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Preparation and properties of novel poly(urethane-imide)s

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A series of poly(urethane-imide)s were prepared by a novel approach. Polyurethane (PU) prepolymer was prepared by the reaction of polyester polyol and 2,4-tolylenediisocyanate (2,4-TDI), and then end-capped with phenol. The PU prepolymer was blended with poly(amide acid) or oligo(amide acid) prepared from 2,2′-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and oxydianiline (ODA) at room temperature in various weight ratios. The blend films obtained by casting and then drying were not transparent, suggesting that phase separation occurred between the polyimide (PI) and PU components. The films became transparent, however, after thermal treatment at 100°C and then 200°C for 1 h each, irrespective of the ratio of the two components. The poly(urethane-imide) films showed good solvent-resistance. Dynamic mechanical analysis of the films showed that glass transition temperatures (T_g) shifted depending on the ratio of PI and PU components. This shift of T_g, along with the transparency of the films, suggests that the PU and PI components employed here are miscible to some extent and that domains of each phase by microphase separation are small. Tensile measurement of the blend films from poly(amide acid) showed that the films are plastic or elastic, depending on the ratio of the components. Thermal stability of the PU was found to increase by the incorporation of polyimide component. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(urethane-imide); polyimide; polyurethane)

INTRODUCTION

Polyurethane (PU) is a versatile polymer and can be easily prepared by a simple polyaddition reaction of polyol, isocyanate and chain extender. The tailor-made properties from supersoft flexible foam to tough elastomers and to long-wearing coatings have resulted in many end applications[1–4]. Unfortunately, the conventional PU is known to exhibit poor thermal stability, which limits its applications. For example, the acceptable mechanical properties disappear above 80–90°C and thermal degradation takes place at temperatures above 200°C[5].

Attempts to improve the thermal stability of PU have been made over a long period. One of the methods used to improve the thermal stability of PU is the chemical modification of its structure by blending or copolymerizing with more thermally stable polymers. Some of these examples are poly(urethane-urea)[6,7], poly(urethane-epoxy)[8–10] and polyurethane–diacetylene[11]. Recently, more attention has been paid to modification by heterocyclic groups. Polyimides are an important class of heterocyclic polymers with remarkable heat resistance and superior mechanical, electrical and durable properties[12–15]. Various attempts to incorporate polyimide units into PU have been made. Reaction of isocyanate-terminated PU prepolymer with acid dianhydride is the method most often utilized to introduce the imide function into the PU backbone[16–20]. The linear poly(urethane-imide) elastomers were obtained, which showed considerably better mechanical properties than the typical linear PU and excellent thermal stability. A modified method was also utilized, in which an acid dianhydride was reacted with aminoethanol to give hydroxyl-terminated imide monomer, which was then reacted with isocyanate-terminated PU prepolymer[21]. Heat-resistant thermoplastic poly(urethane-imide) elastomer with low compression permanently set at high temperature was prepared. Another modified method is the reaction of isocyanate-terminated PU prepolymer with aromatic diamines and dianhydride to prepare PU with imide groups in the backbone[22]. Intermolecular Diels–Alder (DA) reaction of 4-methyl-1,3-phenylenebis(2-furanylcarbamate) with various bismaleimides is also reported to give a series of poly(urethane-imide)s[23–26]. The prepared poly(urethane-imide)s were used as processable matrix resin for glass-fibre composite. The composite exhibited very low void content, good chemical resistance and excellent mechanical properties. All of the poly(urethane-imide)s obtained by the previous studies are linear. Therefore, the solvent-resistance to ordinary organic solvents is poor.

Here, we report our approach to preparing a novel type of poly(urethane-imide). Our approach is based on the reaction between PU prepolymer and poly(amide acid) which is a precursor of polyimide. Poly(urethane-imide) prepared by our novel method has 3-dimensional network structure, and is expected to have properties different from those of linear poly(urethane-imide)s.
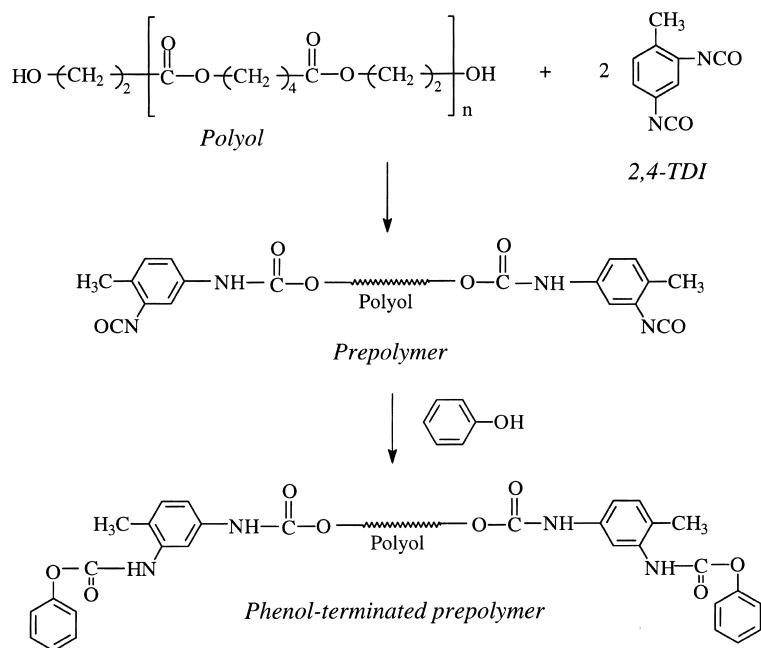
EXPERIMENTAL

Materials

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

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6FDA + ODA

Oligo(amide acid) (n= 1 and 5)
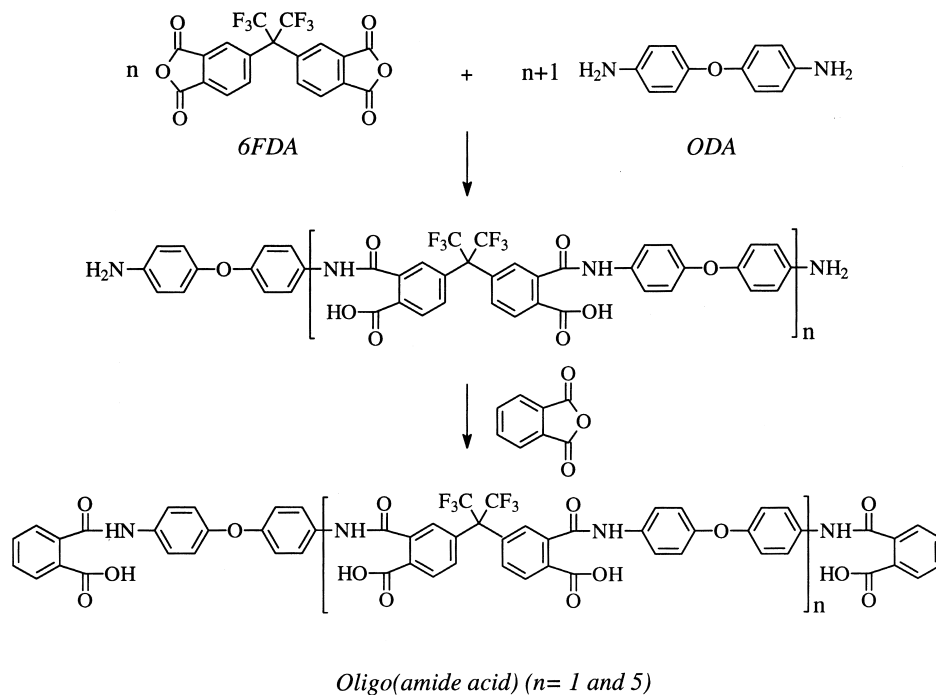
Scheme 1 Preparation of poly(amide acid)

Polyol + 2 *2,4-TDI*

Prepolymer

Phenol-terminated prepolymer

Scheme 2 Preparation of polyurethane prepolymer

mixture of acetic anhydride/acetic acid (30/70), followed by sublimation. Pyromellitic dianhydride (PMDA) was purified by recrystallization from acetic anhydride, followed by sublimation. Oxydianiline (ODA) was purified by sublimation. N-Methyl-2-pyrrolidone (NMP) was purified by distillation under reduced pressure. Phthalic anhydride was purified by sublimation before use. Tolylene-2,4-diisocyanate (TDI), kindly delivered by Nippon Polyurethane Ltd, was used as received. Polyethylene adipate (MW *ca.* 1000, OH number in KOH: 113) (PEA), kindly delivered by Nippon Polyurethane Ltd, was dried *in vacuo* at 80°C for one night before use. Phenol was used as received.

Preparation of poly(amide acid) and oligo(amide acid)

Poly(amide acid) was prepared by the reaction of an equimolar amount of 6FDA and ODA in NMP[27]. ODA (3 mmol, 0.6006 g) was dissolved in NMP (17.4 g) under a nitrogen atmosphere. An equimolar amount of 6FDA (3 mmol, 1.3327 g) was added, followed by stirring at room temperature for 2 h. Poly(amide acid) was also prepared from PMDA and ODA by the same method.

Viscocities of the poly(amide acid)s were 0.93 dL g^{-1} and 1.1 dL g^{-1} for 6FDA/ODA and PMDA/ODA, respectively, at a concentration of 0.5 g dL^{-1} in NMP.

Amine-terminated oligo(amide acid)s with various degrees of polymerization ($n = 1$ and 5 corresponding to $DP = 3$ and 11, respectively) were prepared by adjusting the stoichiometry of the dianhydride and diamine monomers. Then, they were reacted with phthalic anhydride, as shown in *Scheme 1*, to give phthalic anhydride-terminated oligo(amide acid)s[28].

Preparation of polyurethane prepolymer

Polyurethane prepolymer was prepared by the reaction of TDI and polyol (PEA) in a molar ratio of 2:1. Dried PEA (5 mmol, 5.00 g) was placed in three-neck flask equipped with a mechanical stirrer and melted by heating at *ca.* 50°C. TDI (10 mmol, 1.74 g) was added dropwise at that temperature. The mixture was kept stirred at 80°C for 2 h under nitrogen atmosphere. Finally, phenol (10 mmol, 0.94 g) was added and stirred at 80°C for 3 h to end-cap the prepolymer as shown in *Scheme 2*. Blocked PU prepolymer obtained as viscous liquid was diluted with NMP into a 50% solution.

Preparation of the blend solutions and cast films

Poly(amide acid) solution (10% in NMP) and PU prepolymer solution (50% in NMP) were mixed in various weight ratios. For example, a blend of the poly(amide acid) solution and PU prepolymer solution in 5:1 (weight ratio) gives a solution of PI/PU ratio of 50/50. The blend solution was cast on a glass plate, then solvent (NMP) was evaporated under vacuum at 50°C for 16 h. The cast films were thermally treated at 100°C and 200°C for 1 h each.

Model reactions

The reaction between poly(amide acid) and PU pre-polymer was investigated by model reactions between phenyl isocyanate and benzanilide or benzoic acid. Benzanilide (5 mmol, 0.995 g) was dissolved in THF (4 g), then phenyl isocyanate (5 mmol, 0.600 g) was added. The mixture was refluxed in THF for 6 h. Then, solvent was evaporated in rotary evaporator and dried at 50°C for 5 h. The reaction in toluene was also performed similarly.

The reaction between benzoic acid (5 mmol, 0.661 g) and phenyl isocyanate (5 mmol, 0.600 g) was also performed similarly.

Measurements

The i.r. spectrum was recorded on JEOL FT/IR 400. Differential scanning calorimetry (d.s.c.) was performed with a Rigaku Thermal Analysis Station, TAS 100, equipped with a d.s.c. cell base at a heating rate of 10°C min^{-1} under a nitrogen atmosphere. Thermogravimetric analyses (t.g.a.) were carried out with a Seiko I TG/DTA 300, at a heating rate of 5°C min^{-1} under Ar. Dynamic viscoelastic measurement was carried out with a Rhevibron Model DDV-01FP from −50°C to 400°C. Tensile properties were investigated using an Imada Seisaku-sho Model SV-3 at room temperature.

RESULTS AND DISCUSSION

Preparation of the poly(urethane-imide)

Polyurethane prepolymer solution and poly(amide acid) or oligo(amide acid) solution were mixed in various weight ratios. All the blend solutions were clear and transparent at any weight ratio. After drying, the cast films became opaque. This indicates that phase separation occurred between the two components. After the heat treatment at 200°C, however, all the films based on 6FDA/ODA became transparent. The films based on PMDA/ODA were, however, opaque even after the heat treatment. This suggests the difference of phase separation between poly(urethane-imide) based on PMDA/ODA and that based on 6FDA/ODA. The domains of phase separation should have become very small in the case of 6FDA/ODA, but relatively large in the case of PMDA/ODA.

During the heat treatment of poly(urethane-imide), end-capped phenol was released and isocyanate comes out to react with poly(amide acid), giving poly(urethane-imide). The splitting reaction of PU prepolymer was confirmed to occur at 120°C by d.s.c. and t.g.a.[29]. The reaction between PU prepolymer and poly(amide acid) or oligo(amide acid) occurs at the interface of the separated phase. The changes in the i.r. spectra before and after the 200°C treatment are shown in *Figure 1*, to confirm the formation of poly
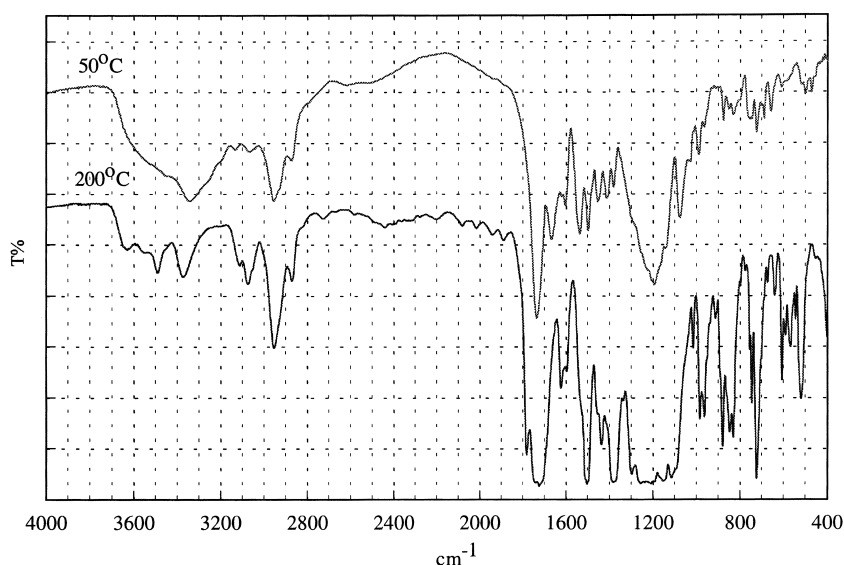
Figure 1 Infrared spectrum of poly(urethane-imide) based on 6FDA/ODA at PI/PU 30/70

(urethane-imide) based on 6FDA/ODA. After 200°C treatment, the absorption of amide acid (1680 cm^{-1}) disappeared and absorptions due to the imide function appeared at 1780, 1380, 720 cm^{-1}, and the urethane function appeared at 3340 and 1740 cm^{-1}.

To investigate the reaction between poly(amide acid) and PU prepolymer, the reaction between phenyl isocyanate and benzanilide or benzoic acid was examined as model reactions. In the reaction between benzanilide and phenyl isocyanate, the i.r. spectra of the products were the same as the starting material after refluxing in THF and also in toluene. In the case of benzoic acid, the i.r. spectra of starting material and products were different. For the product refluxed in THF, the absorptions of benzoic acid became smaller and many new absorptions appeared, including large anhydride adsorption at 1800 cm^{-1}. For the product refluxed in toluene, the absorptions of anhydride became smaller and the adsorptions of phenyl urea became large. According to the above results, it was found that benzoic acid reacts with phenyl isocyanate, giving anhydride and diphenyl urea as shown in *Scheme 3*. They are considered to react at higher temperatures to give benzanilide[2]. These model reactions clearly indicate that isocyanate reacts with carboxylic groups in the poly(amide acid).
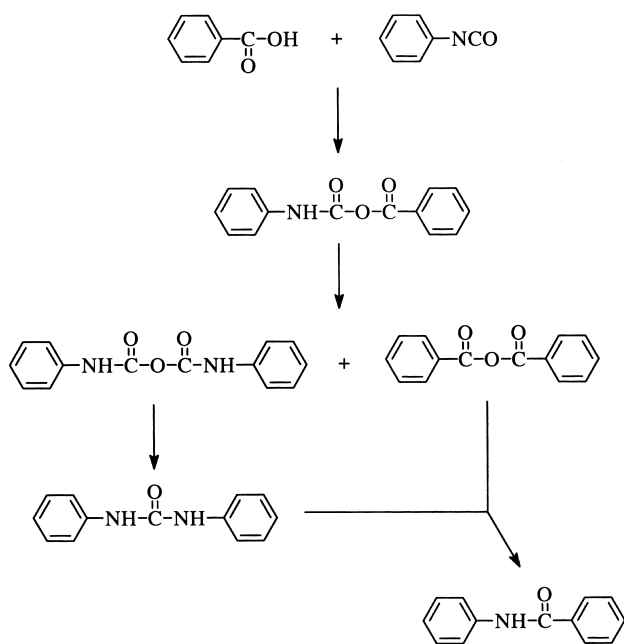
Scheme 3 Model reactions

Table 1 Solubility of poly(urethane-imide) for PI/PU 10/90

Solvent	Solubility	
	Poly(urethane-imide)[a]	Polyimide[b]
Hexane	×	×
Toluene	×	×
Dichrolomethane	◇	×
Acetone	◇	△
THF	◇	○
NMP	◇	○

×, insoluble; ◇, swelling; △, partially soluble; ○, soluble
[a]6FDA/ODA was used as the imide component
[b]6FDA/ODA imidized at 200°C for 1 h

Solvent-resistance of the poly(urethane-imide)

Solvent-resistance of the poly(urethane-imide)s was investigated. The films were immersed into various solvents as hexane, toluene, dichloromethane, acetone, THF and NMP for 7 days. The results of poly(urethane-imide) (PI/PU = 10/90) based on 6FDA/ODA were compared with that of 6FDA/ODA polyimide in *Table 1*. All the films did not change at all in hexane and toluene, but swelled in dichloromethane, acetone, THF and NMP. It should be mentioned that 6FDA/ODA polyimide was soluble in such solvents as THF and NMP, partially in acetone, but poly(urethane-imide)s were not soluble. Therefore, it was shown that the poly(urethane-imide) prepared by our method has excellent solvent-resistance. The reason for the excellent solvent-resistance is considered to be the formation of a network structure between the PU and PI.

Tensile properties of poly(urethane-imide)

Tensile properties of poly(urethane-imide) films based on 6FDA/ODA are summarized in *Table 2*, and some examples are shown in *Figure 2*. When poly(amide acid) was used as the PI component, the properties of the films changed from

Table 2 Tensile properties of poly(urethane-imide) films from 6FDA/ODA

PI component	PI/PU ratio[a]	*E* (MPa)	σ (MPa)	Elongation (%)	State[b]
Polyimide	100/0	2500	101	7.0	P
Polyimide	90/10	2400	92	8.7	P
Polyimide	70/30	2400	43	1.6	P
Polyimide	50/50	1400	20	1.4	P
Polyimide	30/70	117	11.5	170	P
Polyimide	20/80	11.8	9.3	332	E
Polyimide	10/90	5.4	6.1	294	E
DP = 3	20/80	4.3	4.2	376	E
DP = 3	10/90	2.5	3.0	292	E
DP = 11	20/80	7.4	6.6	192	P
DP = 11	10/90	2.9	3.5	341	E

[a]Weight ratio of poly(amide acid) or oligo(amide acid) and PU prepolymer
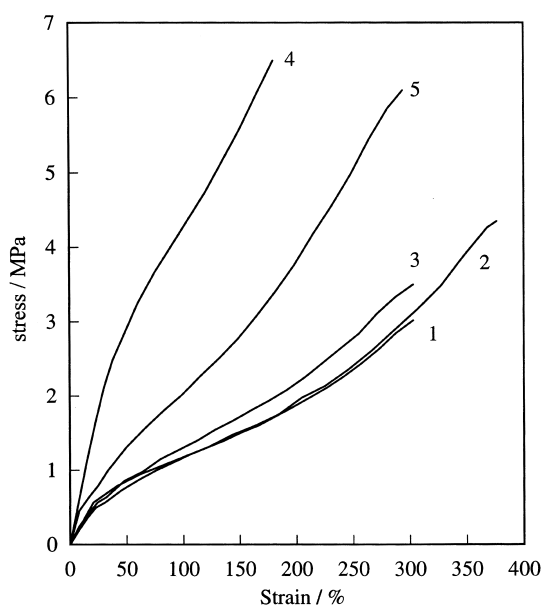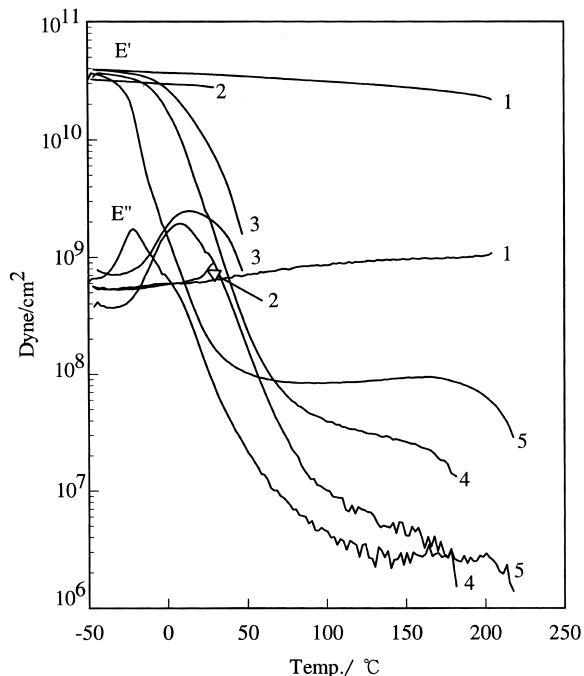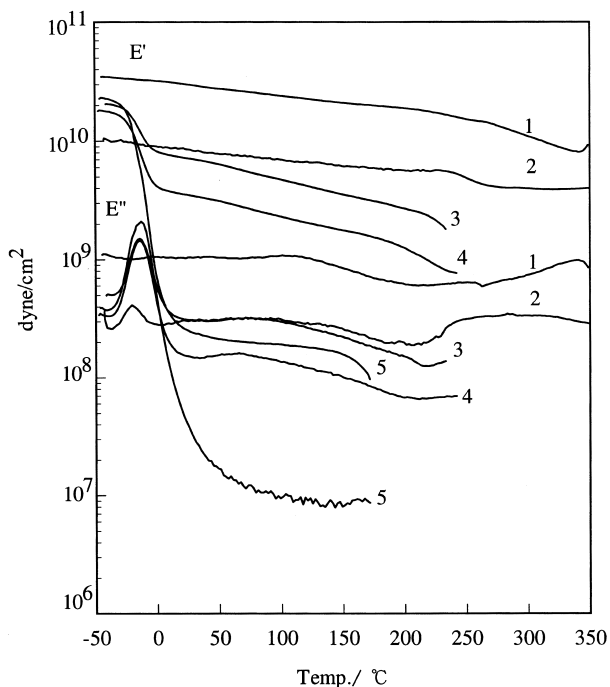[b]E, elastic; P, plastic

Figure 2 Tensile properties of poly(urethane-imide) based on 6FDA/ODA: (1) *DP* = 3, PI/PU 10/90; (2) *DP* = 3, PI/PU 20/80; (3) *DP* = 11, PI/PU 10/90; (4) *DP* = 11, PI/PU 20/80; (5) polyimide, PI/PU 10/90

plastic (PI/PU = 90/10 and 70/30) to brittle (PI/PU = 50/50), then to elastic (PI/PU = 20/80 and 10/90) with the increase in PU ratio. Films for PI/PU 20/80 and 10/90 are typical elastomers whose elongations were more than 300%, and they almost returned to original after breaking. The film for PI/PU 50/50 was brittle and the elongation became the smallest. With further increase in the PI/PU ratio, elongation became large.

The difference in phase separation results in different tensile properties of poly(urethane-imide) films between 6FDA/ODA and PMDA/ODA. For example, poly(urethane-imide) films based on PMDA/ODA showed elasticity only for a PI/PU ratio of 5/95[29], but poly(urethane-imide) films based on 6FDA/ODA showed elasticity even at a PI/PU ratio of 20/80. This is considered to come from the smaller phase separation and better developed network structure in the case of 6FDA/ODA.
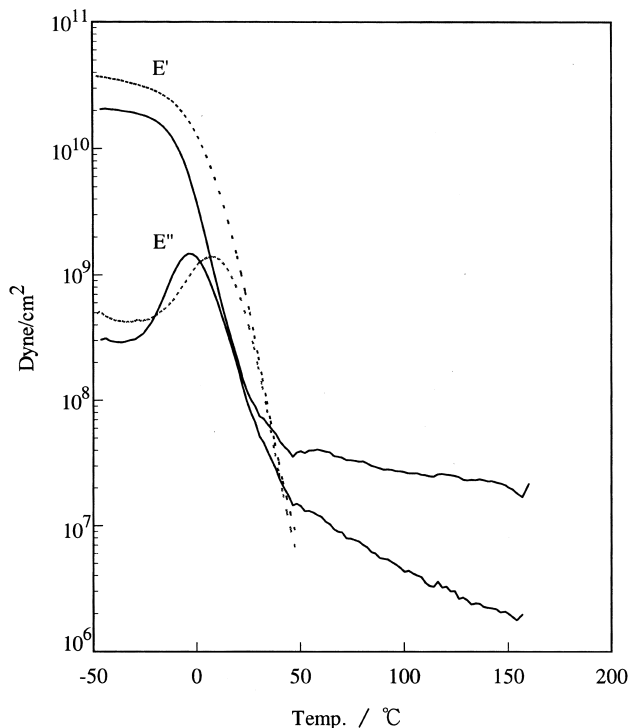

Figure 3 Viscoelastic properties of poly(urethane-imide) based on 6FDA/ODA: (1) PI/PU 90/10; (2) PI/PU 70/30; (3) PI/PU 30/70; (4) PI/PU 20/80; (5) PI/PU 10/90
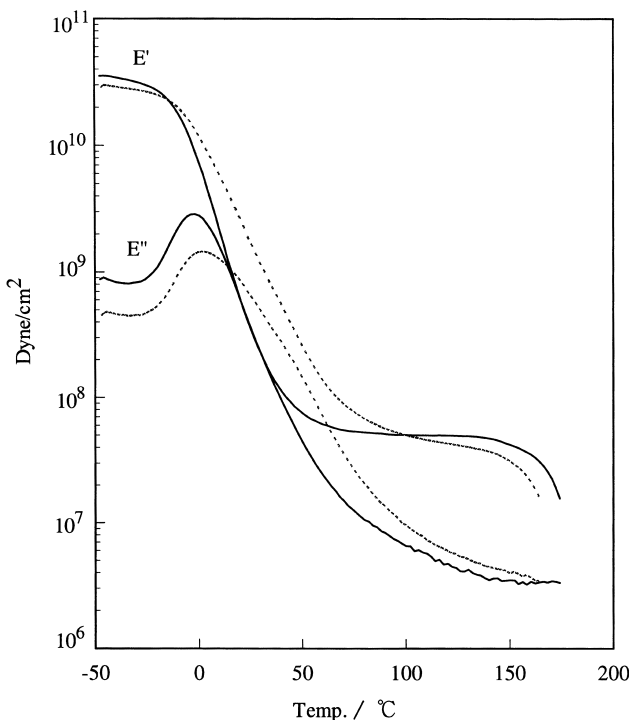

Figure 5 Viscoelastic properties of poly(urethane-imide) based on 6FDA/ODA of *DP* = 3: (- - -), PI/PU 10/90; (———), PI/PU 20/80

Figure 4 Viscoelastic properties of poly(urethane-imide) based on PMDA/ODA: (1) PI/PU 90/10; (2) PI/PU 70/30; (3) PI/PU 30/70; (4) PI/PU 20/80; (5) PI/PU 10/90

Figure 6 Viscoelastic properties of poly(urethane-imide) based on 6FDA/ODA of *DP* = 11: (- - -), PI/PU 10/90; (———), PI/PU 20/80
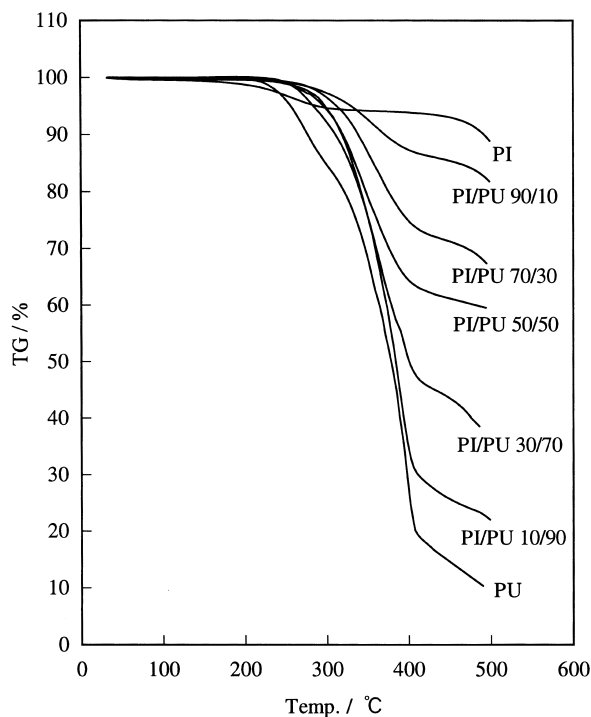
Figure 7 T.g.a. of poly(urethane-imide) based on 6FDA/ODA

Table 3 D.s.c. of poly(urethane-imide) from 6FDA/ODA

	PI/PU ratio	Onset temp. (°C)	Max. temp. (°C)	Endotherm (cal.g^{-1})	T_g (°C)
Polyimide	100/0	—	—	—	340
Polyimide	90/10	341	376	10.3	—
Polyimide	70/30	301	344	16.8	—
Polyimide	50/50	246	334	32.4	—
Polyimide	30/70	250	335	39.8	—
Polyimide	10/90	290	340	52.5	—
Polyimide	0/100	220	320	64.4	—
DP = 3	20/80	302	360	21.4	240
DP = 3	10/90	300	357	31.2	245
DP = 11	20/80	309	360	17.3	260
DP = 11	10/90	317	380	40.7	235

Figure 8 T.g.a. of poly(urethane-imide) based on 6FDA/ODA oligo (amide acid): (- - -), *DP* = 3; (———), *DP* = 11

Also from oligo(amide acid), elastic poly(urethane-imide)s were obtained at PI/PU = 10/90 and 20/80. When the PI/PU ratio is above 20/80, tough films were difficult to make, probably because of the low molecular weight of oligoimide.

Viscoelastic properties of poly(urethane-imide)

Viscoelastic analysis of the poly(urethane-imide) films based on 6FDA/ODA are shown in *Figure 3*. 6FDA/ODA polyimide has a T_g of 320°C after 200°C treatment. As shown in *Figure 3*, the T_g shifted, depending on the ratio of the two components: T_g was − 21°C for PI/PU 10/90, + 8°C for PI/PU = 20/80, and + 16°C for PI/PU = 30/70. The T_g based on the PU component was not observed for PI/PU 70/30 and PI/PU 90/10. The plateau of the storage modulus E' decreased with the increase in the PU component up to PI/PI 70/30. With a further increase in PU component, PI/PU 20/80 and 10/90 for example, poly(urethane-imide) has an extension plateau up to 190°C. The viscoelastic analyses of poly(urethane-imide) films based on PMDA/ODA are shown in *Figure 4*. In this case, T_g was almost constant, irrespective of the PI/PU ratio. Thus, this viscoelastic analysis confirmed that phase separation between PI and PU was smaller in the case of 6FDA/ODA than that based on PMDA/ODA.

Viscoelastic analyses of the poly(urethane-imide) based on 6FDA/ODA oligo(amide acid) are shown in *Figures 5 and 6*. In the case of poly(urethane-imide) from *DP* = 3 (*Figure 6*), we found that the film for PI/PU 10/90 was broken after T_g. But for *DP* = 11 (*Figure 7*), modulus was retained to more than 150°C after T_g and almost the same for PI/PU = 20/80 and 10/90. We can say that with the increase in the molecular weight of imide, a better network was formed.

Thermal stability of poly(urethane-imide)

The t.g.a. of poly(urethane-imide) based on 6FDA/ODA poly(amide acid) and oligo(amide acid) are shown in *Figures 7 and 8*, respectively. The t.g.a. in *Figure 7* shows that the initial decomposition temperatures of

poly(urethane-imide) are higher than that for PU. For example, the film for PI/PU = 10/90 that showed the property of elstomer exhibited 5% weight loss at 290°C, which is *ca*. 40°C higher than that of conventional PU. Poly(urethane-imide) based on oligo(amide acid) showed 5% weight loss at more than 260°C. These t.g.a. results were in agreement with the decomposition temperatures observed by d.s.c. (*Table 3*). The onset of decomposition appeared at 220°C for PU. The onset temperature became higher by modifying with polyimide. With the increase in PI component, the endotherm due to the decomposition became smaller, but the onset temperatures did not change so much. This indicates that the heat resistance of PU was improved by the introduction of polyimide.

CONCLUSIONS

A series of poly(urethane-imide)s were prepared by mixing PU prepolymer and poly(amide acid) or oligo(amide acid) solutions, followed by thermal treatment. Transparent poly(urethane-imide) films were obtained when 6FDA/ODA poly(amide acid) was used. They showed excellent solvent-resistance due to the formation of network structure. Films changed from plastic (PI/PU 90/10) to brittle (PI/PU 50/50) to plastic, then to elastic (PI/PU 20/80 and 10/90) with the increase in PU component. Phase separation in the

poly(urethane-imide) based on 6FDA/ODA was much smaller than in the poly(urethane-imide) based on PMDA/ODA. Inclusion of only 10% PI component improved the decomposition temperature of PU for more than 40°C, and the film was elastic in property.

ACKNOWLEDGEMENTS

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