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Preparation and characterization of poly(urethane–imide) films prepared from reactive polyimide and polyurethane prepolymer

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Abstract

A novel type of poly(urethane–imide) was prepared by a reaction of a polyurethane prepolymer and a soluble polyimide containing hydroxyl functional group. Polyurethane prepolymer was prepared by a reaction of polyester polyol and 2,4-tolylenediisocyanate and then end-capped with phenol. Soluble polyimide was prepared by the two-step synthesis from 2,2′-bis (3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 3,3′-diamino-4,4′-dihydroxybiphenyl (AHBP). Soluble polyimides having various content of hydroxyl functional groups were prepared similarly by using diamine mixtures of AHBP and oxydianiline. Cast films were obtained from blend solutions of the polyurethane prepolymer and the polyimide. The cast films were thermally treated at various temperatures to give a series of transparent poly(urethane–imide) films. By changing the ratio of polyurethane and polyimide components, poly(urethane–imide) films having various properties from plastic to elastomer were prepared. Dynamic mechanical analysis showed that lower glass transition temperature (T_g) of the films shift to high temperature with the increase of polyimide component, suggesting that the two polymer components are miscible to some extent. Thermogravimetric analyses indicated that the thermal degradation of poly(urethane–imide) occurs at ca. 270°C, which is ca. 30°C higher than the conventional polyurethane, confirming that the introduction of polyimide component improved the thermal stability of polyurethane. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(urethane–imide); Polyurethane prepolymer; Reactive polyimide

1. Introduction

Polymer alloys, blend and composites have been receiving increasing attention because of the continued need for engineering polymers with improved properties. Combination of existing polymers offers a mean of engineering into novel materials having certain combination of desired properties exhibited individually by each component polymer. Polyurethane is becoming increasingly important as engineering materials, because it has excellent abrasion resistance and properties of both elastomer and plastics [1–4]. The conventional polyurethane, however, are known to exhibit poor resistance to heat, e.g. the acceptable mechanical properties (strength, moduli, etc.) disappear above ca. 80–90°C and thermal degradation takes place above 200°C [5]. The poor heat-resistance of polyurethane limits its applications.

Research focused on improving the thermal stability of polyurethane has been tried by various ways. One method to improve the thermal stability of polyurethane is a chemical modification of their structure by highly thermally stable heterocyclic groups. Polyimide is an important class of heterocyclic polymers with remarkable heat-resistance and superior mechanical, electrical, and durable properties [6–10]. The introduction of polyimide or oligoimide unit into polyurethane has been attempted by various approaches. Reaction of isocyanate-terminated polyurethane prepolymer with acid dianhydride was the method most often utilized to introduce imide function into polyurethane backbone [11–15]. A modified method was also utilized, in which acid dianhydride was reacted with aminoethanol to give hydroxyl-terminated imide monomer, which was then reacted with isocyanate-terminated polyurethane prepolymer [16]. Another modified method is the reaction of isocyanate-terminated polyurethane prepolymer with aromatic diamines and dianhydride to prepare polyurethane containing imide groups in the backbone [17]. Intermolecular Diels–Alder (DA) reaction of 4-methyl-1,3-phenylene-bis(2-furanylcarbamate) with various bismaleimides is also reported to give poly(urethane–imide)s [18–21]. Poly(urethane–imide)s obtained by these methods are linear, which should result in poor solvent-resistance to ordinary organic solvents.

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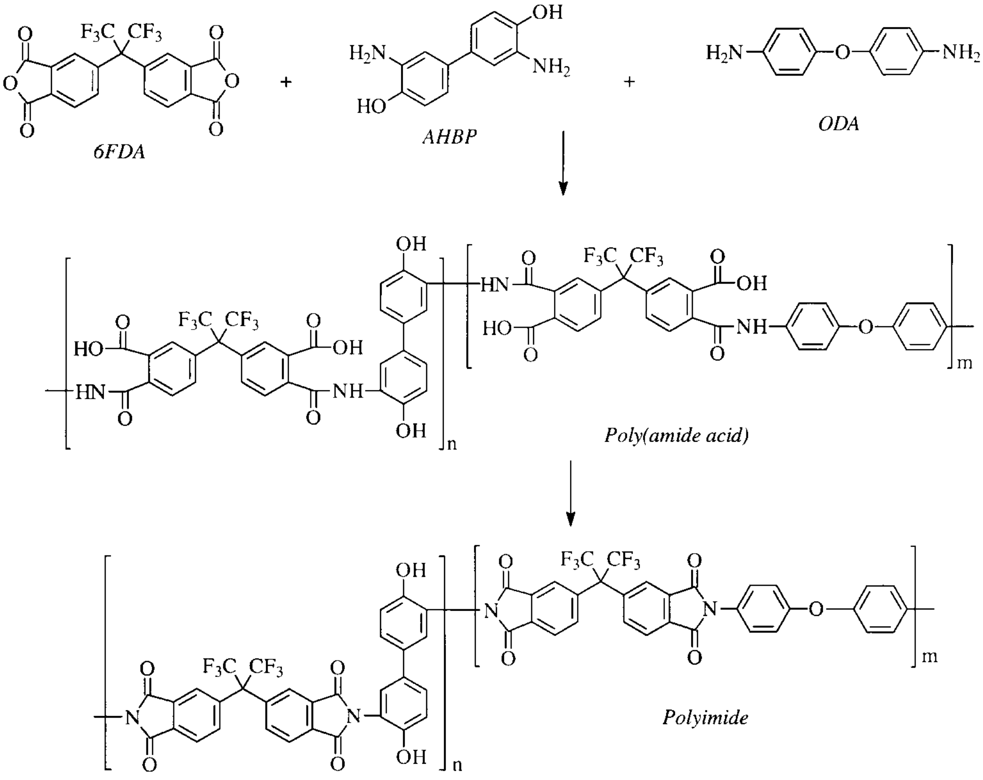


Scheme 1. Preparation of polyimides.

Very recently, we reported a novel approach to prepare a series of poly(urethane–imide)s. Our approach is based on the reaction of polyurethane prepolymer and poly(amide acid) which is a precursor of polyimide [22,23]. The prepared poly(urethane–imide)s have network structure and showed improved thermal stability and excellent solvent-resistance. The poly(urethane–imide) films were plastic or elastomer depending on the ratio of the two components. The properties can be easily controlled by changing the ratio of two components. The domain of phase separation was also found to be controlled by selecting appropriate combination of chemical structure. The formation of urethane–imide linkage in the novel method is based on the reaction between in-situ generated isocyanate group in the polyurethane prepolymer and carboxylic group in the poly(amide acid). The imidization occurs at similar temperature range, and the structure of the poly(urethane–imide) cannot be well-defined. The evolution of water at imidization and evolution of carbon dioxide produced during the reaction between the polyurethane prepolymer and poly (amide acid) also could influence the reaction and properties of the obtained films.

In this report, we intended to prepare poly(urethane–imide)s that have well-defined structure via simple reaction. For that purpose, we examined another novel approach which is based on the reaction between terminal isocyanates in the polyurethane prepolymer and pendent hydroxyl groups in polyimides that are soluble in organic solvents.

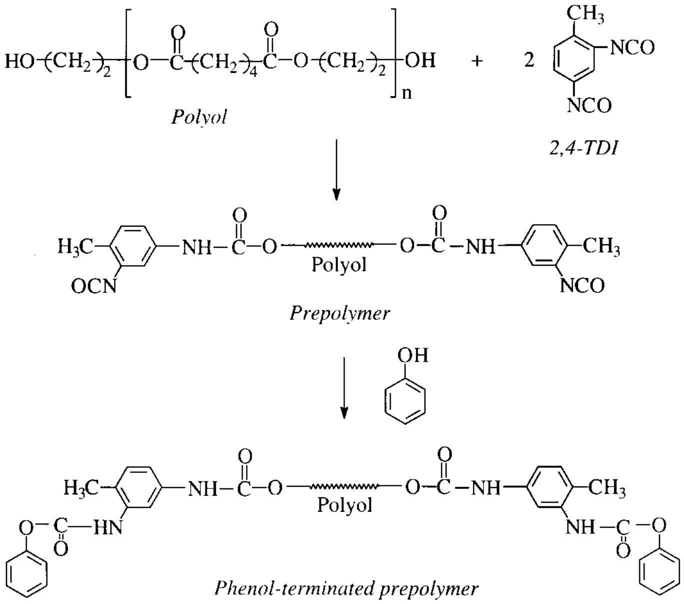
2. Experimental

2.1. Materials

2,2′-Bis (3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) was purified by recrystalization from a

Table 1
Formulation of polyimide and viscosity of poly(amide acid) and polyimide

Code	6FDA mmol (g)	AHBP mmol (g)	ODA mmol (g)	η_{red} (dL/g) poly(amide acid)	η_{red} (dL/g) PI
PI_{10}	3.0 (1.3327)	3.0 (1.0988)	—	0.53	0.32
PI_{21}	3.0 (1.3327)	2.0 (0.7325)	1.0 (0.2002)	0.62	0.45
PI_{11}	3.0 (1.3327)	1.5 (0.5494)	1.5 (0.3003)	0.73	0.50
PI_{12}	3.0 (1.3327)	1.0 (0.3663)	2.0 (0.4004)	0.60	0.39
PI_{01}	3.0 (1.3327)	—	3.0 (0.6006)	0.65	0.49



Scheme 2. Preparation of polyurethane prepolymer.

mixture solvent of acetic anhydride and acetic acid (7.5 : 1, weight ratio), followed by sublimation. Oxydianiline (ODA) was purified by sublimation. N-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure. 3,3′-Diamino-4,4′-dihydroxybiphenyl (AHBP) (Tokyo Kasei Organic Chemicals) was used as received. Tolylene-2,4-diisocyanate (TDI) was used as received from Nippon Polyurethane Ltd. Polyethylene adipate (M.W. ca 1000, OH number in KOH: 113), delivered by Nippon Polyurethane Ltd., was dehydrated in vacuo at 80°C for one night before use. Phenol was used as received.

2.2. Preparation of a series of soluble polyimides contaiing hydroxyl groups

Various kinds of soluble polyimides were prepared by the reaction of equal molar amount of 6FDA and diamine mixtures of AHBP and ODA in NMP as shown in Scheme 1.The content of hydroxyl groups in the polyimide was controlled by adjusting the ratio of diamine monomers, AHBP and ODA as 1 : 0, 2 : 1, 1 : 1, 1 : 2 and 0 : 1 (in molar ratio) as shown in Table 1. Here, we designated polyimide as PI_{10}, PI_{21}, PI_{11}, PI_{12} and PI_{01} to indicate the ratio of diamines.

As a typical example, the preparation of PI_{11} is shown below. AHBP (1.5 mmol, 0.5494 g) and ODA (1.5 mmol, 0.3003 g) were dissolved in NMP (19.6 g) under nitrogen atmophere. Equimolar amount of 6FDA (3 mmol, 1.3327 g) was added as one portion, followed by stirring at room temperature for 2 h. The obtained solution was added into 1000 ml of water to precipitate poly(amide acide), which was filtered, washed with water and dried in vacuo at 50°C for 16 h. Viscosity of the poly(amide acid) was 0.73 dL/g at the concentration of 0.5 g/dL in NMP. Dried powder of poly(amide acide)was imidized in vacuo at 100°C and 200°C for 1 h each. Formation of polyimide containing hydroxyl groups was confirmed by IR from the absorptions of the imide function at 1780, 1380, 720 cm^{-1} and hydroxl group at 3400 cm^{-1}. Viscosity of the polyimide was 0.50 dL/g at the concentration of 0.5 g/dL in NMP.

2.3. Preparation of polyurethane prepolymer

Polyurethane prepolymer was prepared following the Scheme 2. TDI (20 mmol, 3.58 g) was added into dehydrated polyethylene adipate (10 mmol, 10.00 g), and reacted at 80°C for 2 h under nitrogen atmosphere to give polyurethane prepolymer as a viscous liquid. Phenol (20.4 mmol, 1.92 g) was added into the liquid at 80°C for 3 h to give polyurethane prepolymer endcapped with phenol. Then,

Table 2
Formulation of poly(urethane–imide)s

Code	Content of NCO (mol/g)	Content of OH (mol/g)	Weight ratio PI : PU	PU (%)
PU/PI_{10}	1.30×10^{-3}	3.19×10^{-3}	1.0 : 2.5	71
PU/PI_{21}	1.30×10^{-3}	2.15×10^{-3}	1.0 : 1.7	63
PU/PI_{11}	1.30×10^{-3}	1.62×10^{-3}	1.0 : 1.4	58
PU/PI_{12}	1.30×10^{-3}	1.08×10^{-3}	1.0 : 0.8	44

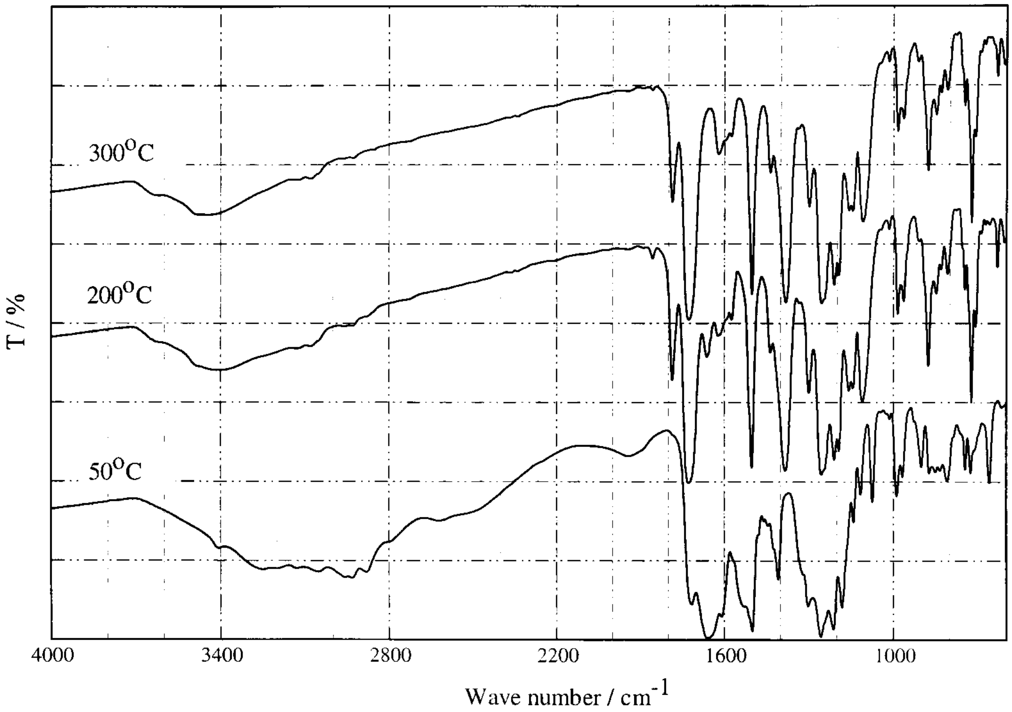


Fig. 1. IR spectra of polyimide, PI_{11}, treated at various temperatures.

polyurethane prepolymer was dissolved in NMP to give a 50% solution.

2.4. Preparation of poly(urethane–imide))films

Polyimide was dissolved in NMP to give a 5% solution. Then, polyimide solution and polyurethane prepolymer solution were mixed so that the amount of hydroxyl functional groups in polyimide and isocyanate groups in polyurethane prepolymer are equal for the stoichiometic reaction, as shown in Table 2. The blend solutions were cast on a glass plate, and solvent (NMP) was evaporated under vacuum at 50°C for 16 h. The cast films were then thermally treated at 100°C and 200°C for 1 h each. Poly(urethane–imide)s from corresponding polyimides were designated as PU/PI_{10}, PU/PI_{21}, PU/PI_{11} and PU/PI_{12}.

2.5. Measurements

Viscosity of poly(amide acid)s and polyimides were measured using Ubbelohde viscometer at a concentration of 0.5 g/dL in NMP. IR spectra were recorded on a JEOL Model IR 810. Dynamic viscoelastic measurements were carried out with a Rheovibron Model DDV-01FP from −50°C to 400°C at 35 Hz at a heating rate of 4°C/min in liquid nitrogen. Thermogravimetric analyses (TGA) were carried out with a SEIKO I TG/DTA 300 at a heating rate of 5°C/min under Ar. Tensile properties were investigated using an IMADA Seisaku-sho Model SV-3 at room temperature with a cross-head speed of 1 mm/min, using film samples about 2 cm long.

3. Results and discussion

3.1. Preparation of poly(urethane–imide)

We intended to prepare a series of novel poly(urethane–imide)s by a simple reaction between hydroxyl functional groups in a polyimide and terminal isocyanates in a polyurethane prepolymer. For that propose, we needed a series of soluble polyimides having hydroxyl groups. Thus, we used 6FDA as one component since 6FDA is known to give soluble polyimide [24]. The content of hydroxyl functional groups was controlled by changing the ratio of AHBP and ODA. After thermal treatment at 300°C, the solubility of the polyimide powder was not so good probably because of the strong hydrogen bonding between the hydroxyl groups in the polyimide. Therefore, we used polyimides after 200°C treatment, which was easily soluble in organic solvents such as THF, DMAc and NMP. From the IR spectra shown in Fig. 1, polyimides treated at 200°C and 300°C are almost same, and we can say that thermal treatment at 200°C gave almost completely imidized powder. As shown in Table 1, viscosity of poly(amide acid)s and polyimides was 0.53–0.73 dl/g and 0.32–0.50 dl/g. The lower viscosity of the polyimides after 200°C treatment can be rationalized by partial hydrolysis of polymer chains during imidizaton [25]. Partial hydrolysis is confirmed by the appearance of 1840 cm^{-1} in the IR spectra of the polyimide treated at 200°C (Fig. 1) which is assigned to the anhydride.

The addition of isocyanate-terminated plyurethane prepolymer into soluble polyimide causes gelation as a result of

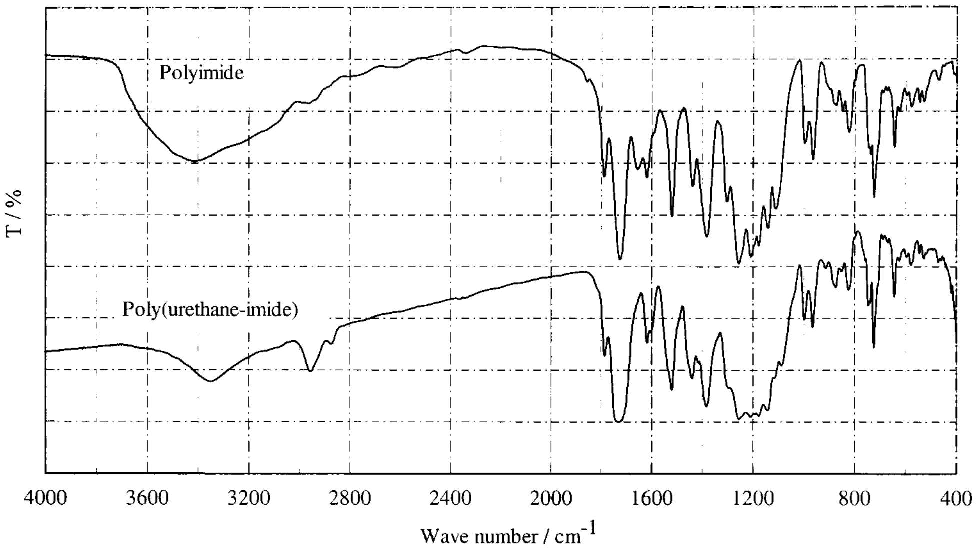


Fig. 2. IR spectra of polyimide, PI_{10} and poly(urethane–imide), PU/PI_{10}, after being treated at 200°C.

the formation of network. In order to prevent gelation during mixing, isocyanate groups were protected with phenol. All the blend solutions were clear and transparent. Films were cast on glass plates from the solution. After drying, the cast films became opaque which means phase separation. The films became transparent, however, after heat treatment at 200°C.

During the heat treatment of the cast films at 200°C in vacuo, endcapped phenol is released and is evaporated. The splitting reaction of phenol from polyurethane prepolymer was confirmed to occur at 120°C by DSC and TGA [22]. The isocyanate groups that were generated by the removal of phenol react with hydroxyl groups in the polyimide, giving poly(urethane–imide). The reaction between polyurethane prepolymer and hydroxyl groups in polyimide occurs at the interface of the separated phase. The progress of the reaction was confirmed by the IR of the cast films. After 200°C treatment of poly(urethane–imide), as shown in Fig. 2, the absorption of hydroxyl groups in polyimide at 3400 cm^{-1} almost disappeared. A small absorption of poly(urethane–imide) at 3340 cm^{-1} is based on the N–H of urethane. The characteristic absorption of NCO at 2270 cm^{-1} was not observed in the Fig. 2. These IR spectra confirms that generated isocyanate groups reacted with hydroxyl groups in the polyimide to form poly(urethane–imide), though other reactions such as the formation of allophanate by a reaction of generated isocyanate with urethane linkage cannot be denied because of the similarity in IR.

3.2. Solvent-resistance of the poly(urethane–imide)s

Solvent-resistance of the poly(urethane–imide) films was investigated. The films were immersed into various solvents as hexane, toluene, dichloromethane, acetone, THF and NMP for one week. The solubility of poly(urethane–imide)s was compared with that of polyimide in Table 3. All the polyimides used as one component were partially soluble in acetone and easily soluble in such solvents as THF and NMP. All the poly(urethane–imide) films, however, did not change at all in hexane and toluene, and only swelled in dichloromethane, acetone, THF and NMP. The only exception is PU/PI_{12} which dissolved in NMP. Therefore, it was shown that the poly(urethane–imide) films prepared by our method has excellent solvent-resistance. The reason

Table 3
Solubility of polyimide and poly(urethane–imide)s

Solvent	Solubility[a]							
	PI_{10}	PI_{21}	PI_{11}	PI_{12}	PU/PI_{10}	PU/PI_{21}	PU/PI_{11}	PU/PI_{12}
Hexane	×	×	×	×	×	×	×	×
Toluene	×	×	×	×	×	×	×	×
Dichloromethane	×	×	×	×	◇	◇	◇	◇
Acetone	△	△	△	△	◇	◇	◇	◇
THF	○	○	○	○	◇	◇	◇	◇
NMP	○	○	○	○	◇	◇	◇	○

[a] × insoluble; ◇ swelling; △ partially soluble; ○ soluble.

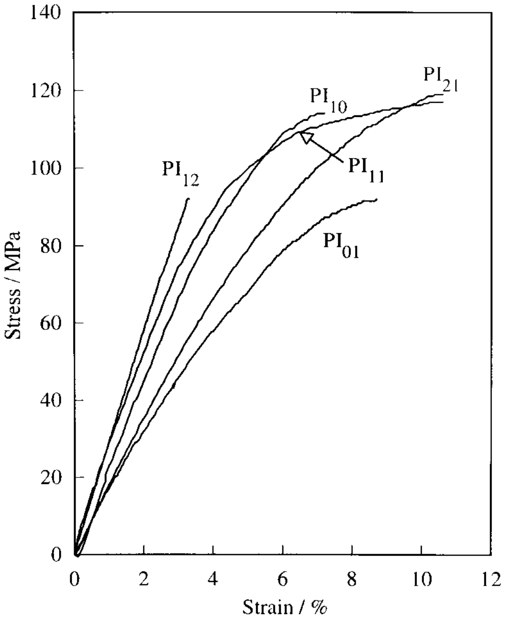


Fig. 3. Tensile properties of polyimide films.

for the excellent solvent-resistance is considered to be caused by the formation of network structure between the polyurethane and polyimide. For PU/PI_{12}, the amount of hydroxyl groups in polyimide is the lowest and thus the crosslink density is the lowest, resulting in dissolution in NMP.

3.3. Tensile properties of poly(urethane–imide) films

Tensile properties of polyimide films with various content of hydroxyl groups are shown in Fig. 3. All the polyimides containing hydroxyl groups (PI_{10}, PI_{21}, PI_{11}, PI_{12}) had higher modulus from 3.0 to 3.5 GPa than PI_{01} (2.4 GPa).

Tensile properties of poly(urethane–imide) films are shown in Table 4 and Fig. 4. The poly(urethane–imide) films showed various properties depending on the ratio of PI/PU and the nature of polyimide used. Films of PU/PI_{12}, PU/PI_{21} and PU/PI_{10} were plastic but film for PU/PI_{11} was elastic and elongation was c.a. 340%. The film almost returned to original after break. The initial modulus of PU/PI_{11} was 11.6 MPa, much lower than other poly(urethane–imide) films and tensile curve showed opposite S pattern, a typical elastomer pattern. Moduli for PU/PI_{12}, PU/PI_{21} and PU/PI_{10} were 297, 186 and 118 MPa, respectively. The curve for PU/PI_{12} was little different from others. As hydroxyl groups in PI_{12} is the lowest, it makes the reaction of polyurethane prepolymer and hydroxyl groups difficult, leading to very low crosslink density.

Table 4
Tensile properties of polyimide and poly(urethane–imide) films

	E (MPa)	σ (MPa)	Elongation (%)
PI_{10}	3500	114	7.2
PI_{21}	3200	119	10.6
PI_{11}	3500	117	10.6
PI_{12}	3400	116	5.0
PI_{01}	2400	92	8.7
PU/PI_{10}	118	14.3	158
PU/PI_{21}	186	35	192
PU/PI_{11}	11.6	14.3	340
PU/PI_{12}	297	15.4	118

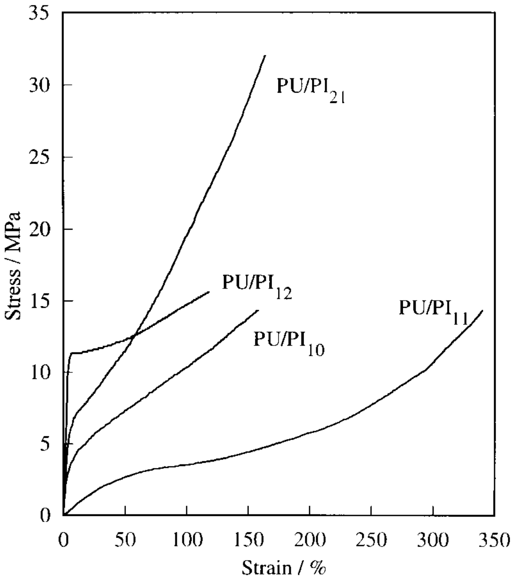


Fig. 4. Tensile properties of poly(urethane–imide) films.

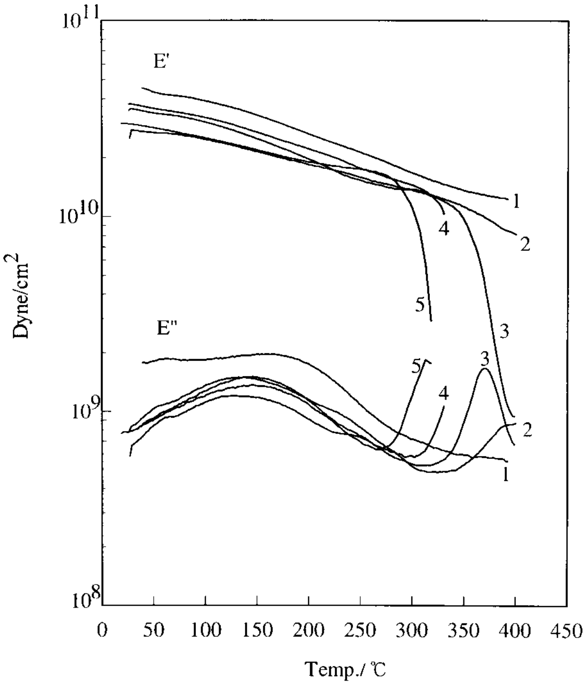


Fig. 5. Viscoelastic properties of polyimide films.1. PI_{10}; 2. PI_{21}; 3. PI_{11}; 4. PI_{12}; 5. PI_{01}.

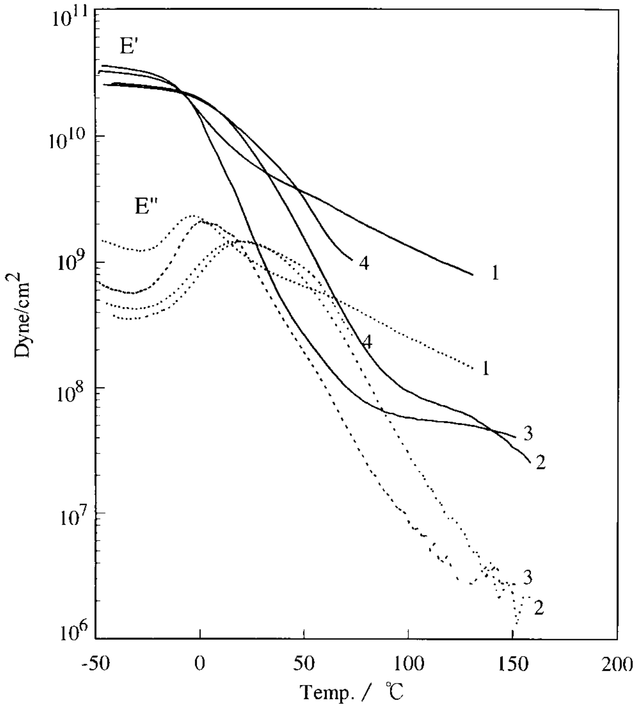


Fig. 6. Viscoelastic properties of poly(urethane–imide) films.1. PU/PI_{10}; 2. PU/PI_{21}; 3. PU/PI_{11}; 4. PU/PI_{12}.

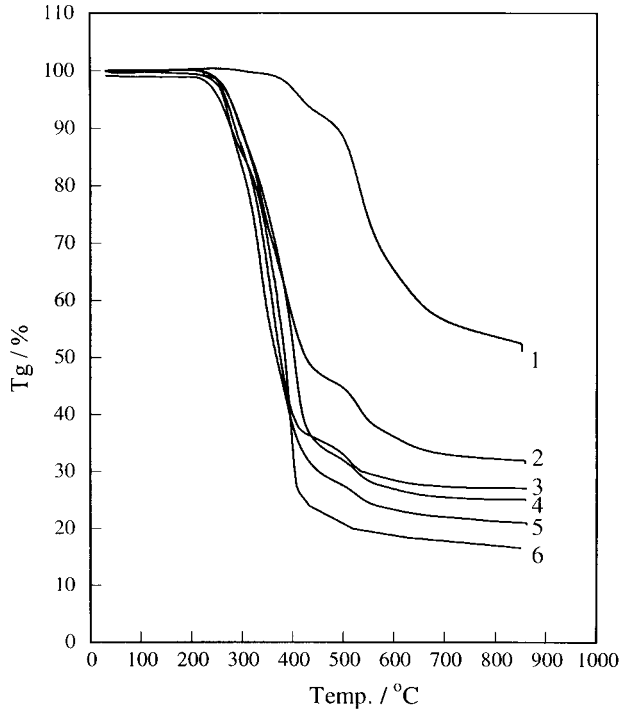


Fig. 7. TGA of poly(urethane–imide)s.1. PI_{10}; 2. PU/PI_{12}; 3. PU/PI_{11}; 4. PU/PI_{21}; 5. PU/PI_{10}; 6. PU.

3.4. *Viscoelastic properties of poly(urethane–imide) films*

Viscoelastic analysis of the polyimide films are shown in Fig. 5. The glass transition temperatures (T_g) of polyimides estimated from the maximum of E$''$ shifted depending on the ratio of diamines. Polyimide with higher content of AHBP had higher T_g as a result of the stronger hydrogen bonding and higher rigidity of the polymer backbone. The T_g for PI_{10} is more than 400°C.

Viscoelastic analysis of the poly(urethane–imide) films are shown in Fig. 6. T_g of poly(urethane–imide)s shifted to higher temperatures with the increase of polyimide component: T_g was − 5°C for PU/PI_{12}, 0°C for PU/PI_{11}, 18°C for PU/PI_{21} and 20°C for PU/PI_{10}. This suggests miscibility between polyurethane and polyimide to some extent. The film for PU/PI_{11} showed a wide plateau of storage modulus from c.a. 70°C to 150°C, which showed microphase separation between soft and hard segments and also well-developed network structure. Other poly(urethane–imide) did not show the wide plateau in the storage modulus.

Poly(urethane–imide) films prepared through the reaction between poly(amide acid) and PU prepolymer showed wide plateau of storage modulus up to 240°C [22,23]. On the contrary, poly(urethane–imide) films prepared in this study through the reaction between hydroxyl groups in polyimide and PU prepolymer showed plateau of storage modulus up to 150°C. This supports the idea that urethane linkage in poly(urethane–imide) is cut into isocyanate and hydroxyl groups at c.a. 150°C.

3.5. *Thermal stability of poly(urethane–imide)*

TGA of polyimide and poly(urethane–imide)s is shown in Fig. 7. For the polyimide containing hydroxyl groups, as shown in PI_{10} as an example, degradation occurred in two stages. The first stage appeared during 380°C ∽ 450 with 8% weight loss as a result of the degradation of hydroxyl groups, and the second stage appeared above 500°C because of the degradation of imide backbone. TGA for poly(urethane–imide)s showed that the initial decomposition temperatures (5% weight loss) was about 270°C. The decomposition temperature did not change so much with the content of polyimide component, as shown in Fig. 8. Conventional polyurethanes are known to decompose at ca. 240°C. This indicates that the heat resistance of polyurethane was improved by the introduction of polyimide.

4. Conclusions

A series of poly(urethane–imide) films were prepared by a reaction of a polyurethane prepolymer and hydroxyl groups in a soluble polyimide. Transparent poly(urethane–imide) films were obtained, which suggests some miscibility between polyurethane and polyimide. This was also confirmed from the viscoelastic analysis. Poly(urethane–imide)s showed excellent solvent-resistance as a result of

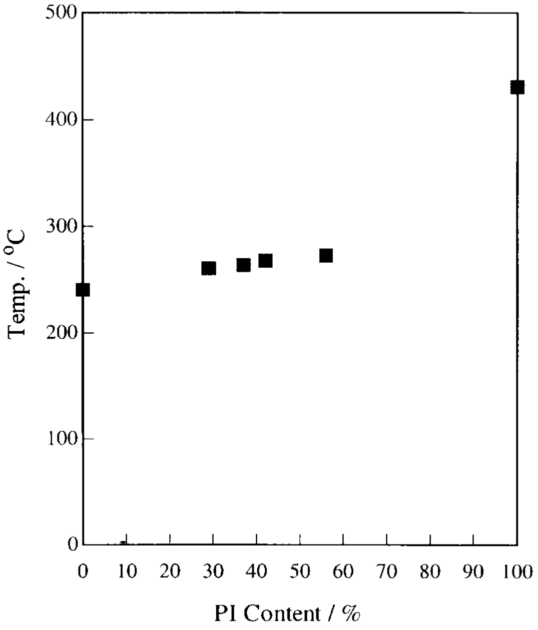


Fig. 8. Temperature of 5% weight loss for poly(urethane–imide) with various polyimide content.

the formation of network structure, and the films had the properties of either plastic or elastomer depending on the chemical structure and crosslink density. Introducing polyimide component into polyurethane improved decomposition temperature of polyurethane for more than 30°C. Urethane linkage in the poly(urethane–imide) are split at ca. 150°C and isocyanate groups are generated. The unique equilibrium reaction of urethane linkage in the poly(urethane–imide) can be applied such as high temperature adhesives.

Acknowledgements

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