Thermal and Mechanical Properties of Poly(urethane-imide)/Epoxy/Silica Hybrids

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ABSTRACT: Improving properties of polyurethane (PU) elastomers have drawn much attention. To extend the properties of the modified PU composite, here a new method via the reaction of poly(urethane-imide) diacid (PUI) and silane-modified epoxy resin (diglycidyl ether of bisphenol A) was developed to prepare crosslinked poly (urethane- imide)/epoxy/silica (PUI/epoxy/SiO$_2$) hybrids with enhanced thermal stability. PUI was synthesized from the reaction of trimellitic anhydride with isocyanate-terminated PU prepolymer, which was prepared from reaction of polytetramethylene ether glycol and 4,4′-diphenylmethane diisocyanate. Thermal and mechanical properties of the PUI/epoxy/SiO$_2$ hybrids were investigated to study the effect of incorporating *in situ* SiO$_2$ from silane-modified epoxy resin. All experimental data indicated that the properties of PUI/epoxy/SiO$_2$ hybrids, such as thermal stability, mechanical properties, were improved due to the existence of epoxy resin and SiO$_2$. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3722–3728, 2010

Key words: poly(urethane-imide); epoxy resin; silica; thermal stability; dynamic mechanical property

INTRODUCTION

Polyurethanes (PUs) have attracted significant attentions for various industrial applications, and some inferior properties of PU, such as the poor thermal stability, low mechanical strength, and water resistance, can be effectively improved by blending or/ and copolymerizing with more thermally stable polymers, such as polyimides (PIs), epoxy resins. It has been reported epoxy-polyurethane composites have some improved properties, such as tensile strength, flexibility, tensile modulus, flexural modulus,[1,2] mostly due to the formation of interpenetrating polymer network structure.[1,3–5] However, in PIs modifying PU, PIs are less used directly as a result of some disadvantage like the lack of processability, although PIs have excellent heat resistance and mechanical properties. Alternatively, chemical modification of PU chains with a thermostable heterocyclic imide group has been mostly accepted,[6,7] resulting in the PU/PI composites with better retention of properties at elevated temperatures than PUs. Among these attempts to incorporate PI units into PUs, reaction of isocyanate or blocked isocyanate-terminated PU prepolymer with anhydride[6,8–12] is mostly used. Because of the existence of the flexible linkages, these corresponding PU/PI composites tend to show fairly good balance of properties including low glass transition temperature, improved solubility, good thermal stability,[13] and even improved ductility.[14]

Introducing silica into PU to form PU hybrids via *in situ* or blending method has also evoked much interests, because they combine the advantages of organic polymers (flexibility, ductility, dielectric strength, etc.) and of inorganic materials (rigidity, high thermal stability, etc).[15–17] This makes PU/SiO$_2$ hybrids possess good mechanical properties, such as medium tensile strength and high elongation. Compared with blending method, *in situ* method through sol–gel process causes much stronger interactions between organic and inorganic phases, correspondingly gives PU/SiO$_2$ much improved properties, and mostly is accepted.

At the same time, PU composites containing imide structure and epoxy resins were reported in our previous works,[18] where the modified PU showed higher thermal stability and much better chemical resistance, due to the existence of imide structure and the interaction between PU and epoxy resins through chemical bonds. Based on these data, here the work in this study was designed to jointly incorporate imide structure, silica and epoxy into PUs for improving the thermal stability, and extending the properties of the new PU/epoxy/silica composite.

TABLE I
List of Raw Materials Used in the Preparation of the Hybrids

Designation	Chemical description	Suppliers
TMA	trimellitic anhydride	Acros Co., Belgium
MDI	4,4′-methylene bisphenylisocyanate (Rubinate® 2020, NCO% = 29.45%,)	Huntsman Co., China
PTMEG	polytetramethylene ether glycol (OH value: 112 mgKOH/g)	Invista Co., China
CX-100	trimethylolpropane tris-(1-(2-methyl) aziridino) propionate (equivalent weight 166 g/eq)	DSM NeoResin, The Netherlands
EP	diglycidyl ether of bisphenol A epoxy resin (Araldite® GT 7071, epoxide equivalent weight 500–525 g/eq)	Huntsman Co. China
IPTES	3-isocyanatopropyltriethoxysilane	Shinetsu Co. Japan

For that, a carboxyl-terminated poly(urethane-imide), poly(urethane-imide) diacid (PUI), was directly synthesized from the reaction of trimellitic anhydride (TMA) with isocyanate-terminated PU prepolymer based on polytetramethylene ether glycol (PTMEG) and 4,4′-diphenylmethane diisocyanate (MDI). The as-synthesized PUI was then directly polycondensed with silane-modified epoxy resin (diglycidyl ether of bisphenol A) via a polyfunctional aziridine crosslinker and sol–gel process to obtain new PUI/epoxy/SiO₂ hybrids. Chemical structure of PUI was characterized with FTIR and NMR analysis, and the thermal and mechanical properties of the obtained PUI/epoxy/SiO₂ crosslinked hybrids were studied with thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA).

EXPERIMENTAL

Materials

The raw materials used in this study were presented in Table I. TMA was purified by heating at 150°C for 4 h under dynamic vacuum; PTMEG and EP were dried before usage under vacuum at 100°C for 1 h, 60°C overnight, respectively. The others were used as received. All other organic solvent were analytical reagents and purified according to common procedure.

Characterizations

FTIR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer. ¹H- and ¹³C-NMR spectra were done on a Bruker Avance 400 spectrometer at 400 MHz and 100 MHz, respectively. All the NMR experiments used polymer solutions in DMSO-d6.

TGA was obtained from a TGA 951 thermal system at a heating rate of 10°C/min under nitrogen atmosphere from 25 to 850°C.

DMA measurements were carried out on DMA Q800 dynamic mechanical analyzer (TA Instruments) in three-point bending mode on samples size of 10×60 mm^2 with 1.0 ± 0.2 mm in thickness. The experiments were performed from 0 to 150°C at a continuous heating rate of 5°C/min and a frequency of 1 Hz.

Synthesis of poly(urethane-imide) diacid

PUI were prepared according to two procedures described previously,[18–20] as shown in Scheme 1. A 500 mL round-bottom, three-necked separable flask with a mechanical stirrer and condenser with drying tube was used as reactor and the reaction was
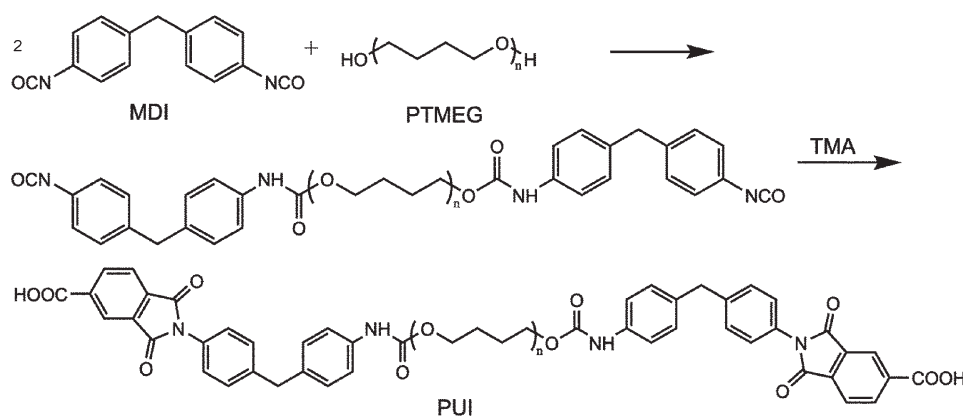
Scheme 1 Preparation routine of PUI.

TABLE II
Compositions of PUI/Epoxy/SiO$_2$ Hybrids with Different Epoxy/IPTES–Epoxy Ratios

Samples	Epoxy/IPTES–epoxy ratio (%)	PUI (g)	Epoxy (g)	IPTES-epoxy (g)	CX-100 (g)
PUI/EP	100	5.00	2.12	0	0.34
PUI/EP/Si20	80	5.00	1.68	0.63	0.34
PUI/EP/Si50	50	5.00	1.05	1.57	0.34
PUI/EP/Si80	20	5.00	0.42	2.51	0.34
PUI/EP/Si100	0	5.00	0	3.14	0.34

carried out in a constant temperature oil bath. 50.00 g (0.05 mol) PTMEG and 28.52 g (0.1 mol) MDI were mixed in 55.00 g dimethylformamide (DMF) and reacted for 4 h at 70°C to obtain PU prepolymer. Subsequently, to cap the terminals of NCO group of prepolymer, a solution of TMA 19.21 g (0.1 mol) in 105.00 g DMF was added dropwise with constant stirring. After addition, the mixture was heated to 80°C and kept for another 2 h, then to 100°C. During these stages, a rather strong evolving of CO$_2$ was observed. After the cease of elution of CO$_2$, the mixture was kept another 30 min at 100°C, then the reaction was stopped, and a yellow solution (37.70 wt %) was obtained. One part of the resulted solution was directly used to prepare PUI/epoxy/SiO$_2$ hybrids 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 50°C for 4 h, a clear and yellow product, PUI, was obtained, which was stored in a desiccator for structural characterizations. The acid value of the product PUI via acid–base titration was 736.70 g/eq. The products were also characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR.

Preparation of silane-modified epoxy (IPTES-epoxy)

The synthesis of silane-modified epoxy was carried out using the following procedure as mentioned,[21]

150 g epoxy resin was dissolved in tetrahydrofuran in the flask (50 wt %), 85.34 g IPTES was added dropwise at 60°C and was then stirred for 4 h until the characteristic peak of the —NCO disappeared.

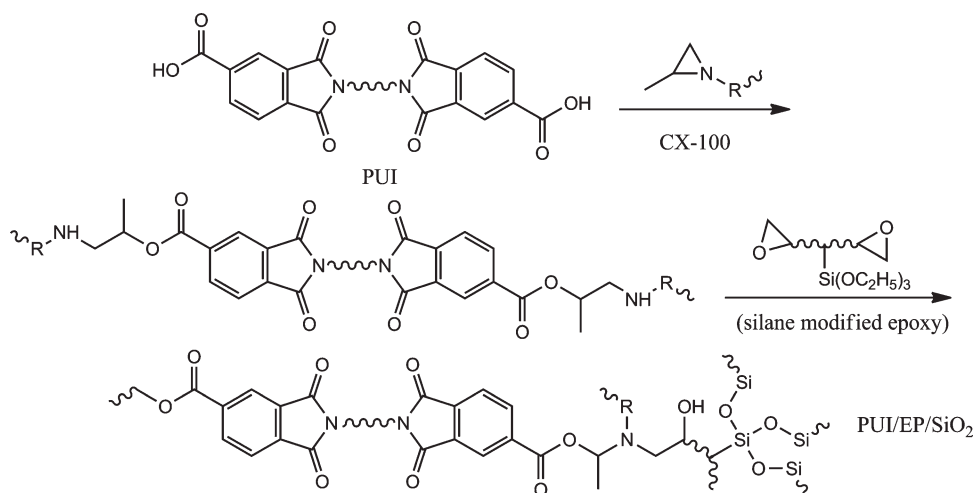## Preparation of PUI/epoxy/SiO$_2$ hybrids

All the PUI/epoxy/SiO$_2$ hybrids were prepared with various epoxy/IPTES-epoxy feed ratios (Table II). A detailed procedure was indicated as follows.

After mixing thoroughly, the as-synthesized PUI solution, CX-100, IPTES-epoxy solution, and epoxy resin solution (50 wt % of toluene) at ambient temperature, the mixture was cast into a Teflon® mold. After 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. Scheme 2 showed the reactions in the curing procedures including the sol–gel process.

RESULTS AND DISCUSSION

FTIR and NMR analysis

The infrared spectra of PU prepolymer and the synthesized PUI were shown in Figure 1. In Figure 1(a), 2271.7 cm^{-1} assigned to —NCO group stretching of

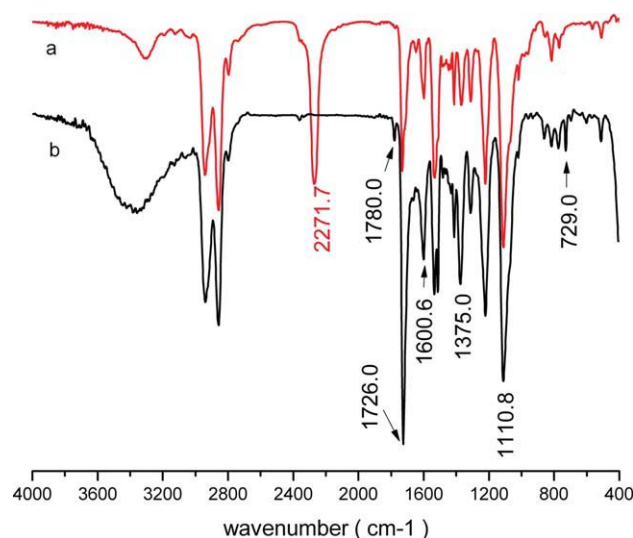**Scheme 2** Curing procedure in PUI/epoxy/SiO$_2$ hybrids.

Figure 1 FTIR spectra of PU prepolymer (a) and the synthesized PUI (b). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the prepolymer could be clearly seen, whereas disappeared in Figure 1(b). Also, the bands at 1780 and 1726 cm^{-1} were assigned to the asymmetric and symmetric stretching vibration of the carbonyl of the imide groups, respectively. The characteristic absorption bands of imide functions at about 1375 (C—N stretching of imide), 1110.8 (imide ring vibration, transverse), 729 cm^{-1} (imide ring deformation) could be seen in Figure 1(b). Besides, some characteristic peaks at 1600.6 cm^{-1} (C-N stretching of amide) and 3300–3600 cm^{-1} (N—H stretching vibrations of amide) could be seen. These confirmed that imide and amide groups were presented in the synthesized PUI backbone.

To further verify the chemical structure of the resultant, ^{1}H- and ^{13}C-NMR were done in DMSO-d6 and shown in Figure 2. In the ^{1}H-NMR spectrum, the peaks around 1.00–1.50 ppm and 3.20–4.00 ppm were assigned to the protons from ether of PTMEG, urethane protons were observed at 9.50 ppm, the aromatic and methyl protons from MDI showed at 7.07–7.45 ppm and 4.05 ppm; the aromatic protons from TMA showed at 8.00–8.30 ppm; a weak and broad peak at 13.80 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, the peaks at 26.54 and 70.17 ppm were assigned to the carbon from ether of PTMEG, 154.03 ppm to carbon from N-amide. The aromatic carbons showed at 118.00–138.00, the peak at 168.04 ppm assigned to carbon from carboxyl and 166.90 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 FTIR and NMR verified the molecular structure of the product, which was as same as designed, although there might be side reactions.

Thermal stability

The thermal stability of the prepared PUI/epoxy/SiO₂ hybrids was evaluated by the TGA method. The results were shown in Figure 3, and Table III summarized the temperatures at the maximum weight loss rate (T_{max}) and weight loss value at T_{max} (W_{max}), as well as the char yield of the hybrids at 800°C. Clearly, the PUI/epoxy/SiO₂ hybrids prepared from silane-modified epoxy resin had higher value of the char yield, and their $T_d^{5\%}$, $T_d^{10\%}$ values evidently increased; the maxim difference was above 60°C for $T_d^{5\%}$ in comparison of PUI/EP with PUI/EP/Si20.

At the same time, two overlapping steps of thermal decomposition were obviously distinguished from the DTGA curves of these hybrids. The first step consisted of a gradual weight loss from room temperature to around 220°C and a minor weight loss in the range of 220–320°C. Assuming a different
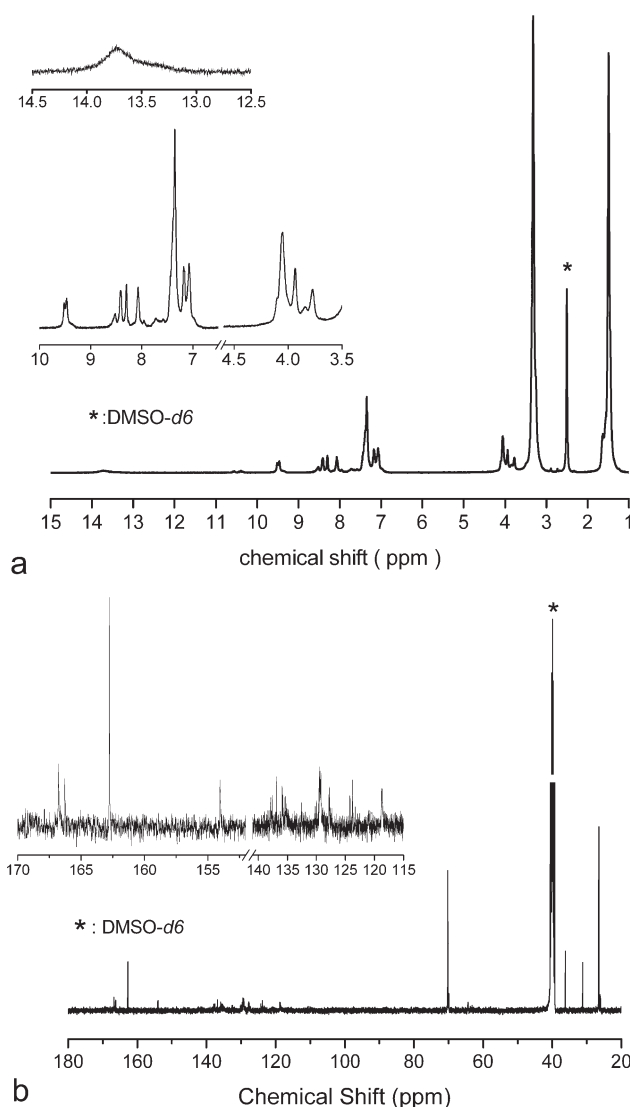

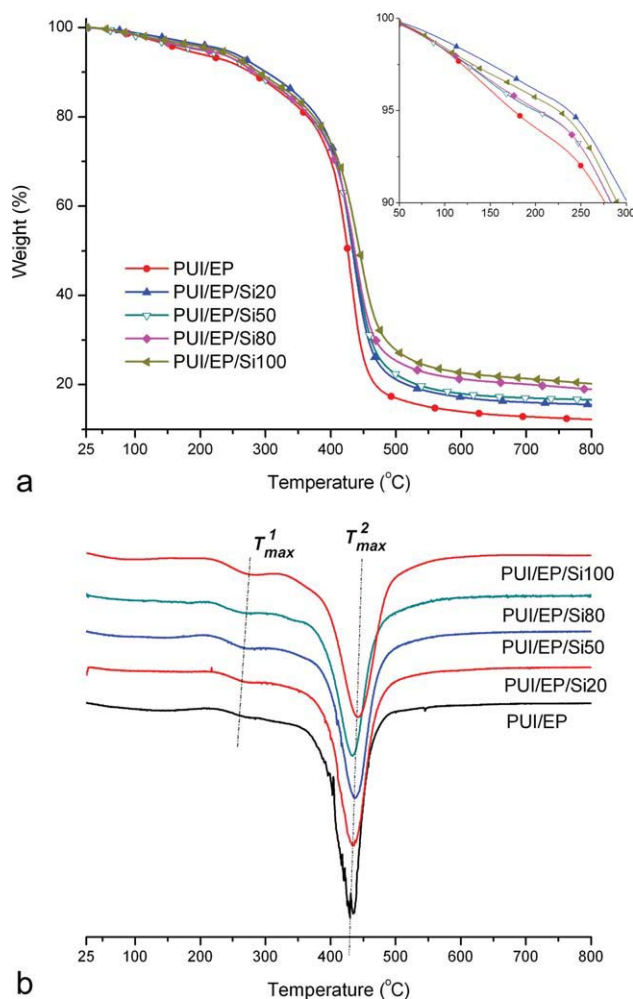**Figure 2** ^{1}H- and ^{13}C-NMR of the synthesized PUI.

Figure 3 Typical TGA curves of PUI/epoxy/SiO$_2$ hybrids. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

bile urethane bonds increased in PUI/epoxy/SiO$_2$ with incorporating IPTES-epoxy, due to the existence of urethane bonds, the T_{max}^1 value of PUI/epoxy/SiO$_2$ increased, whereas W_{max}^1 value decreased. So, the higher thermal stability found in these hybrids in comparison with conventional PUs might have been a result of the shielding effect of the imide and epoxy structures,[18] as well as *in situ* SiO$_2$. The second weight loss at 320–600°C should be caused by the integrated results of decomposition of polyether, epoxy, and imide rings[22–25] and *in situ* SiO$_2$. The same trend of enhancement of thermal stability was observed for the hybrids in the region with increasing the content of more thermally stable *in situ* SiO$_2$ structures. Briefly, all data at Table III showed that the thermal decomposition of these hybrid materials containing silica shift toward the higher temperature range than that of net PUI/EP composite, confirming the enhancement of thermal stability of the hybrids. A reasonable explanation of the phenomenon should be that the hybrid system from IPTES-epoxy had an interpenetrated network nature generated in the sol–gel process, which limited the segmental movement of PUI/EP, leading to the increase in the thermal stability.[24] However, it could be found that all systems had slightly lower $T_d^{5\%}$ value, which might be concerned with the existed lower molecular as mentioned above. As to the reason that the PUI/EP/Si20 system had a highest $T_d^{5\%}$ and $T_d^{10\%}$ value, it might be due to the incompatibility of imide and urethane groups.[25]

Dynamic mechanical properties

Figures 4 and 5 presented the storage modulus (G') and loss tangent (tan δ) versus the temperature, and data are collected in Table IV. PUI/EP and PUI/EP/Si20 exhibited one-step relaxation in the region of 60 to 65°C, attributed to α-type transition (T_g). The others showed two thermal transitions in the region of 64 to 72°C; one transition was attributed to α-type transition, and another one around 44°C was due to melting of crystalline domains of PTMEG segment.

Investigation of tan δ curves showed that increasing content of IPTES-epoxy made the tan δ peak

stability of the urethane units, epoxy chains, the imide units, *in situ* SiO$_2$, and their interactions, urethane groups must be the most labile units and would decompose first to start the initial thermal degradation, so this step should be ascribed to simple depolymerization of urethane bonds besides the evaporation of physically absorbed solvent (such as DMF) and residual monomers, and by-products existing in the hybrid materials at lower temperature.[22] Clearly, although the number of thermally la-

TABLE III
Data on Thermal Stability and Thermal Behavior of the Prepared Hydrids

Sample	T_{max}^1 (°C)	W_{max}^1 (%)	T_{max}^2 (°C)	W_{max}^2 (%)	$T_d^{5\%}$ (°C)	$T_d^{10\%}$ (°C)	CH. Y (%)
PUI/EP	266.7	9.2	429.0	53.3	175.7	276.5	12.0
PUI/EP/Si20	269.8	8.7	435.2	51.5	236.9	301.2	15.4
PUI/EP/Si50	270.1	8.7	438.2	52.5	199.9	283.3	16.5
PUI/EP/Si80	273.9	8.3	437.7	50.9	203.6	283.6	18.4
PUI/EP/Si100	280.2	8.1	442.8	48.9	225.0	289.9	20.2

T_{max}, maximum decomposition temperature; W_{max}, weight loss at T_{max}; $T_d^{5\%}$, temperature at 5 wt % weight loss; $T_d^{10\%}$, temperature at 10 wt % weight loss; CH.Y, char yield at 800°C.
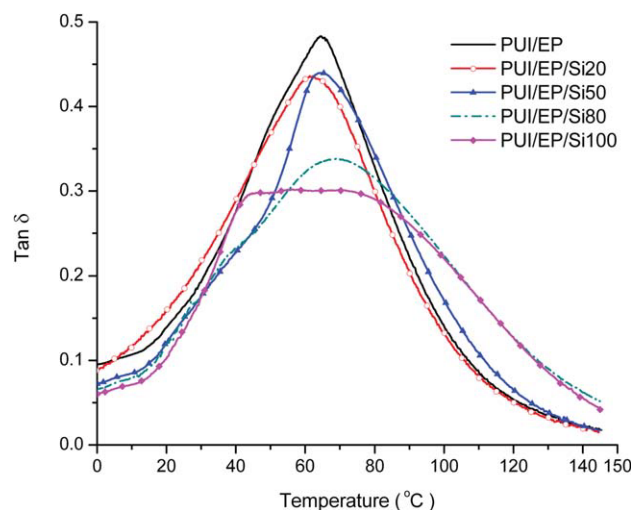
Figure 4 Plot of tan δ versus temperature for prepared hybrids. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

become broader and shift to slightly higher temperature, indicating an increasing restriction of chain mobility due to increasing interaction between organic and inorganic phases. Meanwhile, the broader tan δ peak and the decrease of relaxation strength (the height of the tan δ peak) from 0.48 to 0.3 indicated higher extent of microphase separation for the hybrids as more silica embedded.

While as shown in Figure 5, the storage modulus (G') decreased as the temperature increased. In the glassy region, the decreasing rate of G' became much slower as the increment of silica content. When the temperature was above T_g, higher content of silica resulted in higher G' value, for example, the G' at 100°C for PUI/EP, PUI/EP/Si20, PUI/EP/Si50,
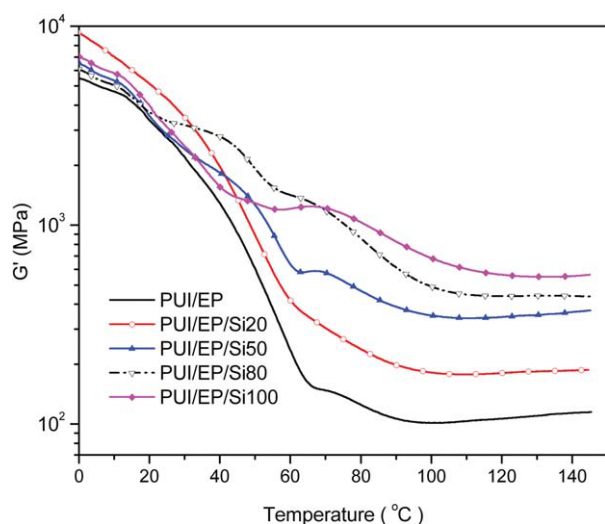

Figure 5 Plot of storage modulus versus temperature for prepared hybrids. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
Data on Dynamic Mechanical Analysis of the Prepared Hybrids

Sample	tan δ[a]	T_g (°C)[b]	T_m (°C)
PUI/EP	0.48	64.1	–
PUI/EP/Si20	0.44	62.3	–
PUI/EP/Si50	0.44	64.9	35.7[c]
PUI/EP/Si80	0.34	69.6	37.5[c]
PUI/EP/Si100	0.30	71.5	44.8

[a] The altitude of tan δ peak.
[b] The maxima of tan δ peak was used for determination of T_g.
[c] Shoulder peak, difficult to determine.

PUI/EP/Si80, and PUI/EP/Si100 were 103.0, 181.5, 347.5, 486.3, and 677.9 MPa, respectively, suggesting that the incorporating silica segments had highly improved the mechanical properties PUI/EP, and the hybrids could maintain good mechanical properties even at high temperature.

CONCLUSIONS

Based on the reaction of isocyanate of PTMEG-MDI PU prepolymer and anhydride of TMA, poly (urethane-imide) diacid (PUI) was directly obtained, structure of which was confirmed with FTIR and NMR spectrometry. The crosslinked PUI/epoxy/SiO$_2$ hybrids containing PUI and epoxy resin with different contents of silane-modified epoxy resin were prepared through the a series of crosslinking reactions, such as the sol–gel process of silane, the interaction among carboxylate of PUI, aziridine, and epoxy groups. Thermal and mechanical properties of the PUI/epoxy/SiO$_2$ hybrids were investigated to study the effect of incorporating *in situ* SiO$_2$. All experimental data indicated that the thermal, mechanical properties of PUI/epoxy/SiO$_2$ hybrids changed depending on the chemical structure of the constituents. As the content of silica increased, PUI/epoxy/SiO$_2$ showed improved thermal stability and higher T_g value, as well higher storage modulus. Of course, because of lower content of incorporated SiO$_2$, the increment of decomposition temperature was still relatively limited. How to extensively improve the stability of the composites will be studied well in the future.

References

1. Chen, C. H.; Chen, M. H. J Appl Polym Sci 2006, 100, 323.
2. Yeganeh, H.; Lakouraj, M. M.; Jamshidi, S. Eur Polym J 2005, 41, 2370.
3. Chen, C. H.; Sun, Y. Y. J Appl Polym Sci 2006, 101, 1826.
4. Okuhira, H.; Iwamoto, N.; Ochi, M.; Takeyama, H. J Polym Sci Part B: Polym Phys 2004, 42, 1137.
5. Stefani, P. M.; Moschiar, S. M.; Aranguren, M. I. J Appl Polym Sci 1998, 68, 1781.
6. Mishra, A. K.; Chattopadhyay, D. K.; Sreedhar, B.; Raju, K. V. S. N. J Appl Polym Sci 2006, 102, 3158.

7. Takeichi, T.; Ujiie, K.; Inoue, K. K. Polymer 2005, 46, 11225.
8. Yeganeh, H.; Barikani, M.; Khodabadi, F. N. Iran Polym J 2000, 9, 249.
9. Iyer, N. P.; Gnanarajan, T. P.; Radhakrishnan, G. J Polym Sci Part A: Polym Chem 2001, 39, 4236.
10. Yeganeh, H.; Shamekhi, M. A. Polymer 2004, 45, 359.
11. Yeganeh, H.; Barikani, M.; Khodabadi, F. N. Eur Polym J 2000, 36, 2207.
12. Gnanarajan, T. P.; Iyer, N. P.; Nasar, A. S.; Radhakrishnan, G. Eur Polym J 2002, 38, 487.
13. Mehdipour-Ataei, S.; Zigheimat, F. Eur Polym J 2007, 43, 1020.
14. Abraham, G.; Packirisamy, S.; Ramaswamy, R.; Thomas, S. Int J Polym Mater 2005, 54, 11071132.
15. Chen, Y. C.; Zhou, S. X.; Yang, H. H.; Wu, L. M. J Sol Gel Sci Technol 2006, 37, 39.
16. Yeh, J. M.; Yao, C. T.; Hsieh, C. F.; Yang, H. C.; Wu, C. P. Eur Polym J 2008, 44, 2777.
17. Jeon, H. T.; Jang, M. K.; Kima, B. K.; Kim, K. H. Colloids Surf A Physicochem Eng Asp 2007, 302, 559.
18. Liu, P. G.; Zhang, Q. F.; He, L. H.; Xie, Q. J.; Ding, H. Y. J Appl Polym Sci 2009, 113, 2628.
19. Król, P. Prog Mater Sci 2007, 52, 915.
20. Meyers, R. A. J Polym Sci Part A: Polym Chem 1969, 7, 2757.
21. Chiang, C. L.; Ma, C. C. M. Eur Polym J 2002, 38, 2219.
22. Hasmukh, P. S.; Hemant, V. S. Eur Polym J 1991, 27, 93.
23. Chattopadhyay, D. K.; Aswini, K. M.; Sreedhar, B.; Raju, K. V. S. N. Polym Degrad Stab 2006, 91, 1837.
24. Sharp, K. G. Adv Mater 1998, 10, 1243.
25. Jiang, B. B.; Hao, J. J.; Wang, W. Y.; Jiang, L. X.; Cai, X. X. J Appl Polym Sci 2001, 81, 773.