

Synthesis and Properties of Poly(Urethane-Imide) Diacid/Epoxy Composites Cured with an Aziridine System

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ABSTRACT: A poly(urethane-imide) diacid (PUI), a diimide-diacid with a soft structure unit, was directly synthesized from the reaction of trimellitic anhydride and isocyanate terminated polyurethane prepolymer. FT-IR and NMR were used to characterize its chemical structure. Then PUI was blended with two types of epoxy resins with different chemical structures, diglycidyl ether of bisphenol A (DGEBA) and novolac epoxy (EPN). After curing the blends with polyfunctional aziridine CX-100, novel polyurethane/epoxy composites were obtained as transparent yellowish films. Thermal, chemical, and mor-

phological properties of the cured composites were investigated using thermal analysis, SEM, TEM, chemical resistance, respectively. All experimental data indicated that epoxy modified PUI composites possessed higher thermal stability than that unmodified PUI, and that modified PUI had much better chemical resistance. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 2628–2637, 2009

Key words: poly(urethane-imide); structure; epoxy resin; composites; morphology; thermal properties; chemical resistance

INTRODUCTION

Various polyurethane (PU) compositions, particularly elastomers, have been shown some unique properties, including excellent elasticity, excellent abrasion resistance, high impact strength, and elongation, which have been widely used in adhesives, coatings, synthetic leather, construction, automotive applications, and shoe soles. However, the poor thermal stability, low hydrolysis resistance of various PUs, particularly the polyesterurethane elastomers¹ had greatly limited their commercial use for lack of mechanical modulus and thermal resistance, especially where the PU compositions were used in a hot and humid atmosphere. To obtain a synergistic well-balanced property profile of the PU elastomers for various applications, various attempts have hence been made to improve the thermal and mechanical properties of the PU elastomers.² An effective way to improve the thermal stability of PUs was the modification of their structures by blending or copolymerizing with thermally more stable polymers. Polyimides were a class of aromatic heterocyclic polymers with excellent heat resistance and mechanical properties. However, their some disadvantages such as brittleness and low processability limited their application in modifying PU. As alter-

natives to those polyimides, chemical modification of PU chains with a thermostable heterocyclic imide structure had been mostly accepted for improving thermal stability^{1–9} due to the unique properties of polyimides mentioned above. The combination of flexible PU and thermostable polyimides had resulted in composites with better retention of properties at elevated temperatures than PUs and, at the same time, imparted some flexibility to polyimides.

Epoxy resin was another resin used to improve PU thermostability, because of their high thermal resistance, high tensile strength and modulus, and good chemical resistance. Compared to the deficiencies of each individual resin, epoxy-PU composites had some improved properties, such as tensile strength, flexural strength, tensile modulus, flexural modulus^{10,11} mostly due to the formation of interpenetrating polymer network (IPN)^{10,12–14}. Although a lot of works had been done on the synthesis and properties of PU-epoxy composites, most of them had focused on improving the brittleness of epoxy resins, their thermostability had a little report,¹⁰ possibly due to the lower temperature stability of PU-epoxy composites than that of pure cured epoxy resins, leading to a reduction in the useful temperature range and overall resin modulus. The reasons could result from the poor thermal stability of PU.

Similarly, imide-diacids, new compounds having concurrently rigid imide structure and reactive carboxyl acid, had shown a promising application in improving PU's thermal stability¹⁵ and modifying

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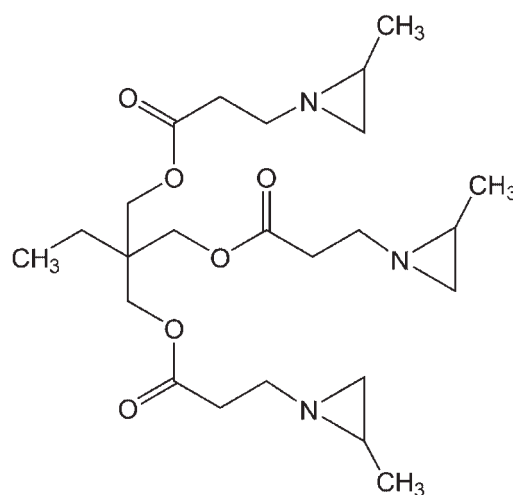
epoxy resin to improve thermal properties, mechanical properties.^{16–24} However, some of the drawbacks to the employment of these high performance compounds, especially diimide-diacids, were their high melting temperatures and lower solubility in common solvent, correspondingly, an elevated reaction temperature was always needed, such as in addition reaction between carboxylic of diimide-diacids and epoxy groups of epoxy resins including DGEBA and EPN. And also, epoxy-imides were generally brittle in nature, which limited their room temperature adhesive strength. On contrary, diimide-diacids containing soft blocks such as oligomers had much improved solubility and lower glass transition temperature, due to the existence of the flexible linkages, so its corresponding polymers showed nice balance of properties including low glass transition temperature, improved solubility, good thermal stability,²⁵ and even improved ductility.²⁶

Based on imide structure incorporating soft PU chain and epoxy modifying PU mentioned above, here imide structure and epoxy resin were jointly incorporated into PU to extend the properties of the new PU/epoxy composite. For that, a diimide-diacid containing flexible ether was firstly synthesized through direct reaction of two moles of trimellitic anhydride (TMA) with one mole of NCO-terminated PU prepolymer. Chemical structure of the resultant was characterized with FT-IR and NMR analysis. The resultant was then directly polycondensed with different types of epoxy resins (DGEBA and EPN) via a polyfunctional aziridine crosslinker to obtain PU/epoxy composites containing rigid imide structure and flexible ether unit. The microstructure and the some properties of the PU/Epoxy composites were studied by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and chemical immersion. The thermal stabilities of the generated materials were also discussed with thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

TMA from Acros Co. was purified by heating at 150°C for 4 h under dynamic vacuum. Isocyanate terminated PU prepolymer (PU, Rubinate[®] 9272, a polyether PU prepolymer, NCO % = 8.5 %, Huntsman Co., China), polyfunctional aziridine CX-100 (chemical name: trimethylolpropane tris-(1-(2-methyl) aziridino) propionate, structure shown as Scheme 1, equivalent weight: 166, DSM NeoResins) were directly used. Epoxy resins, namely, Araldite[®] GT 7071 (DGEBA, epoxide equivalent weight: 500–525 g/eq, difunctional) and DEN 431 (EPN, epoxide equivalent weight: 172–179 g/eq, polyfunctional)



Scheme 1 Chemical structure of CX-100.

manufactured and supplied by Huntsman Co., China and Dow Co., China, respectively, were used as received. All other organic solvent were analytical reagents, and purified according to common procedure except toluene, which was directly used without any treatment. 50% (wt %) toluene solution of GT 7071 and DEN 431 was obtained, respectively, before usage.

Synthesis of poly(urethane-imide) diacid (PUI)

The PUI resin, resultant from PU prepolymer reacting with TMA, was prepared directly by reaction of Rubinate[®] 9272 PU with TMA in *N,N'*-dimethylformamide (DMF) without any catalyst. Details about the preparation were given below. A solution of TMA 15.36 g (80 mmol) in dry DMF (40 mL) was heated in a 500 mL flask equipped with a mechanical stirring bar, a dropping funnel, a condenser and an argon inlet in an oil bath at 50°C. A solution of Rubinate[®] 9272 42 g (40 mmol) in DMF (60 mL) was added dropwise with constant stirring. After addition, the reaction mixture was kept for 30 min at this temperature, then heated to 80°C and kept for another 5 h, then to 100°C. During these stages, a rather strong evolving of CO₂ was observed. This corresponded to the formation of the imide rings by elimination of CO₂ from the C7-cyclic intermediates obtained during the reaction of isocyanate groups with aromatic dianhydrides.^{27,28} After the cease of elution of CO₂, the mixture was kept another 30 min at 100°C, then the reaction was stopped, and a yellow solution (35.3 wt %) was obtained. One part of the resulted solution was directly used to prepared PU-epoxy as following. Another part of solution was poured into 200 mL of water to precipitate the polymer. After washed twice in cold water and dried under dynamic vacuum at 90°C for 4 h, a clear and yellow product, PUI, was obtained, which was

TABLE I
Recipe for the Preparation of PU-Epoxy Resins

Run	Epoxy type	PUI content (g) (wt % ^a)	Epoxy content (g) (wt % ^a)	CX-100 (g)
PUI	–	5.0 (100)	0	0.44
PUI/EP	DGEBA	5.0 (70.2)	1.5 (29.8)	0.44
PUI/EPN	Novolac	5.0 (79.0)	0.94 (21.0)	0.44

^a Weight content in total weight of PUI + epoxy.

stored in a desiccator for structural characterization. Characterization was done by estimation of the acid value via acid–base titration. The acid value of 617.5 g/eq for the product corresponded closely to the theoretical values (673.1 g/eq), which confirmed the completeness of the imidization reaction.

Preparation of PUI/epoxy composites

All the PUI/epoxy composites were prepared from stoichiometric mixtures of PUI, epoxy resin (DGEBA and EPN), and the crosslinker CX-100. A detailed procedure was indicated as following.

After mixing thoroughly 5.0 g of PUI solution obtained as above with equal equivalence of CX-100, epoxy resin solution at ambient temperature, the mixture was cast on to a PTEF mould and the solvent evaporated at room temperature for 24 h. The films formed were then heated in oven at 60°C for 24 h. The obtained films were transparent and yellow in color, and stored in a desiccator for characterizations. The detailed formulation was shown in Table I, where PUI/EP would be the composite with DGEBA and PUI/EPN would be the composite with Novolac epoxy.

Polymer characterizations

FT-IR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer using thin polymeric films cast on KBr disks. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz and 100 MHz, respectively. All the NMR experiments used polymer solutions in DMSO-d₆.

Morphology of the fractured surface of the sample with a thickness of 1–1.5 mm was studied with a JSM 5600 LV SEM. The samples were cooled in liquid nitrogen, fractured with a sharp blow, and the fractured section was coated with gold before examination. Transmission electron micrographs (TEM) were taken with an H-800 TEM at an accelerating voltage of 20 kV. TEM specimens were stained with RuO₄ and sectioned with a diamond knife at ambient temperature.

The thermal stability of the cured composites films was assessed by thermogravimetric analysis using a TGA 951 thermal system. For the analysis, films were cut into small pieces and about 10 mg of sample was

taken and heated at a constant rate of 10°C /min in nitrogen atmosphere from 25 to 750°C. Differential scanning calorimetry (DSC) was performed from 25 to 200°C at a heating rate of 10°C/min under nitrogen atmosphere with NETZSCH DSC 200.

Water and toluene resistances of the cured films were measured as follows.²⁹ Dry films (20 × 10 mm²) were immersed in deionized water and in toluene for 7 days to study water resistance and xylene resistance at 25°C. After immersion, the samples were blotted with a laboratory tissue and weighed *m_s*. Later, samples were dried under dynamic vacuum for 24 hrs at ambient temperature and weighed again (*m_d*). Weight change (Δm) was calculated as:

$$\Delta m(\%) = \frac{(m_s - m_d)}{m_d} \times 100$$

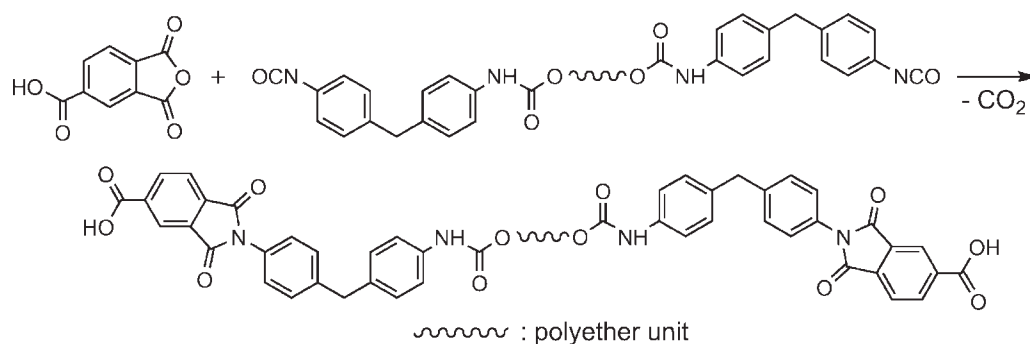
Chemical resistance of cured specimens was performed in acid (10 wt % H₂SO₄), alkali (10 wt % NaOH), and salt (10 wt % NaCl) solutions. Samples with a size of 30 × 30 mm² were weighted (*m_i*) and immersed in afore-mentioned solution of 250 mL in sealed bottles at room temperature, respectively. After 7 days, all of samples were taken off, cleaned with water stream, continually soaked in water for 1 week to remove all of salt in the sample, then treated as those in water, lastly their weight were obtained (*m_s*). Weight change (Δm) used to indicate the chemical resistance of all samples was gotten according to the following equation,

$$\Delta m(\%) = \frac{(m_s - m_i)}{m_i} \times 100$$

RESULTS AND DISCUSSION

Synthesis and structure characterizations of PUI

Diimide-diacids, including the synthesis of diimide-diacid containing flexible units,²⁵ was always obtained from reacting two moles of TMA with one mole of diamine via thermal imidization or chemical imidization. In the present work, the poly(urethane-imide) diacid (PUI) was directly obtained from NCO-terminated PU prepolymer with TMA. Compared with the traditional route involving diamine



Scheme 2 Synthesis of PUI.

and anhydride,²⁵ the advantage of using isocyanate instead of the conventionally used amine was that imidization was achieved in a single-step at a relatively lower temperature (such as 80°C³⁰), avoiding handling polyamic acid intermediates, so providing a very efficient way of combining the chemistry of PUs with that of polyimides. The method was therefore utilized to introduce imide function into the PU backbone and corresponding PU-imide,^{1,3,9,31–35} offering a very broad range of macromolecular architectures.³⁶

Scheme 2 gave a simple route to show the reaction of TMA and PU prepolymer, from which PUI was directly obtained.

Clearly, during the route above, the two reactions should be considered including isocyanate reacting with carboxylic acid and anhydride. It was well known that isocyanate could react carboxylic acid to form amide and simultaneously release CO₂. However, it was only some catalyst³⁷ at lower temperature or higher temperature (such as 120°C) without catalyst³⁸ that favored the reaction of carboxylic groups with diisocyanate. Also, there existed much higher reactivity of anhydride compared to carboxylic acid when reacting with isocyanate was accepted.³⁸ Therefore, to make the main reaction (anhydride reacting with –NCO) proceed smoothly, while restraining the side reaction such as –NCO reacting with –COOH of TMA during chain-extending reaction, here a three-step chain-extending procedure without the addition of catalyst was used, involving a reaction at 50°C followed by a reaction at 80°C, then at 100°C. That was to say, lower temperature made most of isocyanates be captured by the anhydride group of TMA resulting in seven-member-ring intermediate (there was an intermediate of seven-member-ring between the reaction components and the imide compound²⁸), the intermediate was then transferred into imide structure at a higher temperature, giving the carboxylic acid-ended polyimide oligomers. Here the results of FT-IR, NMR below and the acid value, much close to the theoretical values, supported the formation of

the expected compounds except a trace of the resultant from the reaction between –COOH and –NCO.

FT-IR spectroscopy

FT-IR is a convenient instrument to trace the reaction of isocyanate with anhydride to prepare PU-imide copolymer.³⁹ The FT-IR spectrum for PUI prepared from Rubinate[®] 9272 PU prepolymer and TMA was shown in Figure 1. The characteristic peak at 2274.8 cm⁻¹ (N=C=O group stretching) of PU prepolymer and peak as 1862.5 cm⁻¹ of TMA (C=O stretching of anhydride) were not observed, whereas the absorption bands at 1778.4 cm⁻¹ and 726.3 cm⁻¹ were clearly noticed, which were characteristic bands of imide bonds (stretching vibration of the carbonyl groups of five-membered imide rings, out-

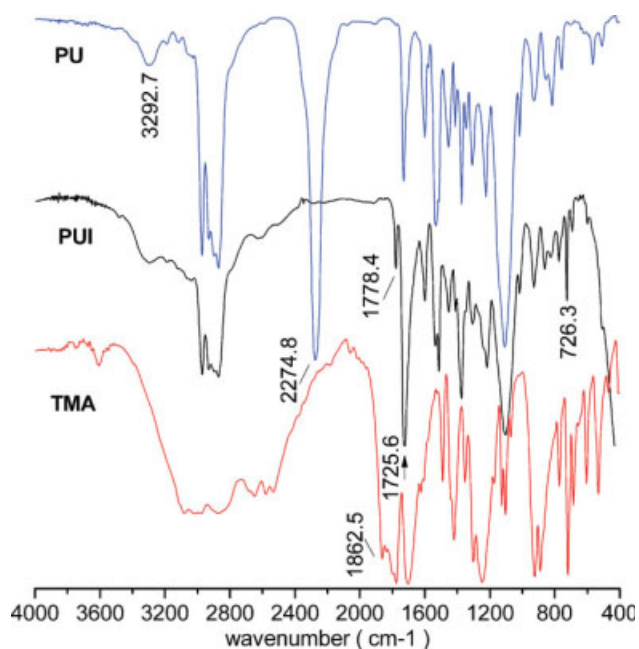


Figure 1 FT-IR spectra of TMA, PU prepolymer, and their resultant (PUI). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

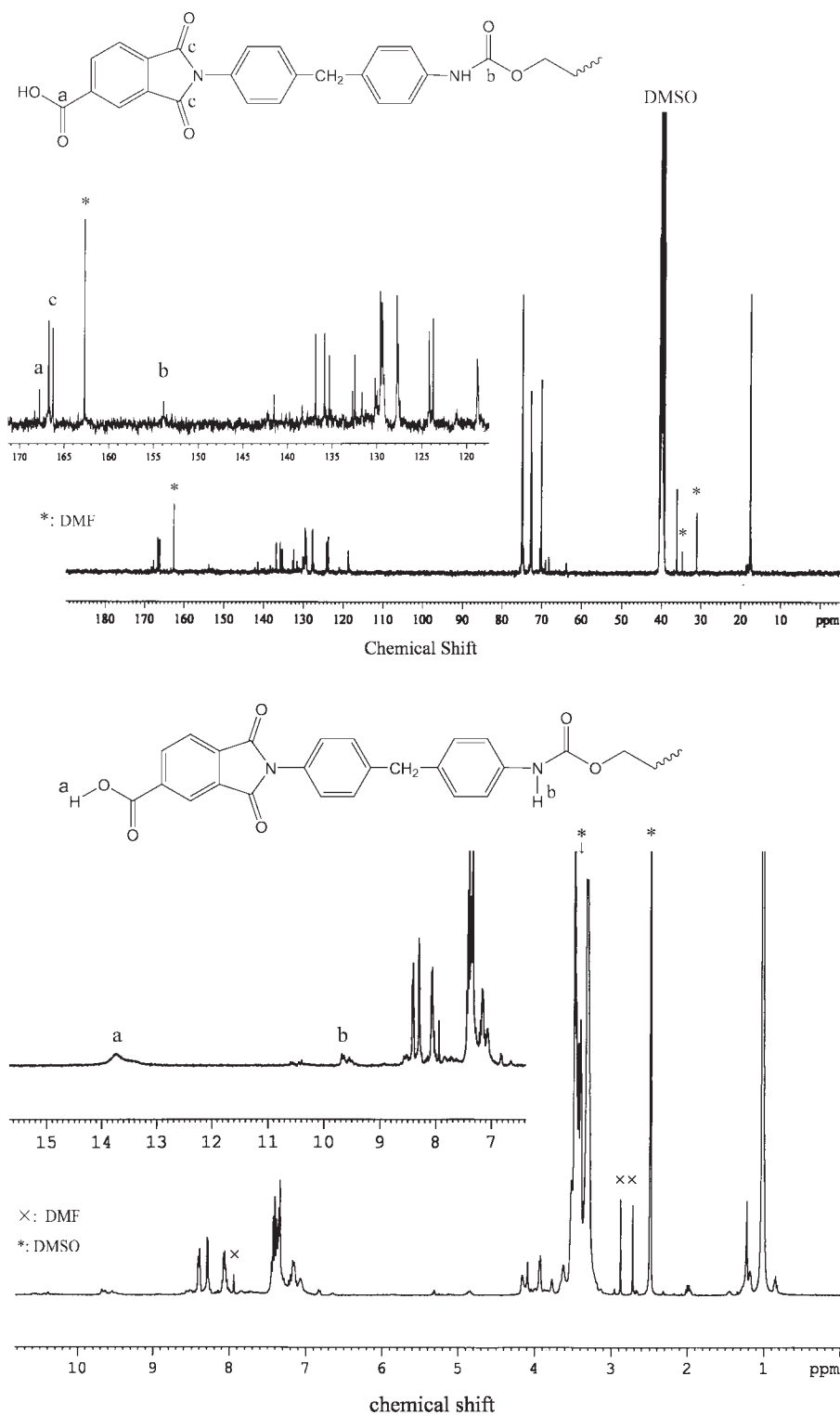
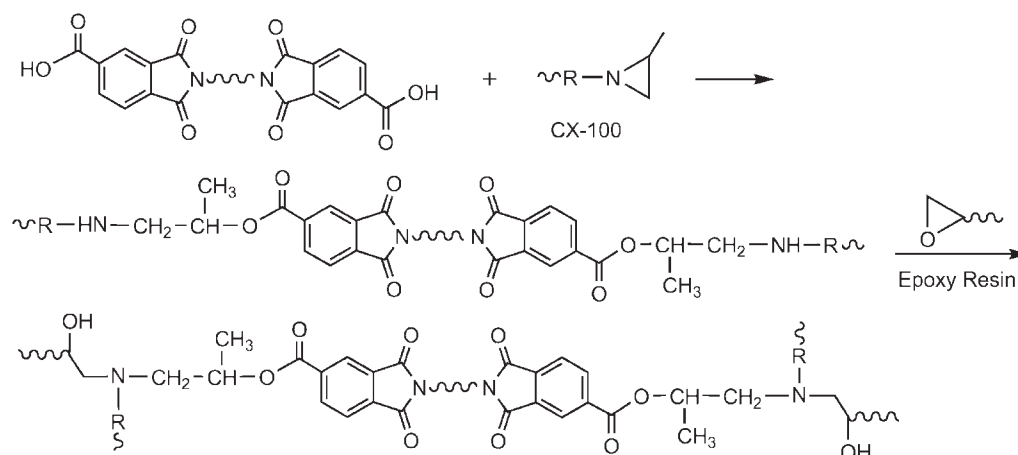


Figure 2 ^1H NMR and ^{13}C NMR spectra of PUI.

of-plane deformation of the imide $\text{C}=\text{O}$ groups, respectively), confirming that imide group was introduced to synthesize PU-imide backbone; and the absence of residual anhydride and $-\text{NCO}$ also indicated that the NCO groups were completely reacted with anhydride groups. Of course, urethane groups were also easily identified by their four main

characteristic bands as followings: 3292.7 cm^{-1} ($-\text{NH}$ groups stretching, broad), 1725.6 cm^{-1} (the amide I band, very strong intensity), 1534.7 cm^{-1} (the amide II band, medium intensity), and 1217.5 cm^{-1} (the amide III band, strong intensity). Moreover, the polyether soft block was also easily characterized by peaks of medium intensity appearing in



Scheme 3 Curing of PUI/epoxy composite.

the spectral region $2800\text{--}3000\text{ cm}^{-1}$ typical of the methylene stretching, and a strong band at 1108.9 cm^{-1} corresponding to the stretching vibration of the ether groups. The characteristic peak of —COOH of PUI could be found in the region of around 1725.6 cm^{-1} and 3292.7 cm^{-1} , although they were overlapped with other groups.

NMR analysis

To further verify the chemical structure of the resultant, ^1H and ^{13}C NMR of the sample were done in DMSO- d_6 and shown in Figure 2. In the proton spectrum, apart from some characteristic peak could be found, for example, urethane protons were observed at 9.68 ppm; the aromatic protons from the MDI of Rubinate[®] 9272 showed at 7.13–7.44 ppm; the aromatic C–H groups from TMA showed at 8.03–8.52 ppm; the peaks around 0.83–1.22 ppm and 3.42–4.17 ppm were assigned to the methylene protons from ether of Rubinate[®] 9272, a weak and broad peak at 13.81 ppm was also observed, which was characteristic position of O–H of acid, indicating the existence of carboxylic acid in the product.

Similarly, in the carbon spectrum, 153.8 ppm assigned to carbon from *N*-amide, 167.8 ppm to carbon from 1-carboxyl and 166.7 ppm, 166.3 ppm to carbon from C=O of *N*-imide could be clearly observed, indicating the existence of carboxylic acid and imide group.

These data from NMR, FT-IR, and the acid-base titration fully verified the molecular structure of the product was in accord to proposed structure, although there might exist the side reaction such as —NCO reacting with —COOH of TMA, because the acid value of 617.5 g/eq of the product was slightly smaller than that of the theoretical values 673.1 g/eq.

Curing of PUI/epoxy composites

To decrease the curing temperature, here a polyfunctional aziridine, namely CX-100, was chosen to cure PUI and epoxy resin to give new PU/epoxy composites.

Different from diacid reacting with epoxy at elevated temperature, aziridines reacted very quickly with nucleophilic materials such as carboxylic groups, where the nucleophile attacked and opened the ring to form a secondary amine. The crosslinking reaction of aziridine and carboxylate occurred at a reasonable rate at ambient conditions during the drying process or when pH value dropped below 6,^{40,41} so no heat or catalyst was necessarily needed to complete the cure.⁴² Moreover, the formed secondary amine could react with epoxy groups of epoxy resin much easily, so it here provided a very efficient way of combining the chemistry of PUs with that of polyimides and epoxy resins, offering a very broad range of macromolecular architectures. Scheme 3 showed a simple route of PUI reacting CX-100 to form a secondary amine, secondary amine then reacting with epoxy groups to form a complicated network structure.

Morphological properties

The microstructure of composite was dependent on the interactions between the continuous phase and the dispersion phase. Figure 3 showed the morphology changes after incorporating epoxy resins. Clearly, these three composites had homogeneous structures in this magnification due to the existence of some strong chemical interactions via covalent bond as Scheme 3. To understand the difference, here TEMs shown in Figure 4 were obtained via vapor-staining by RuO_4 . Interestingly, the unmodified PUI system had a uniform structure over the

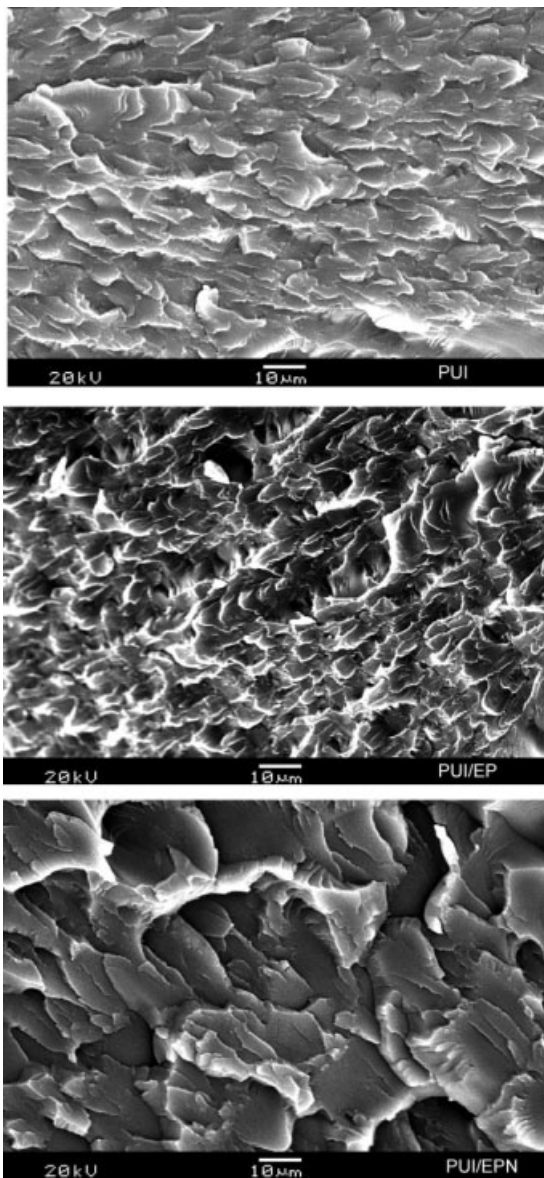


Figure 3 SEM of unmodified PUI, PUI/EP, and PUI/EPN.

entire area; PUI/EP system was much close to uniform except several much faint dark dots, which were too faint to distinguish their existence. Although in PUI/EPN system, very small dark spots with about 200–300 nm in size could be observed, where the dark domain on the photographs was the epoxy resin networks, the white domain was the PUI networks. These phenomena could be thought to be resulted from the following reasons. In epoxy modified PUI system, the difference of solubility parameter value between cured PUI and cured epoxy resins made cured epoxy resins microscopically separate from the cross-linked matrix during curing procedure. However, the existence of covalent bond and other polar groups between PUI and epoxy resins gave some strong

interactions between them, resulting in much faint interface. Especially, in PUI/EP, there might be much more polar groups in PUI/EP than those in PUI/EPN, such as OH groups, that is, the much stronger interface interaction between PUI and EP in PUI/EP made the cured EP much easily disperse well in PUI matrix.

Thermal studies

Thermal behavior and properties of the cured composites were studied by DSC, TGA. The thermal transitions of the composites were shown as

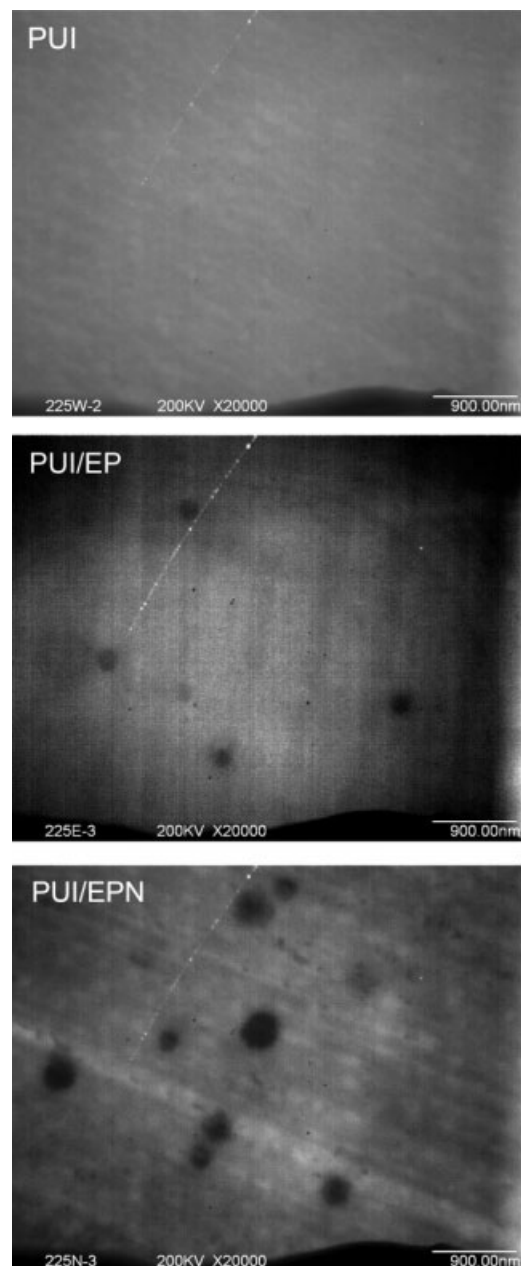


Figure 4 TEM of of unmodified PUI, PUI/EP, and PUI/EPN.

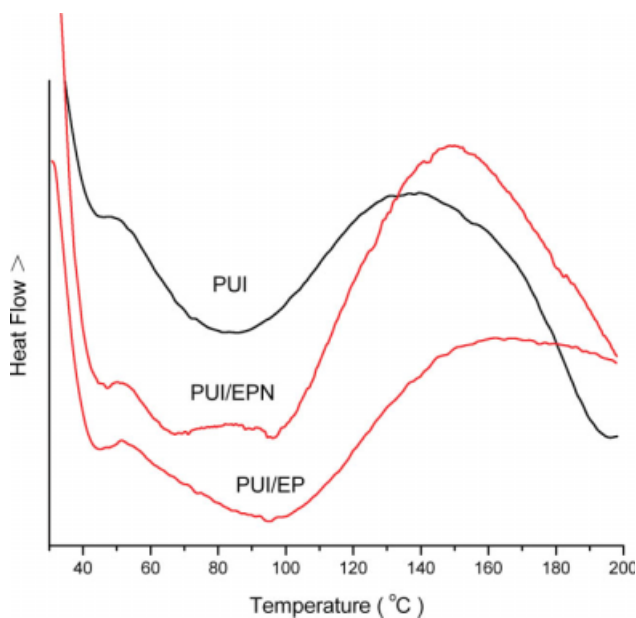


Figure 5 DSC thermograms of the unmodified PUI, PUI/EPN, and PUI/EP composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5. Clearly, none of the composites showed clear melting endotherms in the DSC thermograms. This could be attributed to the amorphous nature of the composites. But there was a distinct difference among them, where the endotherm peak of PUI and PUI/EP was at 84.2°C and 94.8°C, respectively, but PUI/EPN had two peaks at 65.5°C and 95.5°C. This was indicative of the incompatible nature in PUI/EPN, where the EPN and PUI segment domains existed in two-phase morphology. This phenomenon was similar to TEM as above.

TGA analysis was used for evaluation of thermal stability of the cured composites. Figure 6 (a) showed the thermal decomposition of these composites. From Figure 6 (a), it could be shown the epoxy resins modified PUI possessed good thermal stability than unmodified PUI. Due to the existence of epoxy, temperatures at 5 %, 10 % weight loss were greatly improved, from 230.3°C, 276.7°C of unmodified PUI to 257.5°C, 309.6°C of PUI/EPN, 264.7°C, 323.8°C of PUI/EP, respectively.

To understand the difference in the degradation behavior of unmodified PUI and epoxy modified PUI composites, which were difficult to distinguish just from TGA curves, first derivative of thermal gravimetric analysis curve versus temperature thermograms, that is, DTGA curves were obtained with Origin software, and the temperatures at the maximum weight loss rate (T_{max}) and weight loss value at T_{max} (W_{max}) were read from the peak values of the DTGA thermograms, respectively, and listed in Table II. Clearly, it revealed in DTGA that the all

cured polymers had two similar peaks below 400°C, but unmodified PUI had another shoulder peak around 440°C, whose intensity was relatively weaker. These peaks could be attributed to several different degradation stages as following.

Decomposition of unmodified PUI showed a three-step decomposition profile with the onset of the first step around 175°C, maximum rate of weight loss at 238.7°C, corresponding to the simple decomposition of the urethane segment.¹ The second stage of degradation corresponded to the decomposition of soft polyether segment, which started above 300°C and the maximum rate of weight loss at 380.1°C. The third step corresponds to the degradation of advanced fragments produced after the

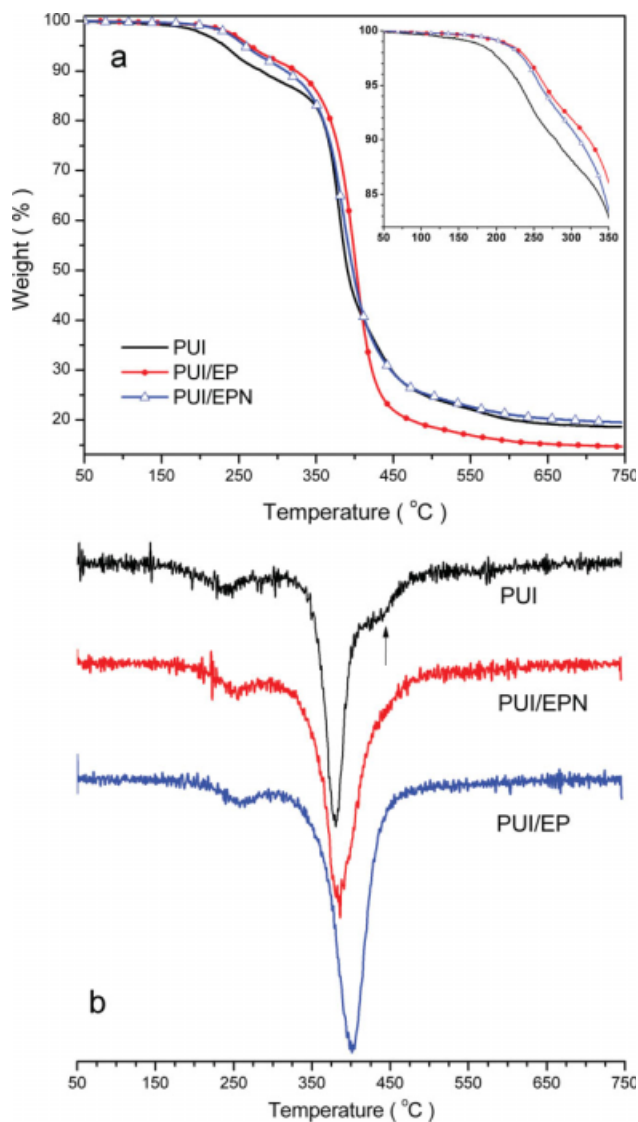


Figure 6 Dynamic thermograms of the unmodified PUI, PUI/EPN, and PUI/EP composite materials (a) and first derivative curves of the dynamic thermograms of the materials (b) in nitrogen. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Thermal Gravimetric Analysis of PUI/Epoxy Composite Films in N₂ Atmosphere

Sample	$T_d^{5\%}$ (°C)	$T_d^{10\%}$ (°C)	T_{max}^1 (°C)	W_{max}^1 (%)	T_{max}^2 (°C)	W_{max}^2 (%)	T_{max}^3 (°C)	W_{max}^3 (%)	Residual at 750°C (%)
PUI	230.3	276.7	238.7	5.8	380.1	38.3	443.5	69.0	18.6
PUI/EPN	257.5	309.6	255.6	4.6	385.7	39.2	–	–	19.5
PUI/EP	264.7	323.8	260.9	4.6	401.2	48.7	–	–	14.7

$T_d^{5\%}$, Temperature at 5 wt % weight loss; $T_d^{10\%}$, Temperature at 10 wt % weight loss; T_{max} , maximum decomposition temperature; W_{max} , weight loss at T_{max} .

second decomposition step as well as the decomposition of imide rings. This third step of thermal decomposition started above 410°C and ended above 470°C with char residues. Compared with unmodified PUI, epoxy modified PUI showed only a two-step decomposition profile. Similarly, their first steps were corresponded to the decomposition of the urethane segment. In terms of the second stage degradation of the two systems, it could be attributed to the integrated results of decomposition of polyether, epoxy, and imide rings, resulting in that the peak width of the second stage degradation of the two systems was much bigger than that of unmodified PUI. In the two profiles, the onset temperature of the first step was obviously higher than that of unmodified PUI, and the temperature at the maximum rate of weight loss (T_{max}) was much improved. These could be attributed to the following reasons: (1) modified PUI had higher crosslinking density than pure PUI, which would be discussed below; (2) cured epoxy self had much high heat resistance. Accordingly, higher crosslinking density and existence of cured epoxy also jointly improved the T_{max} value at the second decomposition.

Chemicals resistance

For different reasons, chemical resistance is always tested in coating applications by methods⁴³ such as immersion and rub testing. Here, the solvent resistance of the three cured films was tested with immersion test. The weight change of samples was listed in Table III, and it was also experimentally shown that the color of samples was not any changed after immersed in toluene, water, and 10% NaCl, and less

TABLE III
The Solvent Resistance of Cured Free Films

Solvent	Weight change (Δm)		
	PUI	PUI/EP	PUI/EPN
Toluene	+48.38	+40.82	+40.27
Water	–12.04	–3.78	–4.40
10% H ₂ SO ₄	–17.58	–2.62	–0.29
10% HCl	–8.54	–2.92	–0.23
10% NaCl	–2.02	–3.09	–1.33
10% NaOH	Dissolved	Disrupted	Disrupted

thinned after immersed in 10% H₂SO₄ and 10% HCl. However, after immersed in 10% NaOH, the PUI sample was completely dissolved to form a white sol; the PUI/EPN and PUI/EP samples were disrupted and changed to white and soft solids. The chemical resistance data showed epoxy modified PUI had much better chemical resistance than unmodified PUI in the order of PUI/EPN > PUI/EP > PUI.

Generally, solvent resistance depended primarily on polarity of cured network resins. Immersion in toluene was usually used to access the crosslink density of polymer networks.⁴⁴ Obviously, epoxy modified PUIs had higher crosslinking degrees than PUI self did. The higher crosslinking degree caused a good chemical resistance as shown Table III, because the higher degree of crosslinking indicated the less free volume and segmental mobility remain available in the polymer. Also, the epoxy modified PUI based on novolac epoxy showed much better chemical resistance, this could attributed to high epoxy functionalities of novolac epoxy, which resulted in high crosslinking density of network, decreasing its exposure to environment. However, the chemical resistance in alkaline aqueous solution indicated these cured polymers possessed bad or lower resistance to alkaline aqueous solution although they had good crosslinked networks. The property could be referred to the hydrolysis of ester group –COO–, resulted from –COOH reacting with aziridine, which might be much sensitive to OH[–] compared with H⁺ when ester group hydrolyzed by alkaline or acid catalysis.

CONCLUSIONS

Poly(urethane-imide) diacid (PUI) was successfully synthesized by directly reacting TMA and isocyanate terminated PU prepolymer. FT-IR and NMR were used to characterize the chemical structure of the resultant. Two novel epoxy resins composites, PUI/EP, and PUI/EPN cured with polyfunctional aziridine were prepared. Unlike unmodified PUI cured with aziridine system, both PUI/EP, and PUI/EPN had inhomogeneous morphologies, where nano-sized EP and EPN dispersed well in PUI matrix. Due to incorporating epoxy resins, the crosslinking

density of epoxy modified PUI had greatly been improved, resulting in the improvement of their properties, such as thermal property, solvent resistance. Compared with unmodified PUI, temperatures at 5%, 10% weight loss were greatly improved, from 230.3°C, 276.7°C of unmodified PUI to 257.5°C, 309.6°C of PUI/EPN, 264.7°C, 323.8°C of PUI/EP, respectively. In term of the chemical resistance, the sequence was: PUI/EPN > PUI/EP > PUI.

Work is in progress to assess their other properties such as mechanical, thermomechanical properties, and the effect of epoxy content, and will be presented in the future. Therefore, it is believed that such material would be hopeful for making novel lower temperature-curing sealants, coatings and adhesives for some special purposes.

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