

# Polyurethane-Modified Epoxy Resin: Solventless Preparation and Properties

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**ABSTRACT:** A polyurethane-modified epoxy resin system with potential as an underfill material in electronic packaging and its preparation procedure were studied. The procedure enabled the practical incorporation of an aliphatic polyurethane precursor, synthesized from poly(ethylene glycol) and hexamethylene diisocyanate without a solvent, as a precrosslinking agent into a conventional epoxy resin. With a stoichiometric quantity of the polyurethane precursor added to the epoxy (ca. 5 phr), the polyurethane-modified epoxy resin, mixed with methylene dianiline, exhibited a 36% reduction in the contact angle with the epoxy-amine surface, a 31% reduction in the cure onset temperature versus the control ep-

oxy system, and a viscosity within the processable range. The resultant amine-cured thermosets, meanwhile, exhibited enhanced thermal stability, flexural strength, storage modulus, and adhesion strength at the expense of a 5% increase in the coefficient of thermal expansion. Exceeding the stoichiometric quantity of the polyurethane precursor, however, reduced the thermal stability and modulus but further increased the coefficient of thermal expansion. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 3094–3103, 2009

**Key words:** crosslinking; polyurethanes; resins; thermal properties; thermosets

## INTRODUCTION

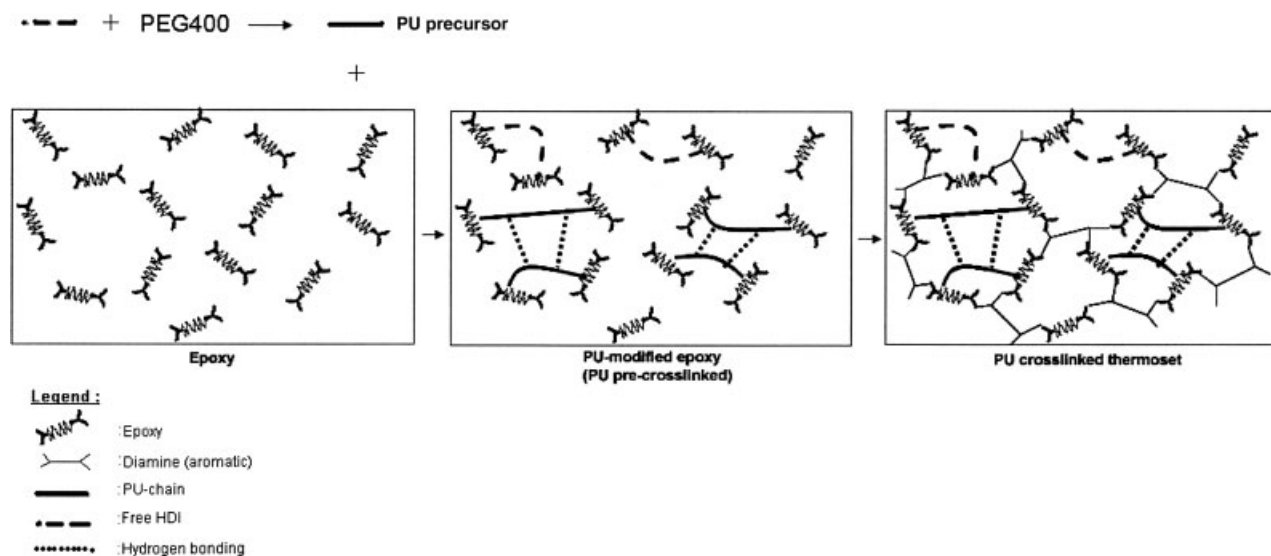
Underfill (UF) materials are vital in electronic packaging to keep solder joints reliable and the whole microchip assembly durable and functional. The materials currently in use are based solely on epoxy polymers because of their ease of processing, low cost, and moisture, heat, and chemical resistance.<sup>1–4</sup> Nevertheless, the coefficient of thermal expansion (CTE) mismatch between a UF material and a die often leads to failure and remains a daunting challenge. The ultimate goal is to reduce the CTE of the UF material to a value as close as possible to that of the solder material. The most common approach is the incorporation of inorganic fillers into the UF matrix, with microsized silica particles being the common choice. However, this practice has its limit: even with the maximum allowable loading, it can hardly reduce the CTE mismatch to the desired level. The availability of nanosized silica primary particles in the range of 10–20 nm has created new prospects and interest in achieving the goal.<sup>5,6</sup> If the

particles can be dispersed well with a size of 10–50 nm in the epoxy matrix, they have the potential to improve the dimensional stability and reduce the CTE mismatch, in addition to increasing the modulus, heat deflection temperature, and barrier to diffusion of solvents.<sup>7</sup> However, the agglomeration of particles, either in a physical fashion as agglomerates or by stronger sintering bonds as aggregates, poses difficulty for the dispersion process.<sup>8</sup> Although attempts to apply high shear stress to the constituent particles to redisperse them in the epoxy matrix remains a challenging approach, studies on improving the silica-epoxy interaction, which is fundamentally important to the dispersion process, via chemical modification of the polymer have not been reported. Chemically modified epoxy may be tailored to produce molecules with chain dynamics that give the right viscoelasticity and other structurally related properties, such as modulus, wetting, adhesion, and thermal stability.

Motivated by this prospect, we undertook this study to chemically incorporate polyurethane (PU) into a commercial epoxy. PU-epoxy systems have been reported previously and are commonly used in the coating industries and structural applications to mitigate the brittle nature of neat epoxy systems.<sup>9–12</sup> To achieve the intended elastomeric characteristics, PUs are often derived from flexible toluene diisocyanate and poly(propylene glycol). However, the

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**Figure 1** Structures of the epoxy, the PU-modified epoxy resin, and its thermoset.

quantity of PU that is added inadvertently results in the formation of PU–epoxy blends. As far as we know, the use of PU–epoxy systems for UF applications has not been explored as the formation of such PU–epoxy blends is catastrophic for UF applications. Here, we intended to add as much PU as could be chemically reacted with the pendant  $\text{—OH}$  of the epoxy chain. Nevertheless, the formation of physical blends was avoided for fear of phase separation. Procedures for preparing a PU precursor and incorporating it as a precrosslinker into the conventional UF epoxy system were investigated. This article reports (1) the preparation of a PU precursor based on poly(ethylene glycol) 400 (PEG400) and hexamethylene diisocyanate (HDI) with an OH/NCO molar ratio of 1 : 3, (2) its subsequent incorporation as a precrosslinker into the epoxy resin, and (3) the properties of the modified epoxy resin and its methylene dianiline (MDA) cured thermosets. Figure 1 illustrates the schematic reaction and structural changes from the monomers to the PU precrosslinked epoxy resin and its thermoset. Microgels

were expected to be present as a result of the precrosslinking reaction.

The 1 : 3 ratio, chosen from a study on a series of OH/NCO molar ratios (1 : 1, 1 : 2, 1 : 3, 1 : 5, 1 : 10, and 1 : 100), yielded a PU precursor with properties that fulfilled the important processing criteria before curing, such as ease of handling and mixing with epoxy, crucial in this solventless system.

## EXPERIMENTAL

### Materials

The materials used in this study are listed in Table I. PEG400 and HDI were used for the synthesis of the PU precursor. MDA and a bisphenol A type epoxy resin (DER331) formed the conventional epoxy resin thermoset system. All reagents were used without further purification, except for PEG400, which was treated to remove traces of water.<sup>13</sup>

**TABLE I**  
Characteristics of the Materials

Material	Structure	Description
PEG400		$M_w = 380\text{--}420$ g/mol
HDI		$M_w = 168$ g/mol
MDA		$M_w = 198$ g/mol
DER331		EEW = 182–192 g/equiv Epoxide concentration (%) = 22.4–23.6

EEW = epoxy equivalent weight;  $M_w$  = weight-average molecular weight.

### Work station setup

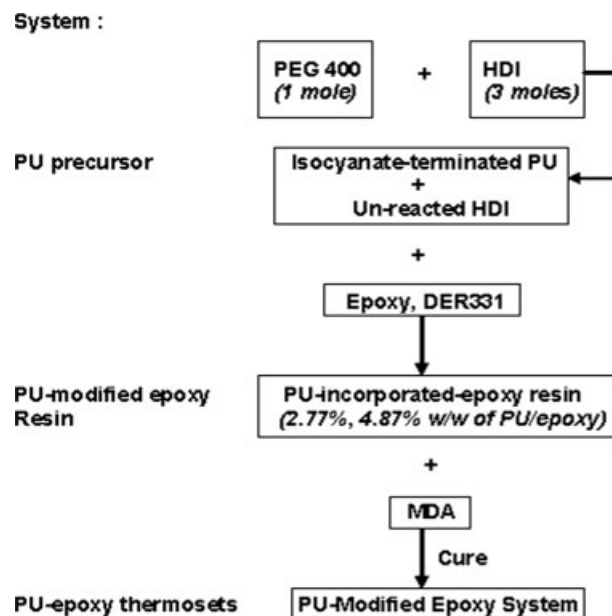
All syntheses were conducted inside a glovebox equipped with a pump and a humidity detector to provide a controlled dry environment. It also provided protection from direct contact with toxic HDI during handling.

### Synthesis of the PU precursor, PU-modified epoxy resin, and PU-epoxy thermosets

The scheme in Figure 2 illustrates the three stages of preparation of the PU-modified epoxy system. All reactions were carried out without a solvent at the ambient temperature with constant magnetic stirring. In the first stage, the PU precursor was prepared from the reaction between PEG400 and HDI with a series of OH/NCO molar ratios. The 1 : 3 molar ratio yielded the PU oligomer (theoretical degree of polymerization = 2) with an isocyanate group at both chain ends in the presence of a small excess of HDI. The second stage involved reacting the resultant precursor with a 1 : 3 molar ratio and the conventional epoxy resin to yield a PU precrosslinked epoxy, which is called here the PU-modified epoxy resin. In the third stage, MDA was added to the PU-modified epoxy resin to affect the actual curing of the main epoxy component, leading to the formation of PU-epoxy thermosets. The control system was obtained by the reaction of stoichiometric ratios of MDA with DER331.

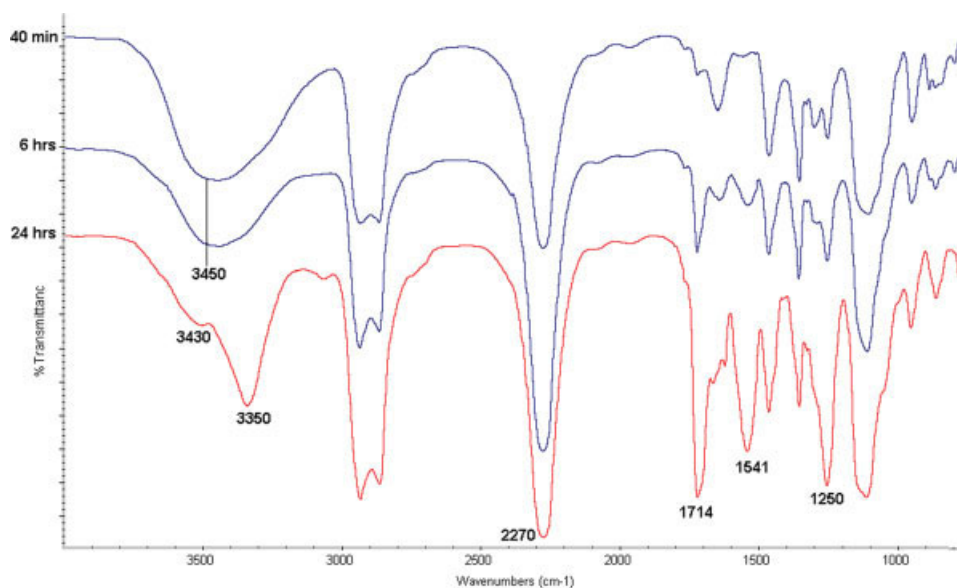
### Characterization

Fourier transform infrared (FTIR) spectra were obtained with a Thermo Nicolet IR200 spectrometer. The samples were directly analyzed on ZnSe plates. Each run was set in the mid-IR range of 4000–750  $\text{cm}^{-1}$  with 10 scans at a resolution of 2  $\text{cm}^{-1}$ . A Mettler-Toledo TGA/SDTA 851 thermal system was used to measure the thermal stability of the samples. The samples were heated from 30 to 600°C at 20°C/min in nitrogen flowing at 30 mL/min. The thermogravimetric analysis (TGA) apparatus was coupled with the FTIR instrument; the purge gas carried the decomposition products from the TGA apparatus through a glass inlet tube and into the flow cell for FTIR measurements. The contact angle was measured with a VCA Optima XE 2500 goniometer, which used an optical system to capture the profile of the samples on the epoxy-amine and silica glass surfaces. The angle that formed between the liquid and solid interface after the liquid stopped advancing was taken as the contact angle. A PerkinElmer Pyris 1 differential scanning calorimeter was used to determine the cure profiles of the epoxy/



**Figure 2** Preparation schematic of the PU-modified epoxy system.

MDA and PU-modified epoxy/MDA mixtures. Mixtures were heated from 50 to 300°C at 20°C/min under a nitrogen atmosphere. The viscosities of the uncured systems of epoxy/MDA and PU-modified epoxy/MDA were measured at 25°C at a shear rate of 10 rpm using a Brookfield DV-II+ digital viscometer with a spindle-and-cup geometry. Readings were taken after it had stabilized. All samples were taken out of -20°C storage and thawed for 30 min before measurement. CTEs of the PU-epoxy thermosets were measured with a PerkinElmer Diamond N5350003 thermomechanical analyzer from 30 to 250°C at 5°C/min under purging nitrogen gas. A PerkinElmer DMA 8000 dynamic mechanical analyzer recorded the storage modulus and glass-transition temperature ( $T_g$ ) of the thermosets in the thermal range of 30–250°C with a single cantilever mode. The bending frequency was fixed at 1 Hz, and the temperature ramp was 3°C/min. Flexural tests were carried out with a Hounsfield instrument in the three-point-bending mode on the basis of the ISO 178 standard. Thermoset strips of 4 mm × 10 mm × 80 mm were supported on a span 64 mm apart and flexed at 2 mm/min. The adhesion strength of the thermosets was carried out by first adhering two 5 mm × 50 mm substrates to the thermosets and then tested with the single lap shear on the same Hounsfield instrument. The substrates were pulled at a speed of 2 mm/min. All characterizations of the thermosets were performed on the PU epoxy cured at 120°C for 2 h with a 1-h postcure at 160°C.



**Figure 3** FTIR spectrum depicting the reaction progress of PEG400-HDI. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

## RESULTS AND DISCUSSION

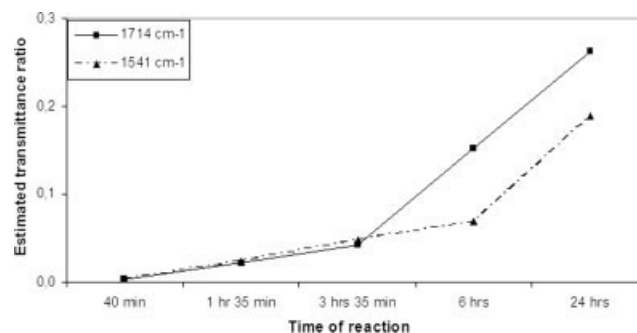
### Reactions

The PU precursor was successfully synthesized and incorporated into the conventional epoxy as a pre-crosslinker to produce a PU-modified epoxy resin. The reaction of the diol and diisocyanate forming the PU precursor was monitored with an FTIR technique to track and determine its completion on the basis of the characteristic frequencies. The initiation of the reaction was signified by the appearance of a urethane group, which was represented by the paired N—H stretching bands at  $\sim 3430$  and  $\sim 3350$   $\text{cm}^{-1}$ , the N—H bending band at  $\sim 1541$   $\text{cm}^{-1}$ , the C=O stretching band at  $\sim 1714$   $\text{cm}^{-1}$ , and the C—O stretching band at  $\sim 1250$   $\text{cm}^{-1}$ .<sup>14–16</sup> On the basis of the spectra shown in Figure 3, this happened 40 min after the diol and diisocyanate were added together. The progress of the reaction can be observed through the FTIR spectra as well, being evidenced by the gradual increase in the intensity with time of the bands at 1714, 1541, and 1250  $\text{cm}^{-1}$ . In an estimated quantitative representation, it can be presented as the area ratio of the 1714- and 1541- $\text{cm}^{-1}$  bands versus the 2900- $\text{cm}^{-1}$  band; the latter originates from the fixed quantity of the C—H group. The plot of the estimated ratio, shown in Figure 4, exhibits a trend that shows a quantitative increment of the C=O and N—H groups, signifying that the reaction is progressing. The completion of the reaction is marked by the disappearance of the O—H band at  $\sim 3450$   $\text{cm}^{-1}$ .<sup>17</sup> For the PEG400-HDI system, 24 h is needed to complete the reaction. Now, the fully formed PU precursor is ready for incorporation

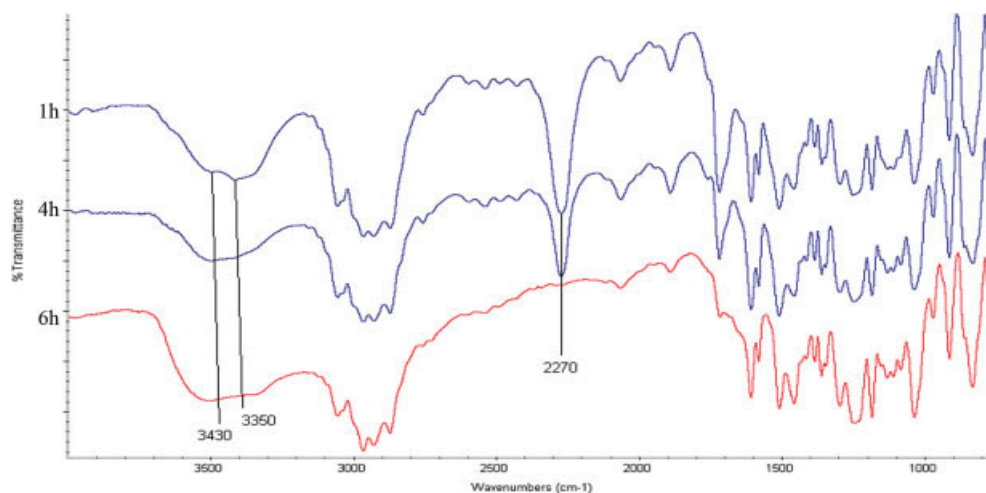
into epoxy via the reaction between the terminal —NCO group of the precursor and the pendant —OH group of the epoxy, forming the —NHCO— linkage. Again, with the FTIR technique, the disappearance of the N=C=O band at 2270  $\text{cm}^{-1}$  evidences the completion of the incorporation reaction (Fig. 5). A successful incorporation process takes 6 h.

### Thermal, physical, and mechanical properties

The basic processing requirements of a UF material include a wide thermal processing window, good wetting capability, and a workable viscosity range for its yet-to-cure system. Application-wise, a low cure onset temperature is appreciated according to Zhang and Wong.<sup>18</sup> As for the cured thermoset, it should be thermally stable, more rigid, and less thermally expanded, possess a high  $T_g$ , and have good adhesion to the substrate.



**Figure 4** Estimated area ratios of different absorption bands against the reference of 2900  $\text{cm}^{-1}$ .



**Figure 5** FTIR spectrum depicting the reaction progress of the PU-modified epoxy resin. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

#### PU-modified epoxy resin

For the yet-to-cure mixture of the PU-modified epoxy and amine, the relevant parameters have been measured and are discussed here.

The first effect of PU incorporation on epoxy is demonstrated by its higher thermal stability versus that of the neat epoxy, as summarized in Table II. Taking the temperature of the first weight loss as the degradation onset temperature ( $T_{d(0)}$ ), which is also a measure of thermal stability, we find that the incorporation of 2.77 or 4.87% (w/w) PU into the epoxy thermally stabilizes the system, enhancing  $T_{d(0)}$  to 200 and 215°C, respectively, from the value of the epoxy (185°C). This means a wider window for processing of the modified epoxy system. The increase can be attributed to the PU precrosslinked epoxy structures forming microgels. The resultant urethane linkage enhances the thermal stability.

The next important effect of PU is the wetting capability of the resin, which is measured through its contact angle. It is evident from Table III that the PU-modified epoxy resins that were mixed with the curing agent MDA had reduced contact angles when

tested on epoxy-amine. For systems with 2.77 wt % incorporated PU or 4.87 wt % incorporated PU, the contact angles with the epoxy-amine substrate were 54.0 and 48.5°, respectively, versus 75.2° for the control epoxy. The maximum reduction at 36% was significant. Here, the epoxy-amine surface simulated the solder mask of the electronic assembly. The effect of the reduced contact angle arose from the interaction between the carbonyl and hydroxyl groups of the incorporated PU with the epoxy-amine surfaces. This trend is much desired in a UF material for ease of coating and adhesion. The results also imply that the PU-modified epoxy system would yield improved adhesion on the solder mask surface. This implication was subsequently confirmed by its adhesion strength values, as shown in Table IV (single-lap-shear analysis). Meanwhile, the wettability of the PU (4.87%)-modified epoxy resins on a silica glass surface was also measured, with the silica glass surface simulating the silica particle surface. The measured contact angle of the modified system was 44.1° versus 51.0° for the control system; that is, there was a significant 14%

**TABLE II**  
Thermal Stability

Epoxy resin system	$T_{d(0)}$ (°C) <sup>a</sup>	$T_{d(0)}$ (°C) <sup>b</sup>	$T_{d(0.5)}$ (°C) <sup>b</sup>	Maximum mass loss rate temperature (°C) <sup>b</sup>
Epoxy	185 ± 0	290 ± 0	410 ± 0	395 ± 0
PU-modified epoxy resin (2.77% PU)	200 ± 0	305 ± 0	413 ± 4	398 ± 4
PU-modified epoxy resin (4.87% PU)	215 ± 0	320 ± 0	415 ± 0	398 ± 3

All values are averages of three measurements.

<sup>a</sup> Epoxy resin.

<sup>b</sup> Thermosets.

**TABLE III**  
Contact Angles, Viscosities, and Cure Temperatures

Epoxy resin system	Contact angle on the silica glass surface (°) <sup>a</sup>	Contact angle on the epoxy-amine surface (°) <sup>b</sup>	Viscosity (P) <sup>b</sup>	Cure onset temperature (°C) <sup>b</sup>	Cure peak temperature (°C) <sup>b</sup>
With 0% PU	51.0 ± 1.5	75.2 ± 1.9	521 ± 13	113 ± 0	179 ± 6
With 2.77% PU	44.1 ± 1.0	54.0 ± 1.4	597 ± 17	104 ± 1	178 ± 1
With 4.87% PU	44.1 ± 0.6	48.5 ± 1.2	715 ± 12	78 ± 1	167 ± 2

<sup>a</sup> Epoxy resin.

<sup>b</sup> Epoxy resin mixed with MDA

reduction. The result implies the ability of the PU-modified epoxy to wet the silica particles, thereby showing potential in promoting deagglomeration of nanosilica particles and improving dispersion. This will be discussed in detail in a future article.

Viscosity measurements revealed that the PU-modified epoxy resin/MDA mixtures, before curing, were more viscous than the control system/MDA. The results are summarized in Table III. The viscosity increased with the content of PU. Microgels associated with the PU precrosslinked structures, which increased with the PU content, were accountable for the observed increase. Nevertheless, the viscosities were still within the processable range.

Figure 6 compares the nonisothermal curing profiles of the PU-modified epoxy and control resins obtained at the heating rate of 20°C/min with differential scanning calorimetry. The analyzed onset and peak temperatures of the curing reaction are summarized in Table III. The results clearly show that the cure onset temperature decreased because of incorporated PU: 78° for 4.87% PU and 104° for 2.77% PU versus 113° for the control system. That is, there was a significant 31% reduction for the epoxy modified with 4.87% PU. The lower cure temperature of the PU-modified epoxy can be attributed to the reduced mobility of the molecular chains induced by the microgels. Physically, the onset translates to the initiation of gelation, which occurred at a lower temperature for the modified epoxy system. Generally, a UF resin that undergoes fast gelation is preferred because this minimizes

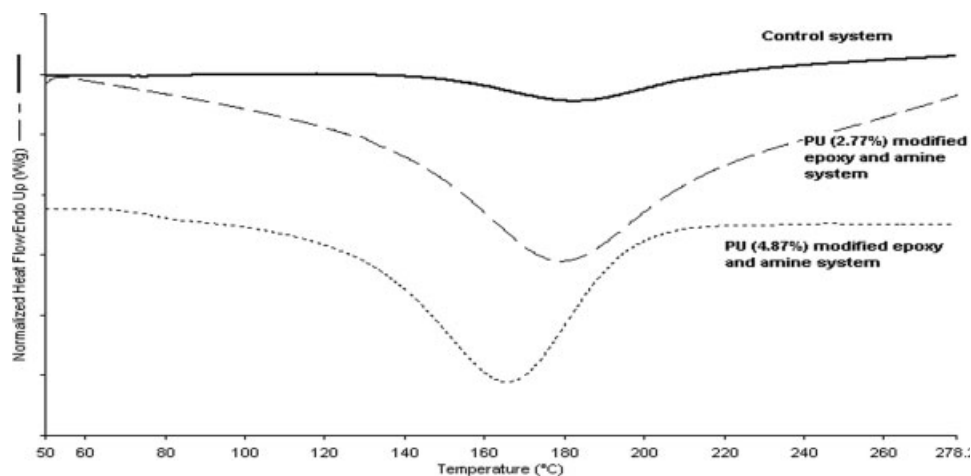
voiding [18]. The PU-modified epoxy system evaluated here has an advantage, in that its curing process starts below the boiling temperature of water, thereby giving no opportunity for any trace of moisture to be trapped within the matrix to vaporize and form voids.

#### Thermosets

The main properties of the thermosets obtained from the PU-epoxy and control epoxy resins are summarized in Tables II, IV, and V. A comparison of the thermal stability data in Table II and Figure 7 shows that the PU-modified epoxy thermosets are more stable than the control. The enhanced thermal stability of the PU-modified thermosets (i.e., 320°C for 4.87% PU) renders them more suitable for use in lead-free applications, for which the maximum reflow temperature is 260°C.<sup>19</sup> The enhancement of the thermal stability can be attributed to the higher overall cross-link density, which contains additional urethane linkages.<sup>20,21</sup> The similarity of the 50% weight loss temperature ( $T_{d(0.5)}$ ) values exhibited by both sample types (Table II) is mainly due to the decomposition of the principal chemical structure of the epoxy-amine network, which dominates both the modified and control epoxy systems. The urethane group in our system appears to degrade at 510°C. This is evidenced by the FTIR spectrum of the evolved gas obtained from the TGA-FTIR measurements. Figure 8 compares the three-dimensional FTIR spectra of the evolved gases for the control and PU-modified

**TABLE IV**  
Single-Lap-Shear and Three-Point-Bending Test Analysis Values

Thermoset system	Single-lap-shear analysis			Three-point-bending test		
	Lap shear (MPa)	Force (N)	Elongation (mm)	Flexural strength (MPa)	Deformation at break (mm)	Flexural modulus (GPa)
Epoxy thermoset (control)	3.27	161	1.80	126	17	70
PU-epoxy thermoset (4.87% PU)	5.65	281	2.25	163	11	85



**Figure 6** Curing profile comparison of representative modified and control systems.

epoxy thermosets. The frequency of interest is  $2400\text{ cm}^{-1}$  for  $\text{CO}_2$  gas. Degradation of the PU-modified thermoset is characterized by a significant release of  $\text{CO}_2$ , which is detected at 24–27 min (corresponding to ca.  $510^\circ\text{C}$ ), as shown in Figure 8(b). The possible reaction giving rise to  $\text{CO}_2$  is decarboxylation of the urethane group according to eq. (1). Although the urethane group in normal homopolymers or physical blends decomposes at lower temperatures ranging from 160 to  $240^\circ\text{C}$ ,<sup>9</sup> this does not happen for urethane in the PU-modified epoxy thermoset. One possible explanation is that a small amount of PU is chemically incorporated into the epoxy matrix as a microgel. To verify this concept, blends containing PU precursors in excess of the stoichiometric quantity (10 and 20 wt % PU) were investigated. One important feature is the immiscibility of the blends, as evidenced by two  $T_g$ 's (to be discussed later). Interestingly, the  $T_{d(0)}$  values of the blends occurred at 260 and  $265^\circ\text{C}$ , respectively, falling within the range limit of the control discussed earlier. This indicates that this is an average effect induced by a structural change due to the incorporation of 4.87 wt % (or

0.009 mol) PU, which enhances the stability, and excess PU, which behaves in a manner typical of immiscible blends.<sup>9</sup> This implies that using quantities of PU that exceed the stoichiometric ratio will not improve performance:

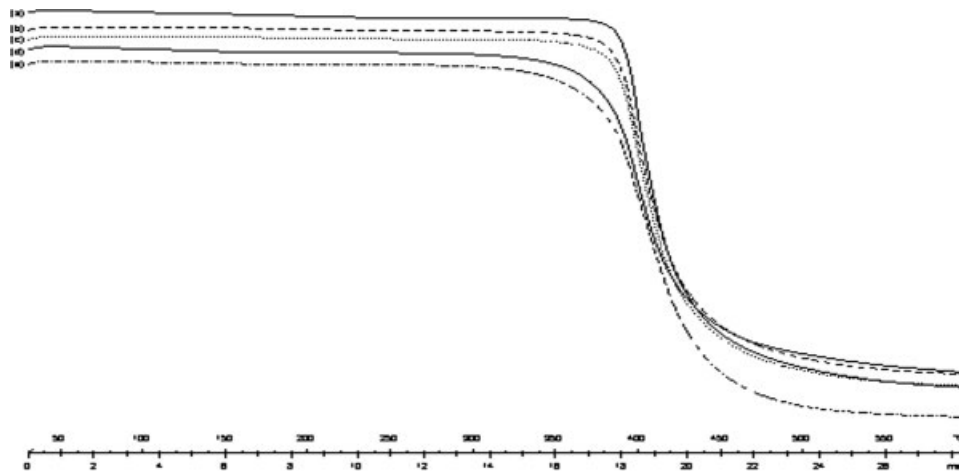


The additional crosslink contributed by the incorporated PU also affects the rigidity of the thermosets. This is characterized by the PU-modified epoxy thermosets exhibiting improved adhesion, higher flexural modulus and strength, and lower deformation at break than the control. The results of the single-lap-shear and three-point-bending-mode flexural tests are summarized in Table IV. The adhesion of 4.87% PU-modified thermosets measured at 5.65 MPa versus 3.27 MPa for the control shows an improvement. Generally, an increase in the crosslink density leads to an increase in the flexural modulus and strength and a decrease in the deformation at break. These results are in good agreement with the notion that chains in PU-modified thermosets are

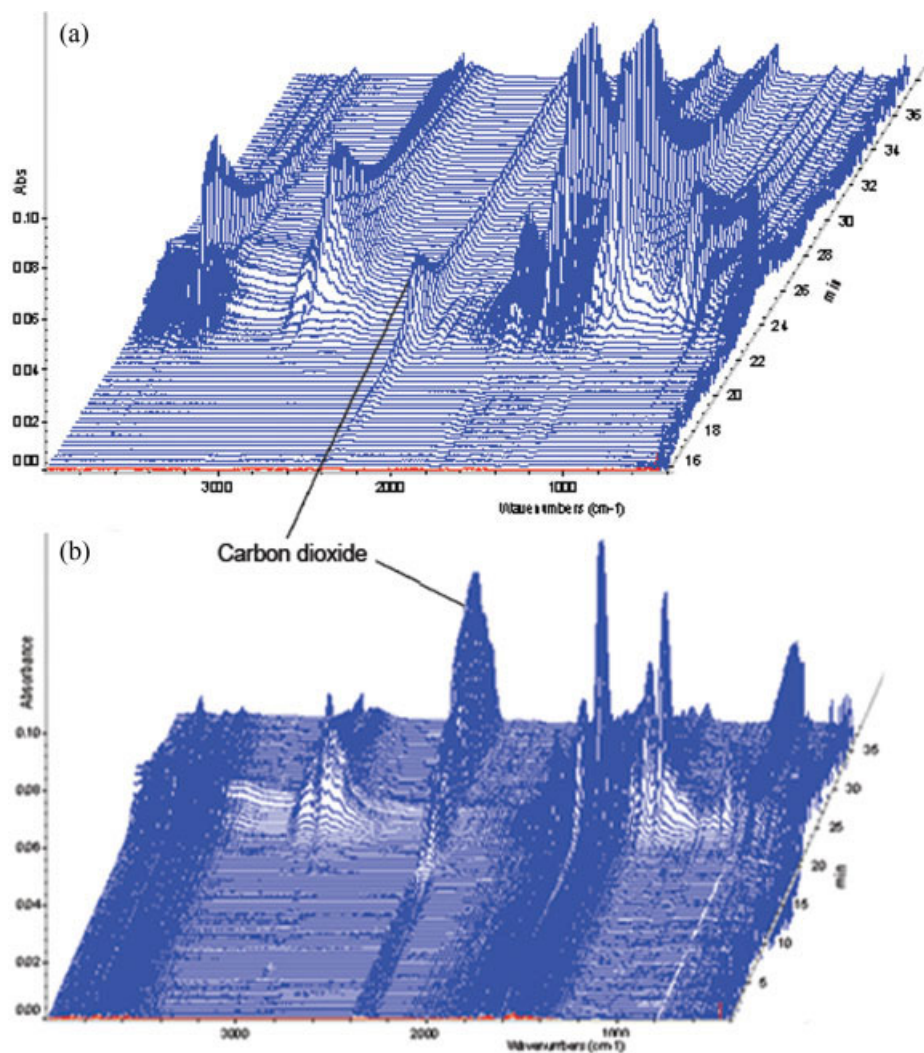
**TABLE V**  
 $T_g$ , CTE, and Storage Modulus Values

Thermoset system	$T_g$ ( $^\circ\text{C}$ )	Storage modulus		CTE	
		Before $T_g$ ( $\times 10^9$ Pa)	After $T_g$ ( $\times 10^7$ Pa)	Below $T_g$ (ppm/ $^\circ\text{C}$ )	Above $T_g$ (ppm/ $^\circ\text{C}$ )
Epoxy (control)	$180 \pm 0$	$1.01 \pm 0.11$	$3.39 \pm 0.34$	$64.4 \pm 0.3$	$158 \pm 1$
PU-epoxy (2.77% PU)	$167 \pm 0$	$1.18 \pm 0.03$	$2.93 \pm 0.13$	$65.9 \pm 0.5$	$171 \pm 1$
PU-epoxy (4.87% PU)	$153 \pm 2$	$1.23 \pm 0.16$	$2.19 \pm 0.06$	$67.8 \pm 0.8$	$168 \pm 1$
PU-epoxy (10% PU)	$139 \pm 0$	$0.92 \pm 0$	$1.49 \pm 0$	$66.9 \pm 0.8$	$161 \pm 3$
PU-epoxy (20% PU)	$90 \pm 0$ $145 \pm 0$	$0.92 \pm 0$	$1.05 \pm 0$	$73.7 \pm 0.2$	$168 \pm 2$

$T_g$  was determined from  $\tan \delta$  of dynamic mechanical analysis, the storage modulus was determined from dynamic mechanical analysis, and CTE was determined from thermal mechanical analysis.



**Figure 7** TGA thermograms of thermoset systems: (a) the control, (b) the PU (2.77%)-modified thermoset, (c) the PU (4.87%)-modified thermoset, (d) the PU (10%)-modified thermoset, and (e) the PU (20%)-modified thermoset.

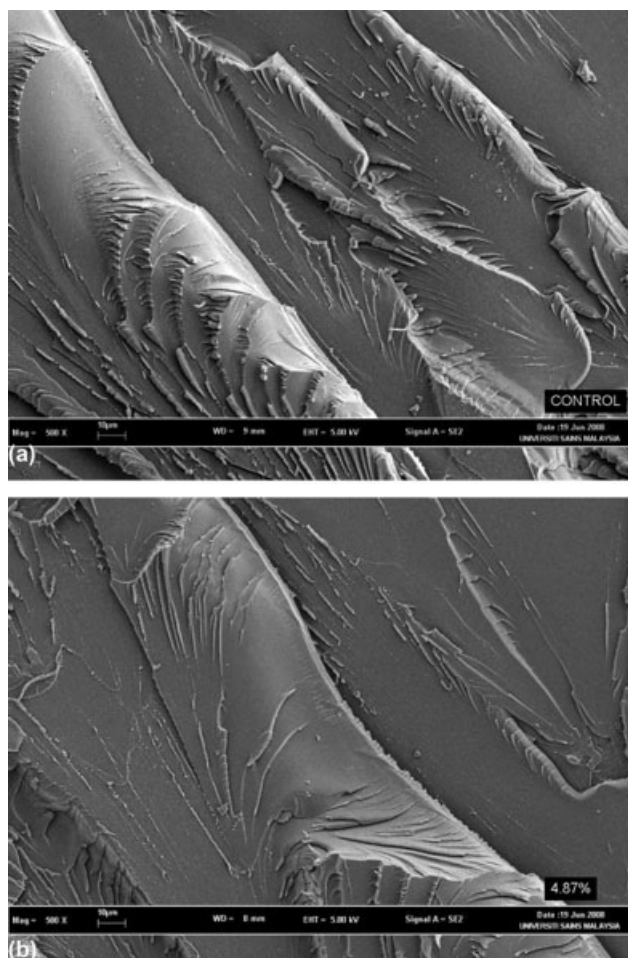


**Figure 8** FTIR spectra of the evolved gas from TGA for (a) the control system and (b) the PU-modified system. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

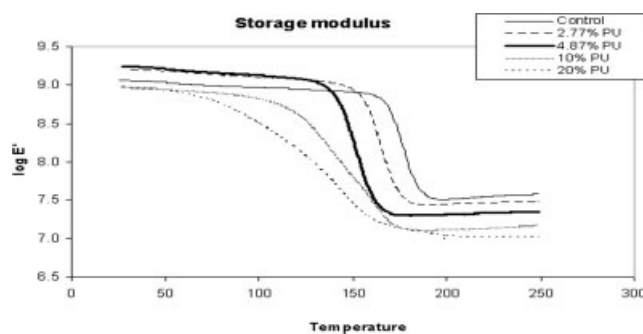


held by additional crosslinks leading to higher overall crosslink density. Figure 9 shows the morphology of fractured surfaces of the thermosets, featuring more closely spaced fracture stripes characteristic of rigid polymers in the control, which confirm the reduced rigidity due to PU.

$T_g$ 's, storage moduli, and CTEs of the PU-modified thermosets are summarized in Table V, whereas dynamic mechanical analysis thermograms depicting the storage modulus of the thermosets are shown in Figure 10. A comparison of the stoichiometric and excess PU-modified thermosets shows the appearance of two glass transitions in the latter. Although this confirms a two-phase nature, there is an obvious decreasing  $T_g$  trend with a higher PU loading, an indication that the systems are not completely immiscible epoxy/PU blends but instead are partially miscible and dependent on the PU loading. This behavior is believed to be influenced by the average effect of the structural change and excess PU, as mentioned earlier. As for the stoichiometric thermosets, a single glass transition can be observed,



**Figure 9** Fractured surface morphology of (a) the control system and (b) the PU-modified system.



**Figure 10** Dynamic mechanical analysis thermograms depicting the storage modulus ( $E'$ ) of the thermoset system.

decreasing with increasing PU loading, and this is influenced mainly by the structural change. In all, the plasticizing effect imposed by PU chains on the thermosets is dominant. As for the glassy storage modulus, it increases with the PU loading for the stoichiometric thermosets. Generally, this is associated with reduced segmental mobility, thus confirming the occurrence of a higher crosslink density with increasing PU content and in comparison with that of the control. However, for the thermosets in which PU was in excess, a reversing trend was noted, with a modulus equal to  $9.2 \times 10^8$  Pa noted for both 10 and 20% PU versus  $10.1 \times 10^8$  and  $12.3 \times 10^8$  Pa for the control and 4.87% PU-modified thermosets, respectively. As for UF applications, the modulus trend is more acceptable if the incorporated PU is within the stoichiometric ratios.

The plasticizing effect of PU is also apparent in the thermosets' CTEs. As shown in Table V, the CTE increases with increasing PU content in both stoichiometric and excess PU thermosets, although it is less differentiated in comparison with the glass transition and modulus. Overall, the trend (CTE1 and CTE2 denote values below and above  $T_g$ , respectively) is not in the desired direction. Nevertheless, the result demonstrates that a small amount of PU (as little as 2.77 wt %) is capable of affecting the CTE of PU-epoxy thermosets.

## CONCLUSIONS

A PEG400-HDI-based PU precursor chemically incorporated into a conventional epoxy system as a pre-crosslinker in stoichiometric ratios improved the thermal stability, contact angle, and cure onset temperature of an epoxy resin. The observed increase in the viscosity was, nevertheless, within the processable range. The PU-epoxy thermosets cured with MDA also showed improved thermal stability and flexural and adhesion strength as well as higher storage modulus, all of which are desirable

properties for UF material applications. The CTE values of the thermosets invariably showed that a small amount of the PU precursor, even as little as 2.77 wt %, affected the CTE of the system, albeit not in the desired direction. Nevertheless, this suggests that with the right PU structures and composition, it is possible to modify the epoxy system into a UF material with suitable CTE and wetting properties that is capable of dispersing nanosized silica particles. The results also show that the incorporation of PU beyond its stoichiometric quantity is not favorable.

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