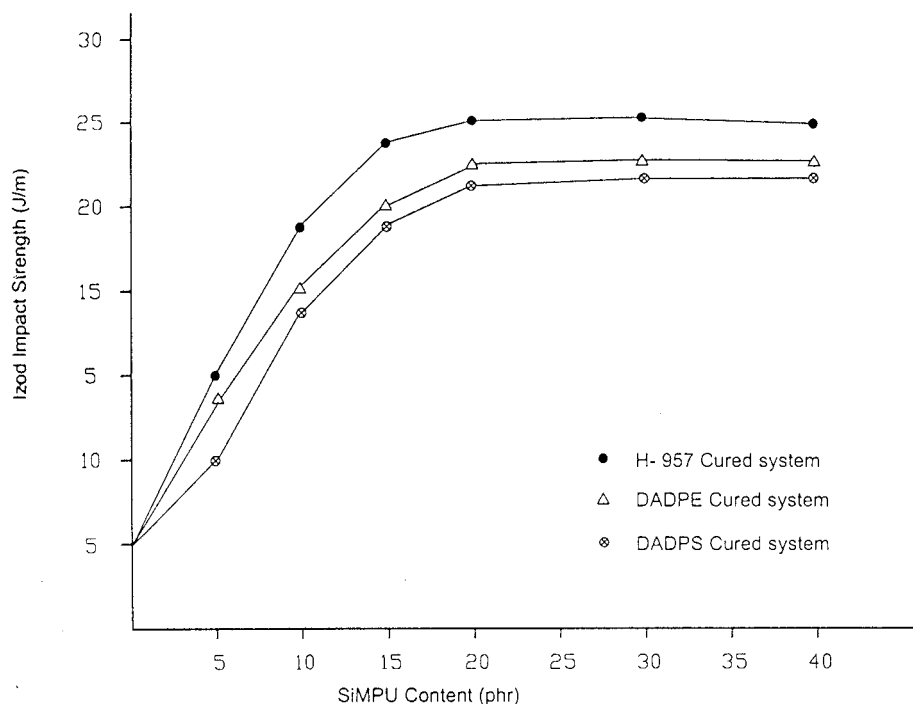


Figure 7 Effect of the SiMPU content on the Izod impact strength of the epoxy-based formulations.

virgin resin. As the peel strength of the resin depended on the flexibility of the cured resin system,²² it was expected that 15 phr SiMPU would better improve the toughness of the resin without a loss of tensile properties.

Impact strength

Figure 7 represents the impact strength of the epoxy resin versus the SiMPU content with different hardeners. In all cases, the impact strength increased with the SiMPU content up to 20 phr, and after that, it leveled off. This can be considered a critical concentration beyond which no significant change can be observed. This improvement in the impact strength could be attributed to an increased degree of entanglement between the epoxy resin and hydroxy-terminated polyurethane oligomer. Urethane (SiMPU) oligomers partially reacted with epoxy-resin-formed extended chain components in the epoxy formulations and consequently reduced the crosslinking density of the resin systems; this was a major cause of the brittleness of the epoxy resins. As a result of this grafting of SiMPU onto epoxy resins, the systems became more flexible and tough, and this provided high impact strength. Beyond 20 phr SiMPU, the virtual leveling off of the impact strength could be explained by the fact that the chain length remained constant; that is, the distance between the crosslinks did not change.

However, the impact strength of the epoxy-SiMPU adduct systems were varied with the hardener. The

flexible amine-formulated hardener H-957 improved the impact strength of the epoxy-SiMPU adduct systems more than the DADPS and DADPE curing systems.

Figure 8 presents K_c versus the SiMPU content with H-957, DADPS, and DADPE hardener systems. In all these cases, K_c increased compared with that of the virgin resin with the concentration of SiMPU. Significantly, it reached $3 \text{ MPa m}^{1/2}$ with the H-957 hardener system; compare this to $0.95 \text{ MPa m}^{1/2}$ for the unmodified system at a critical concentration of 20 phr SiMPU. Above this concentration of SiMPU, the improvement of K_c virtually leveled off, like the impact strength. There was probably no significant interaction between the modifier and epoxy resin above a modifier concentration of 20 phr.

CONCLUSIONS

Synthesized hydroxy-terminated SiMPU oligomers at a 15 phr concentration were very effective in improving the toughness of epoxy resins without the deterioration of the tensile properties of the resins. The impact strength increased continuously and reached a maximum value (five times greater than that of the virgin resin) at a critical modifier concentration (20 phr). K_c reached $3.0 \text{ MPa m}^{1/2}$ (it was $0.9 \text{ MPa m}^{1/2}$ for the virgin resin). Above this concentration of SiMPU, the improvement of both K_c and the impact strength leveled off. There was probably no significant interac-

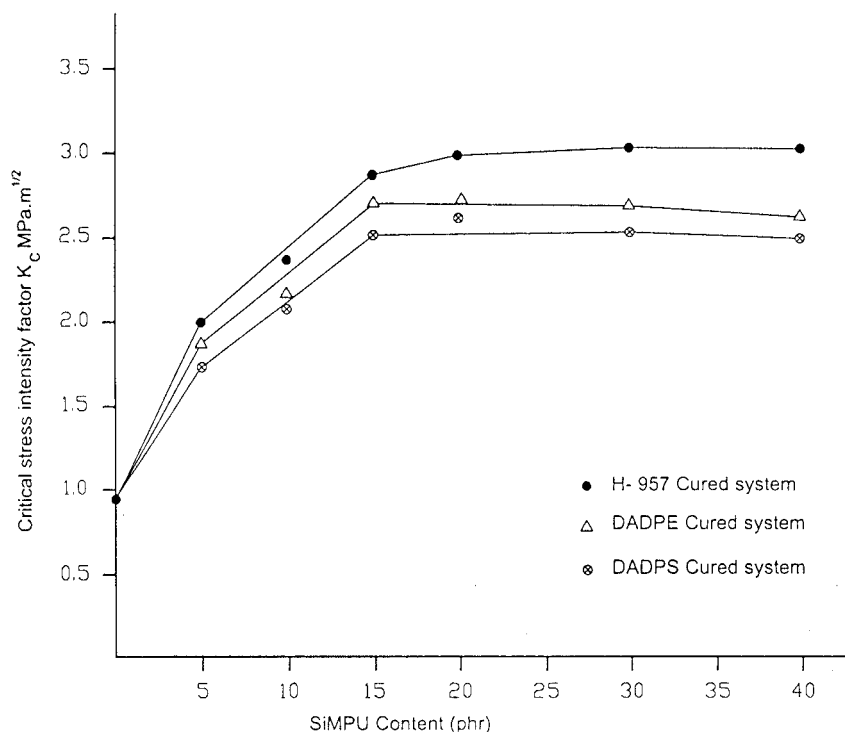


Figure 8 Effect of the SiMPU content on K_c of epoxy-based formulations.

tion between the modifier and epoxy resin above a modifier concentration of 20 phr.

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