

Synthesis and Properties of Elastic Polyurethane-Imide

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ABSTRACT: A new synthesis route for elastic polyurethane-imides (EPIs) has been established by a method involving the use of urea. Various EPIs were synthesized from polyurethane-urea, which was prepared from 4,4'-diphenylmethane diisocyanate (MDI), polyoxytetramethylene glycol (PTMG) and 4,4'-diphenylmethanediamine (MDA), and pyromellitic dianhydride in *N*-methyl-2-pyrrolidone (NMP). Flexible films were cast from these solu-

tions that had different inherent viscosities. Imidization of the EPI films was completed at 200°C for 4 h *in vacuo*. The EPIs were determined by FTIR, ¹H NMR, and ¹³C NMR spectra. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 242–248, 2010

Key words: Polyurethane-imide; Polyurethane-urea; Polyurea method

INTRODUCTION

Polyurethane elastomers (PUEs) prepared from various combinations of polyisocyanate and polyol have been widely used in different fields. These PUEs have varying specifications, such as rubber elasticity, abrasion resistance, adhesion, and so on, but PUEs in general (which are formed from organic polymer material) have a basic problem in terms of heat-resistance. By improving this fundamental property, PUEs may gain some industrial advantage. Therefore, chemists have actively carried out many studies concerning the heat-resistance of PUEs. As representative examples of organic–inorganic hybrids, compound methods involving the use of silica gel or the sol–gel method using metal alkoxides such as tetraethoxysilane have been very popular.¹ However, this approach suffers from two or three problems. For example, metal alkoxide (which is the raw material for this work) is very expensive and processing is difficult because the value of T_g for the resulting composites rises as the amount of raw material used increases.

Polyimides (PIs) have high-temperature stability, excellent electrical and mechanical properties, and good chemical resistance. However, PIs are insoluble and intractable in the fully-imidized form in all cases and severe difficulties arise in processing. Therefore, significant efforts have been made to improve their processability and solubility. We have recently succeeded in synthesizing elastic PIs, which are composites that exhibit processability and solubility, by the

polyurea method^{2–9} and we noted an improvement in the properties of polyurethane when using elastic polyimide. We believe that this method has advantageous in terms of reactivity and formability, as it involves the synthesis of elastic polyurethane-imides (EPIs) via an organic–organic hybrid.^{10–17} As a consequence, the use of EPIs is now receiving attention as a possible technique for improving the processing of PI.

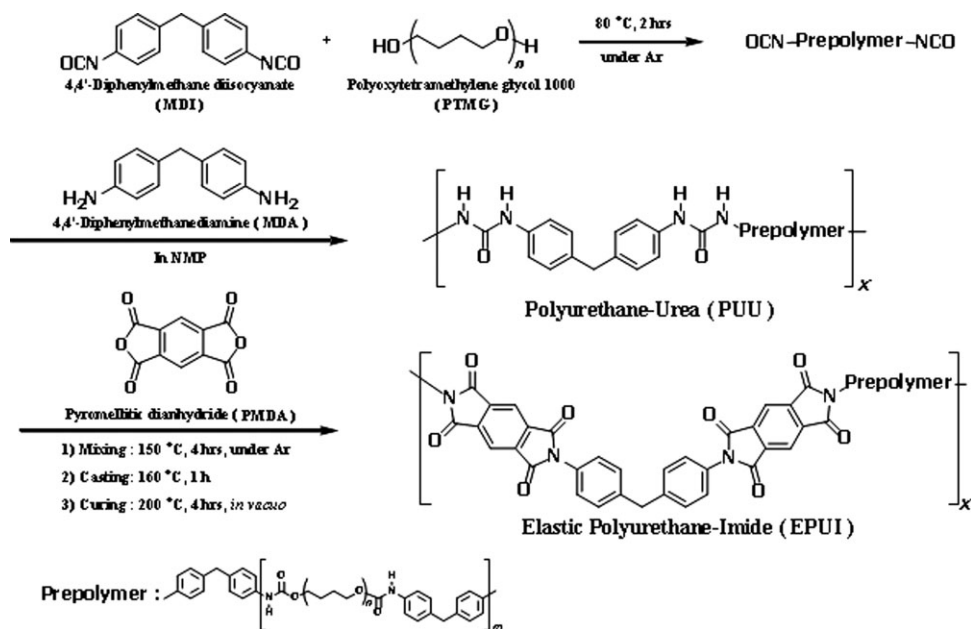
To the best of our knowledge, there have been no reports regarding synthesis using the urea method or the physical properties of derived PUI composites before this work. In this article, we would like to report a new method for the synthesis of PUIs using polyurethane-urea (PUU), which was prepared from 4,4'-diphenylmethane diisocyanate (MDI), polyoxytetramethylene glycol 1000 (PTMG1000) and 4,4'-diphenylmethanediamine (MDA), and acid dianhydride in *N*-methyl-2-pyrrolidone (NMP). We will also describe the properties of PUI composites resulting from the use of the urea method (Scheme 1). The composition of the PI units in the PUI composites was also investigated.

EXPERIMENTAL

Materials

MDI was supplied by Nippon Polyurethane Industry. The MDI was purified by distillation under reduced pressure (267–400 Pa) at 80°C before use. PTMG ($M_w = 1000$) was delivered by Hodogaya Industry. The PTMG was dehydrated *in vacuo* at 80°C for 24 h before use. MDA (Nacalai Tesque) and pyromellitic dianhydride (PMDA, Nacalai Tesque) were used without further purification. NMP (Nacalai Tesque) was kept over a 3 Å molecular sieve.

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Scheme 1 Synthesis of elastic polyurethane-imide (EPUI).

Instrumentation

FTIR spectra were recorded on a JASCO FTIR-5300 using the attenuated total reflection (ATR) method and the transmission method at room temperature ($23 \pm 2^\circ\text{C}$). The ATR spectra were measured by ATR500/M using an ATR prism KRS-5. Thin films ($2\text{--}3\ \mu\text{m}$) were prepared using mechanized centrifugal casting at 100°C for 2 h and the resulting films were cured at 100°C for 24 h *in vacuo*. ^1H (300 MHz) and ^{13}C NMR (75.4 MHz) spectra were recorded on a Varian Unity plus-300 spectrometer using tetramethylsilane (TMS) in chloroform-*d* ($\text{CDCl}_3\text{-}d$) at room temperature ($23 \pm 2^\circ\text{C}$) as an internal standard. The acquisition parameters of the ^{13}C NMR spectra were as follows: spectral width = 18.859 kHz, acquisition time = 1.816 s, recycle delay = 0.185 s, transients = 1024, and spectral frequency = 75.4 MHz. Solid-state ^{13}C NMR experiments were also carried out on a Varian Unity plus-300. Zirconium oxide (ZrO_2) rotors (5 mm o.d.) were used with Kel-F caps for all of the measurements. The NMR measurements were carried out at room temperature ($23 \pm 2^\circ\text{C}$) unless otherwise stated. Cross-polarization with magic angle spinning (CP/MAS) was used to study these materials. Typical parameters for the ^{13}C CP/MAS NMR experiments were as follows: observation frequency 75.4 MHz, acquisition time = 40.32 ms, recycle time = 10.0 s, complex points = 2016, spectral width = 50.0 kHz, and transients = 1024. All of the ^{13}C CP/MAS NMR spectra were externally-referenced to hexamethylbenzene by assigning the methyl signal at 132.07 ppm with respect to the TMS resonance at 0.0 ppm. Tensile tests were investigated using an Orientec RTC-1225A with model-U-4310.

JIS 3-dumbbells were used for the standard samples. The measurement conditions for the tensile tests were as follows: crosshead speed = 100 mm/min at room temperature ($23 \pm 2^\circ\text{C}$). Differential scanning calorimetry (DSC) measurements were performed on a Rigaku Thermo-plus DSC 8230 at a heating rate of $10^\circ\text{C}/\text{min}$ over the temperature range -120°C – 200°C under an Ar atmosphere. Approximately 9.5 mg of each composite was weighed out and sealed in an aluminum pan. The samples were quickly cooled to -120°C and heated to 200°C at $10^\circ\text{C}/\text{min}$. Dynamic mechanical analysis (DMA) was performed on a Seiko Instruments DMS 6100 at a heating rate of $2^\circ\text{C}/\text{min}$ and at a frequency of 10 Hz under an N_2 atmosphere. Atomic Force Microscopy (AFM) experiments were carried out on the dried films at room temperature in air using an Olympus NV 2000. Most of the images were obtained by means of Tapping-mode (ACAFM) with a silicon nitride cantilever (OMCL-AC 240TS-C2; Olympus Optical) with a spring constant of 15N/m and a resonating frequency of 20 kHz. The scanning rates were varied from 1 to 2 Hz. All the images presented in this work were reproducibly obtained over at least three points on the sample surfaces.

Synthesis of elastic polyurethane-imide via polyurethane-urea

Scheme 1 shows the preparation procedure for making the EPUI composites via PUU. The composition of the EPUI composites is shown in Table I. For example, the synthesis of EPUI containing 35% PI can be described as follows.

TABLE I
Synthesis of Elastic Polyurethane-Imides (EPIs)

	Prepolymer 15–65 ^a		PUU15 15–65 ^b				EPI1 ^c			
	MDI ^d (mol)	PTMG 1000 ^e (mol)	Prepolymer (mol)	MDA ^f (mol)	PUU (mol)	PMDA ^g (mol)	Imide content (wt %)		Appearance	
							Calc.	Theo.	Solution	Sheet ^h
EPI 15	1.25	1.00	0.25	0.25	0.50	0.50	15	15	Yellow	Yellow
EPI 25	1.50	1.00	0.50	0.50	1.00	1.00	26	25	Red	Yellow
EPI 35	1.75	1.00	0.75	0.75	1.50	1.50	35	35	Reddish brown	Yellow
EPI 45	2.25	1.00	1.25	1.25	2.25	2.25	47	47	Reddish brown	Reddish brown
EPI 55	2.75	1.00	1.75	1.75	3.50	3.50	55	55	Reddish brown	Reddish brown
EPI 65	3.75	1.00	2.75	2.75	5.50	5.50	66	65	Reddish brown	Reddish brown

^a Various prepolymers containing imide units were prepared at 80°C for 2 h under an Ar atmosphere by bulk polymerization.

^b Various polyurethane-ureas containing imide units were prepared at room temperature (23 ± 2°C) for 24 h under an Ar atmosphere by liquid polymerization.

^c Pyromellitic dianhydride, *Mw* = 218.12.

^d 4,4'-diphenylmethane diisocyanate, *Mw* = 250.26.

^e Polyoxytetramethylene glycol, *Mw* = 1000.

^f 4,4'-Diphenylmethanediamine, *Mw* = 198.26.

^g Various polyurethane-imides containing imide units were prepared at 150°C for 2 h under an Ar atmosphere by liquid polymerization.

^h Various sheets were obtained by casting of the resulting solution (20 g) using a centrifugal casting machine at 160°C, for 1 h, after which the sheets were treated at 200°C for 4 h *in vacuo*.

Prepolymer synthesis

A prepolymer was prepared by bulk polymerization, in which both terminal groups consisted of isocyanate units. MDI (30.435 g, 0.122 mol) and PTMG 1000 (69.565 g, 0.0696 mol) were added to a 500 mL four-necked reaction flask equipped with a stirrer, a gas inlet tube and a gas outlet tube, and were then stirred at 80°C for 2 h under an Ar atmosphere. The completion of the reaction was determined from the concentration of residual isocyanate groups, as obtained by the amine equivalent method.

Polyurethane-urea

PUU was prepared by liquid polymerization. The prepolymer (20 g), MDA, and NMP (200 mL) were added to a well stopped 300 mL glass scientific flask, and then the solution was stirred at room temperature (23 ± 2°C) for 24 h under an Ar atmosphere. Thin sheets were obtained by casting of the resulting solution (20 g) using a centrifugal casting machine at 100°C for 2 h. The following peaks were by FTIR (cm⁻¹) (transmission method): 3314 (NH stretching), 2942 and 2859 (CH stretching), 1732, 1645, and 1597 (C=O of urea), 1537 and 1514 (NH bending), 1111 (CO stretching), and 644 (amide). Figure 1 shows the ¹H NMR (CDCl₃-*d*) spectrum of PUU. In Figure 1, the ¹H NMR spectrum of PUU shows *H_a* at 6.59 ppm (-R¹NHCONHR²-) and *H_{a'}* at 6.91 ppm (-R¹NHCONHR²-), *H_b* at 8.39 ppm (-R³NHCOO-) and *H_{b'}* at 8.80 ppm (-R⁴NHCOO-), *H_c* at 7.40 ppm (aromatic ring), and *H_d* at 7.06 ppm

(aromatic ring). Figure 2 shows the ¹³C NMR and ¹³C CP/MAS NMR spectra of PUU; the ¹³C NMR spectrum shows *C_a* at 153.2 ppm (-R¹HNCONHR²-) and *C_b* at 152.3 ppm (-R³HNCOO-), *C_c* at 134.1 ppm (aromatic ring), *C_d* at 117.6 ppm (aromatic ring), *C_e* at 136.9 ppm (aromatic ring) and *C_f* at 128.1 ppm (aromatic ring). The ¹³C CP/MAS NMR spectrum shows broad resonances at 120.0–145.0 ppm and 175.0–200.0 ppm, corresponding to an aromatic ring, while the resonance of *C_c*–*C_f* overlaps with those of the other carbons. The broadening of this resonance peak (line width) is about 30 ppm, and it is spread over 128 ppm of the aromatic region.

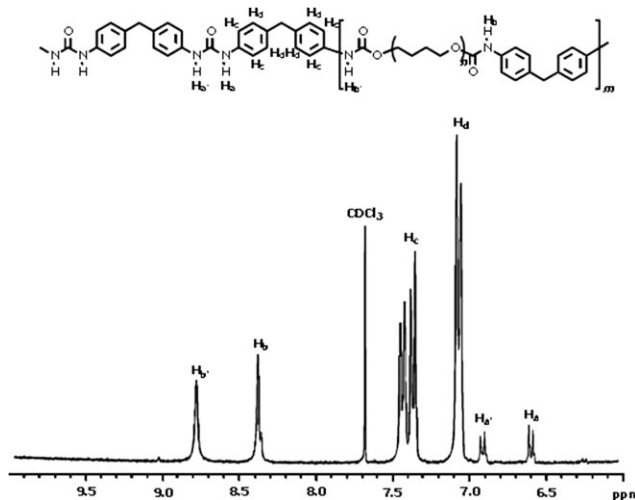


Figure 1 ¹H NMR spectrum of PUU containing 35% imide content.

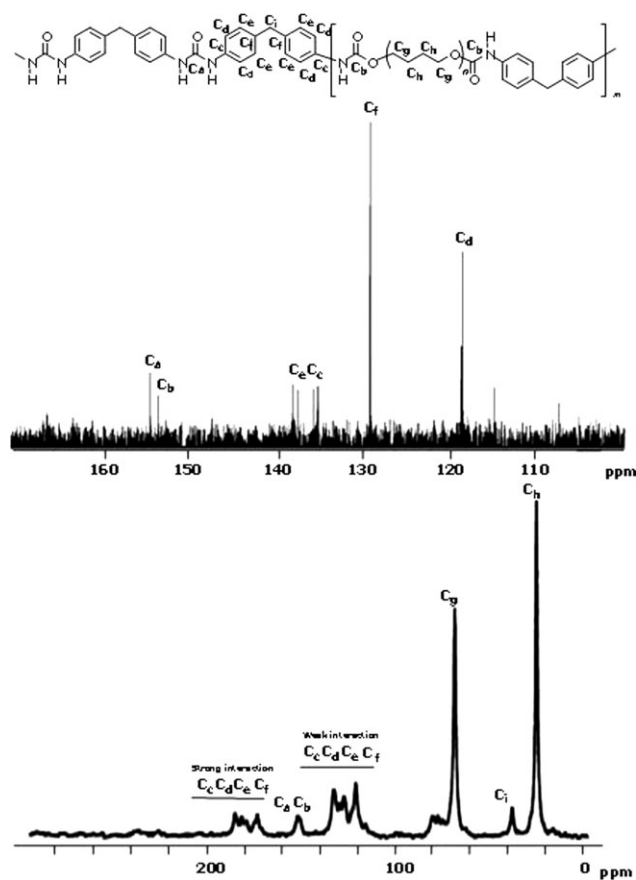


Figure 2 ^{13}C NMR (CDCl_3) (top) and CP/MAS ^{13}C NMR (bottom) spectra of PUU containing 35% imide content.

Elastic polyurethane-imide

EPUI was prepared by liquid polymerization. PUU solution (100 mL) and PMDA were added to a 500 mL four-necked reaction flask equipped with a stirrer, a gas inlet tube and a reflux condenser, and

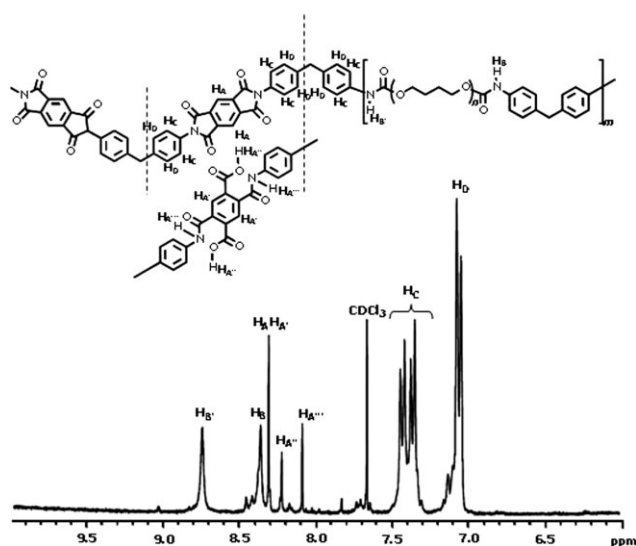


Figure 3 ^1H NMR spectrum of EPUI containing 35% imide content.

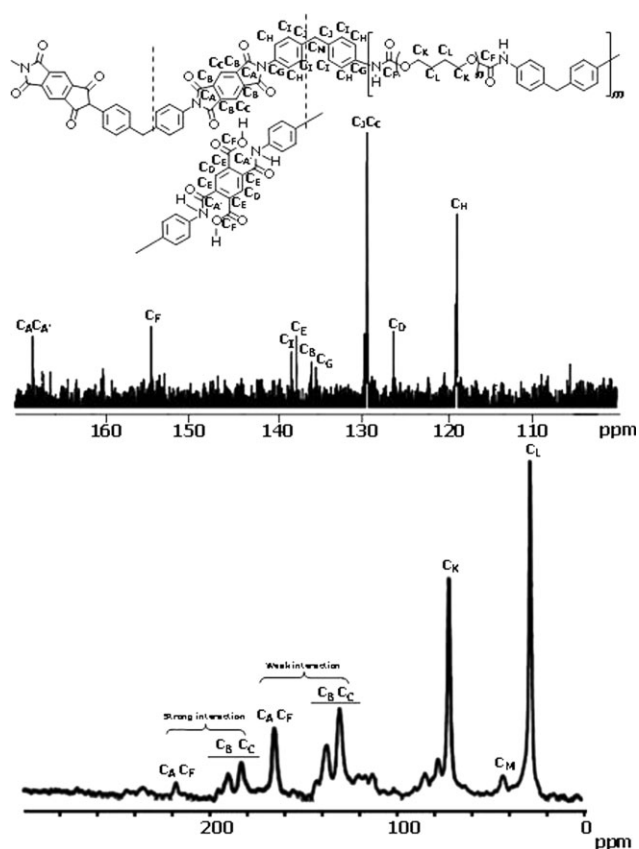


Figure 4 ^{13}C NMR (CDCl_3) (top) and CP/MAS ^{13}C NMR (bottom) spectra of EPUI containing 35% imide content.

the solution was then stirred at 150°C for 2 h under an Ar atmosphere. A test sheet was prepared by casting the resulting solution using a centrifugal casting machine at 160°C for 1 h, after which the sheet was treated at 200°C for 4 h *in vacuo*. The sheet was reddish brown and permeable.

RESULTS AND DISCUSSION

Synthesis of polyurethane-urea

Six prepolymers were prepared from MDI and PTMG1000 by bulk polymerization. The prepolymers were reacted with diamine (MDA) in NMP at

TABLE II
Solubility of Polyurethane-Imide Containing 35% Imide Content

Solvent	Solubility ^a
Hexane	x
Benzene	□
Toluene	□
Acetone	□
THF	□
DMSO	□
NMP	○

^a x insoluble, □ swelling, ○ partially soluble.

TABLE III
Tensile Properties^a of Elastic Polyurethane-Imides (EPUIs)

	M ₁₀ (MPa)	M ₅₀ (MPa)	M ₁₀₀ (MPa)	M ₂₀₀ (MPa)	M ₃₀₀ (MPa)	M ₄₀₀ (MPa)	M ₅₀₀ (MPa)	M ₆₀₀ ^b (MPa)	T _B ^c (MPa)	E _B ^d (%)
PUI 15	2.01	3.39	4.49	5.68	6.69	7.33	8.43	9.17	9.62	644
PUI 25	2.84	6.16	7.78	9.64	10.86	11.91	13.29	14.83	16.13	681
PUI 35	7.92	12.66	15.03	20.02	29.01	40.61	–	–	48.13	466
PUI 45	13.42	20.42	22.67	27.81	36.25	–	–	–	40.19	340
PUI 55	13.42	30.79	31.97	37.27	–	–	–	–	41.19	268
PUI 65	–	–	–	–	–	–	–	–	–	–

^a Tensile properties are measured at room temperature (23 ± 2°C) with a strain speed of 100 mm/min.

^b Mx is the tensile strength at a strain of X%.

^c Tensile strength at breaking point.

^d Elongation at breaking point.

room temperature (23 ± 2°C) to give the various PUUs (Table I). The reactions were completed within 24 h under an Ar atmosphere, and test sheets were easily obtained by casting of the PUU solutions using a centrifugal casting machine.

Synthesis of elastic polyurethane-imide

EPUIs were prepared from PUU and PMDA via the urea method. The results are shown in Table I. The Mws of EPUI containing below 25% imide content are from 55,000 to 60,000 and the Mws of EPUI containing over 35% imide content are from 25,000 to 34,000. The Mw decrease with increasing imide contents in the composites. The hybridization of EPUI 15–65, quantitatively produced polymers with different inherent viscosities at 2 h. The viscosities increased as the amount of PMDA increased. The

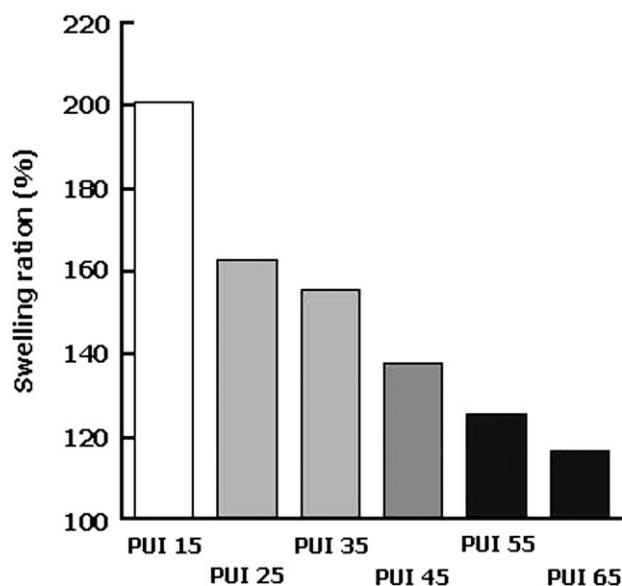


Figure 5 Swelling tests of elastomeric polyurethane-imide composites (EPUIs), measurement conditions: solvent = tetrahydrofuran (THF), measurement temperature = room temperature (23 ± 2°C), measurement time = 24 h.

formation of the sheets was carried out using a centrifugal casting machine. The resulting sheets were treated at 200°C for 4 h *in vacuo* to complete the imide reaction.

Characterization of polyurethane-imide

FTIR (cm⁻¹) (transmission method) measurements gave the following results: 3304 (NH stretching), 2940 and 2859 (CH stretching, aliphatic and aromatic), 1779 (C=O of imide) and 1728 (C=O of imide and urethane), 1599 (NH bending), 1377 (CN stretching), 1113 (CO stretching), and 725 (C=O bending).¹² Figure 3 shows the ¹H NMR (CDCl₃-d) spectrum of EPUI. The ¹H NMR spectrum of EPUI in Figure 3 shows H_A, H_{A'}, H_{A''}, and H_{A'''} at 8.32, 8.20, and 8.09 ppm, and the urea absorptions have disappeared. Figure 4 contains the ¹³C NMR and ¹³C CP/MAS NMR spectra of EPUI, which show peaks at 168.0 and 126.0 ppm that are associated with imide and with urethane. The solid-state ¹³C CP/MAS NMR spectrum shows the imide structure. The peaks for urethane at 129.8, 164.9, 182.6, and 219.0 ppm are associated with the imide structure. The urea peak (155.9 ppm) has disappeared.

TABLE IV
Glass Transition Temperature (T_g) of Elastic Polyurethane-Imides (EPUIs) with DSC^a

	Transition time (min)	T _s ^b (°C)	T _e ^c (°C)	T _g (°C)
PUI 15	1.48	-62	-51	-57
PUI 25	1.80	-66	-48	-56
PUI 35	2.06	-58	-37	-51
PUI 45	1.42	-59	-43	-55
PUI 55	1.63	-63	-46	-55
PUI 65	2.01	-59	-38	-51

^a Differential scanning calorimetry (DSC) measurements were performed at a heating rate of 10°C/min over the temperature range -120°C–200°C under an Ar atmosphere.

^b Transition start temperature.

^c Transition end temperature.

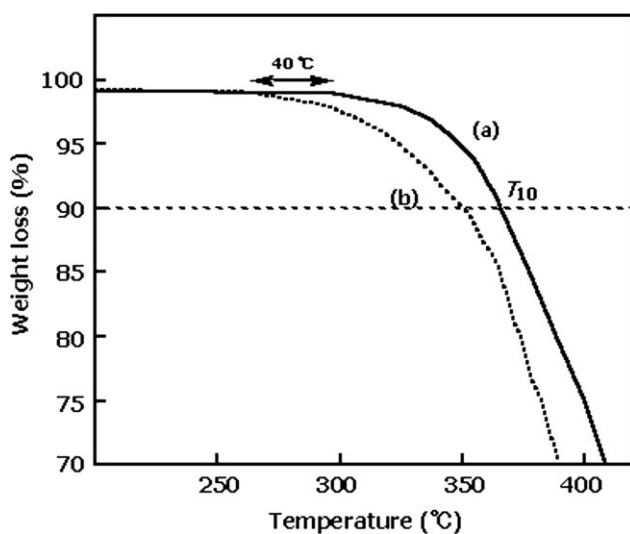


Figure 6 TGA curves of EPUI35 (a) (solid line) and PU (PTMG/MDI) (b) (dotted line) under N_2 at $10^\circ C/min$.

Solvent resistance of the polyurethane-imide

Solvent resistance of EPUI containing 35% imide content was investigated. The film was immersed into various solvents as hexane, benzene, toluene, acetone, THF, DMSO, and NMP. The result shows Table II. The film was partially soluble in NMP. However, the film did not change in hexane, and only swelled in benzene, toluene, acetone, THF, and DMSO. The film shows good solvent resistance. The reason for the good solvent resistance is considered to be uniformly caused by the formation of network structure between the imide and urethane.

Physical properties of polyurethane-imide

The tensile properties of the composites prepared from PUU and PMDA are reported in Table III. In

the case of all the tensile strength and the tensile modulus increase with increasing imide content in the composites. However the elongation at breaking point showed different behavior. The elongation at breaking point of EPUIs containing over 25% imide content in the composites decreases. It suggests that, when the imide content is over 25%, the effect of it is widely put out. Stiffening of the composites occurred with the progress of the imidization process. The PUI containing an imide content of 35% showed the best elastomer behavior among these composites, and this is believed to be because it then adopts a structure with small restrictions in the network caused by aggregation with fellow imide groups.

The results of swelling tests conducted on the EPUIs are shown in Figure 5. In Figure 5, the swelling rate decreased with increasing imide content. This corresponds with the result of the tensile test. It suggests that the network chain density in the composite increases with increasing imide content and crosslinking occurs between the imide segments.

The results of DSC analyses for the composites are summarized in Table IV. One main transition for the composites can be observed in the range between $-60^\circ C$ — $40^\circ C$. The values of T_g for the composites are -57 , -56 , -51 , -55 , -55 , and -51 , respectively. These values are same as determined by the peak temperature in the E' curves.

The thermal stability of the composite (EPUI35) was examined by TGA under air. As shown in Figure 6, the 10% weight loss temperature (T_{10}) for EPUI35 is $340^\circ C$. T_{10} therefore probably depends upon the oxidative degradation of the urethane segment (the unstable segment in the composite) because T_{10} for EPUI is above $400^\circ C$ in air. The formation of the EPUI mainly reduces the mobility of the urethane segment, so the thermal degradation

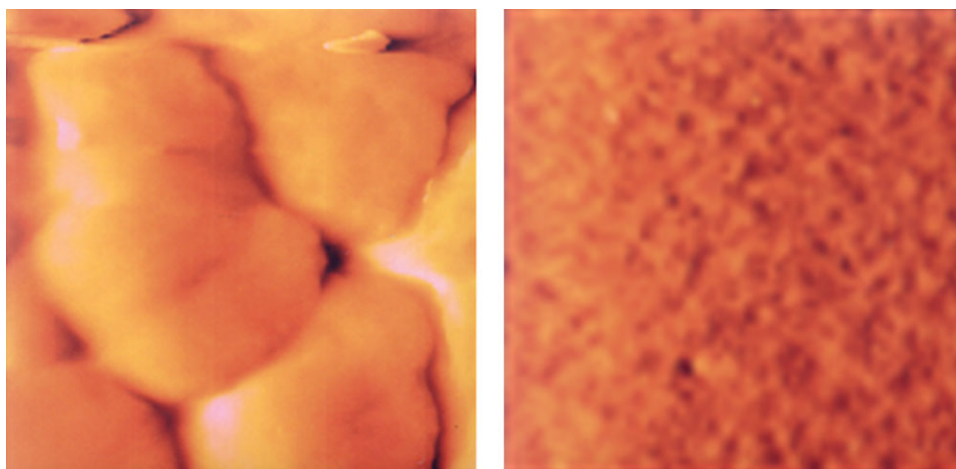


Figure 7 AFM image of PUU (left) and EPUI35 (right), scan range: $30 \times 30 \mu m^2$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

temperature of the composite shifts to higher temperature. The formation of the 35% polyimide hybrid gives a composite with a 20°C higher degradation temperature.

The surface morphology and homogeneity of the PUU and EPUI35 were estimated for the film samples from three transformations of the AFM images (Fig. 7). In comparison with the PUU, EPUI35 shows a flattened surface for the composite and the formation of a more homogeneous surface.

CONCLUSION

EPUIs were successfully prepared, using PUU and PMDA. We examined methods of increasing the degree of compatibility between the urethane and the imide segments that were obtained via the PUU. Their mechanical and thermal properties were investigated.

EPUIs were obtained from PUU and PMDA by the urea method. FTIR and NMR analyses confirmed that the EPUIs had both urethane and imide segments. The use of PMDA possessing a reaction site with a urea group on the PUU precursor improved the degree of compatibility between the urethane and the imide segments. Transparent composites were obtained when the concentration of the imide segment was below 65 wt %. The measured values of the imide content in the composite agreed with the theoretical values. The tensile strength and the tensile modulus increased, and the elongation at breaking point decreased with increasing imide content in the composites. The dynamic mechanical and thermal analyses suggested that network between the imide and the urethane segments occurred uni-

formly in the composites. The formation of the EPUIs had a great influence on the mobility of each contents in the network. TGA analyses indicated that the formation of the 10 wt % imide hybrid gave a composite with a 20°C higher degradation temperature.

We found that EPUI35 had the best elastic properties of all of the composites that we examined.

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