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High performance poly(urethane-imide) prepared by introducing imide blocks into the polyurethane backbone

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Abstract

A series of novel linear poly(urethane-imide)s were synthesized by the reaction between isocyanate-terminated polyurethane (PU) prepolymer and amine- or anhydride-terminated oligoimide. PU prepolymer was synthesized by reacting polyethylene adipatediol of molecular weight 1000 with tolylene-2,4-diisocyanate at the molar ratio of 2:3 or 1:2. Oligoimide was synthesized from the reaction of 4,4′-(hexafluoroisopropylidene) diphthalic acid with 4,4′-oxydianiline at various molar ratios. Equimolar amounts of PU prepolymer and oligoimide were reacted in *N*-methyl-2-pyrrolidone, followed by casting on glass plates and heat treatment at 100 and 150 °C for 1 h each to give linear poly(urethane-imide)s as transparent yellowish brown films. Poly(urethane-imide) films with less of 30% of imide component became elastomer, and films with more than 36% imide component became plastic. The effects of end-groups of oligoimide, molecular weight of oligoimide, and molecular weight of PU prepolymer on the solvent resistance, the tensile properties, viscoelastic properties, and thermogravimetric properties of poly(urethane-imide) films were systematically examined. Solvent resistance and tensile modulus of poly(urethane-imide) films from amine-terminated oligoimides were better than those from anhydride-terminated oligoimides. On the other hand, thermal stability and elongation at break for the poly(urethane-imide) films from anhydride-terminated oligoimides were higher than those from amine-terminated oligoimides.

Keywords: Poly(urethane-imide)s; PU prepolymer; Oligoimide

1. Introduction

Polyurethane (PU) has excellent properties such as oil resistance, cold resistance, and abrasion resistance [1,2]. Therefore, PU is widely utilized in various fields as flexible foams, rigid foams, leathers, coating materials, adhesives, sealants, elastomers, and fibers. However, poor thermal property limits the application of PU in a harsh condition. In order to improve the heat-resistance of PU, various approaches have been attempted. Those include copolymerization and alloying with thermally more stable polymers such as urea [3], epoxy [4], diacetylene [5], and polyimide. Among the thermally stable polymers, polyimide (PI) that is known as a representative thermally stable polymer should be the best candidate both for copolymerization and polymer alloying because of the versatility of PI. The approaches to incorporate imide units into PU can be divided into two approaches.

One approach is the alloying of PU with high molecular weight PI or its precursor poly(amide acid), affording poly(urethane-imide)s with network structure. For example, in the case of blending PU prepolymer with poly(amide acid) [6–8], the isocyanate groups react with the carboxylic groups of poly(amide acid), affording a series of novel poly(urethane-imide) films with remarkably improved heat-resistance. The approach easily affords poly(urethane-imide) films having wide range of properties from elastomers to plastics by changing the ratio or chemical structure of PU and PI. By decomposing the thermally less stable PU domains [9], porous PI films were obtained [10,11]. Other examples include the preparation of poly(urethane-imide) films by the reaction of isocyanate-terminated PU prepolymer with soluble PI containing pendant phenolic hydroxyl groups [12], and the preparation of poly(urethane-amide) by the reaction of isocyanate-terminated PU prepolymer with pendant alcoholic hydroxyl groups of aromatic polyamide [13,14].

The other and the more often used approach for the synthesis of poly(urethane-imide)s is the reaction between isocyanate-terminated PU prepolymer and acid dianhydride, a monomer for the preparation of polyimide, thus giving linear

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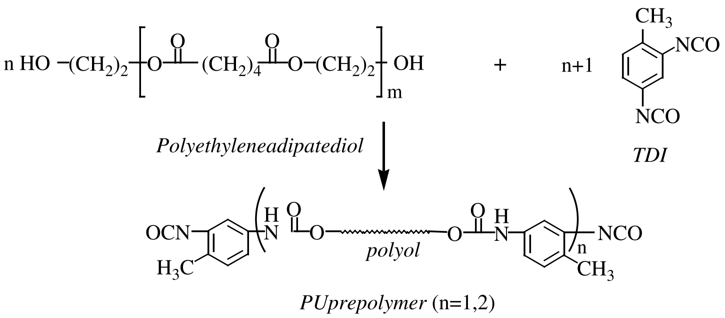


Scheme 1. Preparation of PU prepolymer.

poly(urethane-imide)s [15,16]. Other modified methods include the reaction of isocyanate-terminated PU prepolymer with the hydroxyl group of the amonoalcohol-modified acid dianhydride [17,18], the reaction of isocyanate-terminated PU prepolymer with aromatic diamine and acid dianhydride [19], and the utilization of intermolecular Diels–Alder reaction between the furanyl end-capped PU prepolymer with various bismaleimides [20–22].

Until now, however, there has been almost no report on poly(urethane-imide)s that incorporate imide component as blocks into PU backbone. The only report is from Jeon et al. in which anhydride-terminated oligoimide was use [23]. The novel methodology of introducing imide blocks into the PU backbone could afford flexibility in designing high performance PUs, because of the versatility available in the selection of dianhydride and diamine monomers, in the degree of polymerization for the oligoimide, and in the selection of terminal groups of oligoimide. In this report, we prepared soluble anhydride- and amine-terminated oligoimides, and the imide blocks were introduced into the backbone of PU by reacting with the isocyanate-end groups of PU prepolymer, giving novel type of linear poly(urethane-imide)s. The effects of end-groups of oligoimide, molecular weight of oligoimides, and molecular weight of PU prepolymer on the properties of the linear poly(urethane-imide)s were systematically examined.

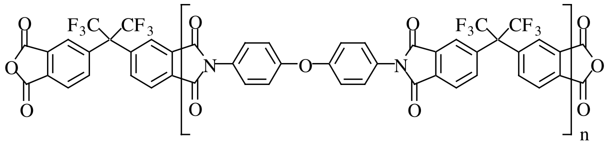
2. Results and discussion

2.1. Synthesis of poly(urethane-imide) films

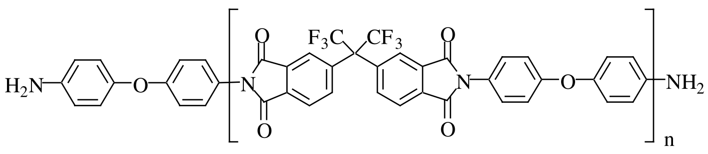
Polyethylene adipatediol of average molecular weight of 1000 was used as a polyol. The polyol was reacted with tolylene-2,4-diisocyanate (TDI), as shown in Scheme 1, at the molar ratio of 1:2 or 2:3, giving PU prepolymer with average MW of ca. 1000 for $n=1$ or ca. 2000 for $n=2$.

Two types of oligoimides (Fig. 1) were prepared from 4,4′-(hexafluoroisopropylidene)diphthalic acid (6FDA) and 4,4′-oxydianiline (ODA). The combination of 6FDA and ODA was selected for the purpose of preparing soluble oligoimides. Anhydride-terminated oligoimides (an series) were prepared by utilizing excess amounts of 6FDA, and amine-terminated oligoimide (am series) were prepared using excess amounts of ODA following the formulation shown in Table1.

The poly(urethane-imide)s were synthesized by reacting isocyanate-terminated PU prepolymer with equal molar amounts of oligoimide at room temperature for 2 h followed by film casting and drying at 50 °C and then heat treatment at 100 and 150 °C for 1 h each. As shown in Scheme 2, the reaction between anhydride-terminated oligoimide and PU prepolymer gives poly(urethane-imide) through the formation of imide linkage, and the reaction between amine-terminated oligoimide and PU prepolymer gives poly(urethane-imide)

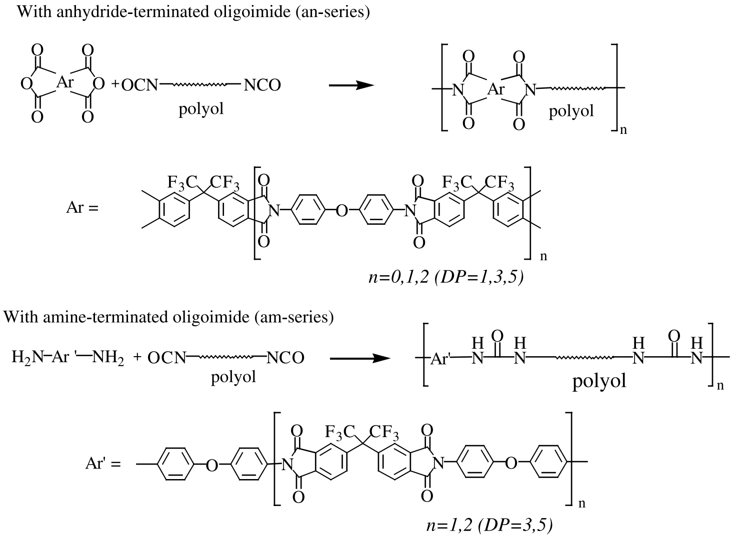


*Anhydride end-capped oligoimide (**an-series**)*
n=0,1,2 (DP=1,3,5)



*Amine end-capped oligoimide (**am-series**)*
n=1,2 (DP=3,5)

Fig. 1. Structure of oligoimides.



Scheme 2. Preparation of poly(urethane-imide)s.

Table 1
Formulation of poly(urethane-imide)s

Code	PU prepolymer		Oligoimide			Imide content %
	n	*g* (mmol)	*n* (DP)	6FDA, *g* (mmol)	ODA, *g* (mmol)	
PUI($n=1$/an-0/25)	1	1.35 (1)	0 (1)	0.44 (1)	0.00 (0)	25
PUI($n=1$/an-1/45)	1	1.35 (1)	1 (3)	0.88 (2)	0.20 (1)	45
PUI($n=1$/am-1/38)	1	1.35 (1)	1 (3)	0.44 (1)	0.40 (2)	38
PUI($n=2$/an-0/15)	2	2.62 (1)	0 (1)	0.44 (1)	0.00 (0)	15
PUI($n=2$/an-1/30)	2	2.62 (1)	1 (3)	0.88 (2)	0.20 (1)	30
PUI($n=2$/an-2/40)	2	1.31 (0.5)	2 (5)	0.66 (1.5)	0.20 (1)	40
PUI($n=2$/am-1/24)	2	2.62 (1)	1 (3)	0.44 (1)	0.40 (2)	24
PUI($n=2$/am-2/36)	2	1.31 (0.5)	2 (5)	0.44 (1)	0.30 (1.5)	36

through the formation of urea linkage. The codes for the poly(urethane-imide)s are shown in Table 1. For example, PUI($n=1$/an-0/25) indicates poly(urethane-imide) that was prepared from PU prepolymer ($n=1$) and an-series oligoimide ($n=0$), and the imide content is 25%. Poly(urethane-imide)s were obtained as yellowish brown transparent films. Typical PU elastomer was prepared, for comparison, by reacting equimolar amounts of PU prepolymer and 1,4-butanediol.

The progress of the reaction between the isocyanate groups of PU prepolymer and end groups of oligoimide was confirmed from IR. Fig. 2 shows the IR spectra for the reaction of PU prepolymer ($n=1$) and anhydride-terminated oligoimide ($n=1$, DP$=3$). The progress of the reaction between the isocyanate group and anhydride group was confirmed from the disappearance of the peaks that originate from the isocyanate (2270 cm^{-1}) and from the anhydride (1848 cm^{-1}) at the stage of 50 °C treatment. This clearly shows that isocyanate groups reacted with anhydride groups at the stage at 50 °C. Fig. 3 shows the IR spectra for the reaction of PU prepolymer ($n=2$) with the amine-terminated oligoimide ($n=2$). The progress of the reaction was similary confirmed from the disappearance of the peaks that originate the isocyanate (2270 cm^{-1}) and the amino group (3450 cm^{-1}) after the 50 °C treatment. Thus, the formation of poly(urethane-imide)s was confirmed from the IR spectra.

2.2. Solubility of poly(urethane-imide) films

The solubility of the poly(urethane-imide) films was examined and the results are summarized in Table 2.

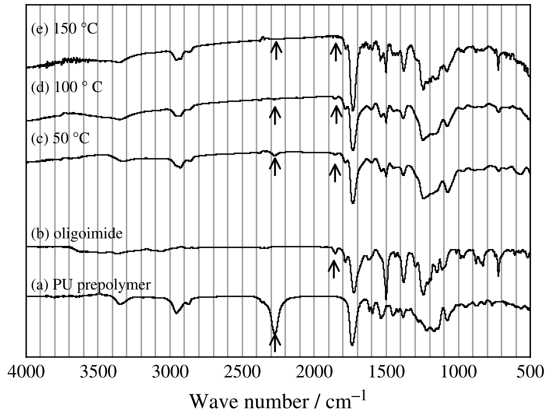


Fig. 2. IR spectra of PU prepolymer (a); anhydride-terminated oligoimide (b); and the blend after thermal treatment at 50 °C (c); at 100 °C (d); and at 150 °C (e).

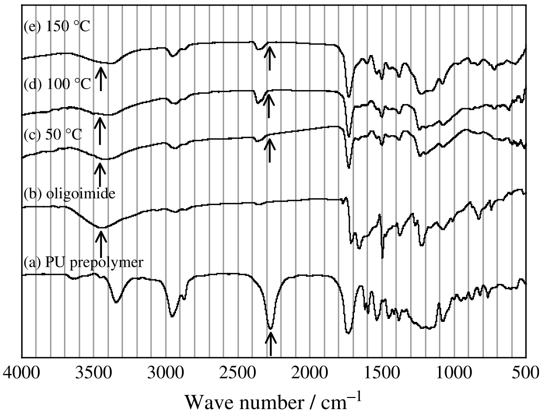


Fig. 3. IR spectra of PU prepolymer (a); amine-terminated oligoimide (b); and the blend after thermal treatment at 50 °C (c); at 100 °C (d); and at 150 °C (e).

Poly(urethane-imide)s prepared from the anhydride-terminated oligoimide dissolved easily in polar solvents such as NMP, *N*,*N*-dimethylformamide (DMF), tetrahydrofuran (THF), acetone, and dichloromethane. On the other hand, poly(urethane-imide)s prepared from the amine-terminated oligoimide showed much less solubility. They did not dissolve in NMP and DMF at room temperature, and were soluble only when heated. They also did not dissolve but only swelled in THF, acetone, and dichloromethane. The an-series of poly(urethane-imide)s are connected through imide linkages. On the other hand, the am-series of poly(urethane-imide)s are connected through urea linkages. The stronger intermolecular interaction between the urea linkage due to the stronger hydrogen-bonding capabilities than the imide linkage should be the reason for the solubility differences.

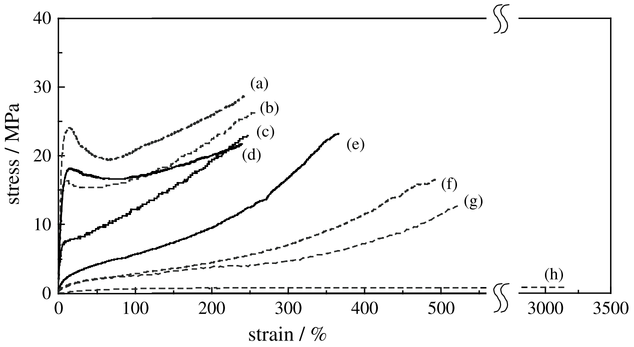


Fig. 4. Stress–strain curves for the poly(urethane-imide) films. (a) PUI($n=1$/an-1/45), (b) PUI($n=2$/an-2/40), (c) PUI($n=2$/am-2/36), (d) PUI($n=1$/am-1/38), (e) PUI($n=2$/am-1/24), (f) PUI($n=2$/an-1/30), (g) PUI($n=1$/an-0/25), (h) PUI($n=2$/an-0/15).

2.3. Tensile properties of poly(urethane-imide) films

Tensile measurements were performed and the results are shown in Fig. 4 in the form of stress–strain curves. Table 3 summarizes tensile modulus, tensile strength, and elongation at break for the films. The films containing less than 30% of imide component were elastomers, except PUI($n=2$/an-0/15). S–S curves for the elastomer films showed reverse S form typical for elastomers. The elongation at break for the elastomer films was as high as in the range of 370–520%. Tensile modulus for the elastomer films was less than 100 MPa. In the PUI($n=2$/an-0/15) film, anhydride monomer was introduced as imide component, which was not effective enough as physical crosslinking points to act as hard segment to induce microphase separation, resulting in no recovery after elongation. On the other hand, the films with more than 36% of imide component became plastic, and higher tensile modulus (420–880 MPa) was observed. The elongation at break of the plastic films were still as high as 240–260%, which indicates that even the plastic films are highly tough.

In Fig. 5, tensile modulus and elongation at break were plotted against the imide content for an-series and for am-series. With the increase of the imide content, tensile modulus increased and the elongation at break decreased for both types of the poly(urethane-imide). There is a clear tendency, however, that am-series have higher modulus and lower elongation at break than the an-series. This difference comes

Table 2
Solubility of poly(urethane-imide)s

Code	NMP	DMF	THF	CH_2Cl_2	Acetone	Hexane
PUI($n=2$/an-0/15)	△	△	△	△	△	×
PUI($n=1$/an-0/25)	○	○	○	○	○	×
PUI($n=2$/an-1/30)	○	○	○	○	○	×
PUI($n=2$/an-2/40)	○	○	○	○	○	×
PUI($n=1$/an-1/45)	○	○	○	○	○	×
PUI($n=2$/am-1/24)	△	△	△	□	□	×
PUI($n=2$/am-2/36)	△	△	□	□	□	×
PUI($n=1$/am-1/38)	△	△	□	□	□	×

○, soluble at room temperature; △, soluble on heating; □, swelling; ×, insoluble.

Table 3
Tensile properties of poly(urethane-imide) films

Code	E (MPa)	σ_b (MPa)	Elongation (%)	State
PUI($n=2$/an-0/15)	0.8	0.8	3140	Viscoelastomer
PUI($n=1$/an-0/25)	20	4.6	522	Elastomer
PUI($n=2$/an-1/30)	70	16	492	Elastomer
PUI($n=2$/an-2/40)	520	26	256	Plastic
PUI($n=1$/an-1/45)	880	29	244	Plastic
PUI($n=2$/am-1/24)	90	24	366	Elastomer
PUI($n=2$/am-2/36)	420	21	247	Plastic
PUI($n=1$/am-1/38)	438	22	242	Plastic

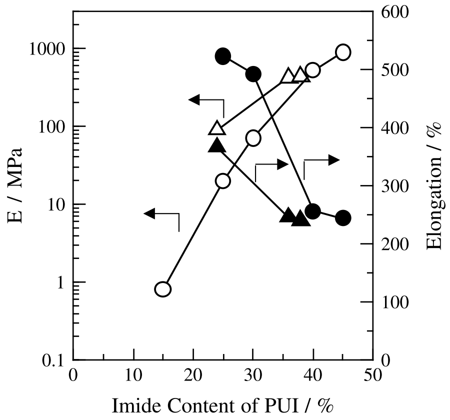


Fig. 5. Tensile modulus and elongation at break for an-series and am-series of poly(urethane-imide) films. ○, tensile modulus for an-series; △, tensile modulus for am-series; ●, elongation at break for an-series; ▲, elongation at break for am-series.

from the higher intermolecular interaction of the urea linkages of am-series than the imide linkages in the an-series, as was observed in the case of solubility difference.

2.4. *Viscoelastic properties of poly(urethane-imide) films*

The dynamic viscoelastic measurements of the poly(urethane-imide) films were performed. Fig. 6 shows the results for elastomers of poly(urethane-imide) films. The rubbery plateau region for the elastomers continued up to ca. 150 °C. In the case of introducing anhydride monomer ($n=0$), the rubbery plateau region ends at ca. 130 °C. On the contrary, in the case of introducing oligoimide (an-1 and am-1), the rubbery plateau region reached to 150–160 °C. The results clearly demonstrate that introduction of oligoimide is an effective approach to enhance the thermal properties of PU elastomers.

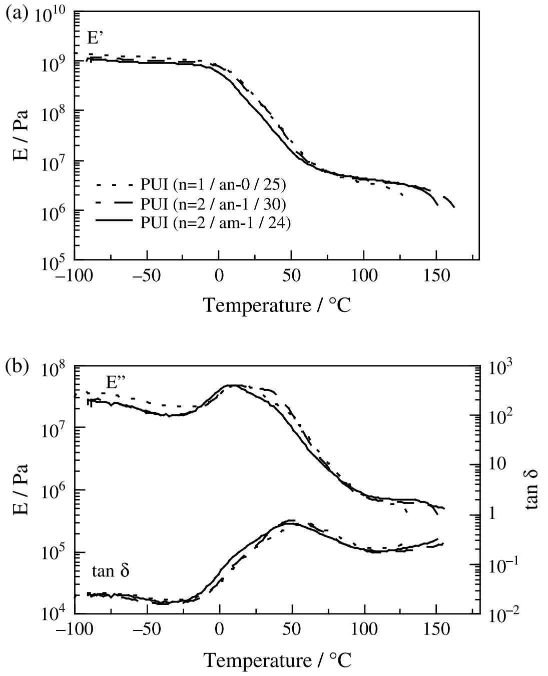


Fig. 6. Viscoelastic analyses of elastomeric poly(urethane-imide) films.

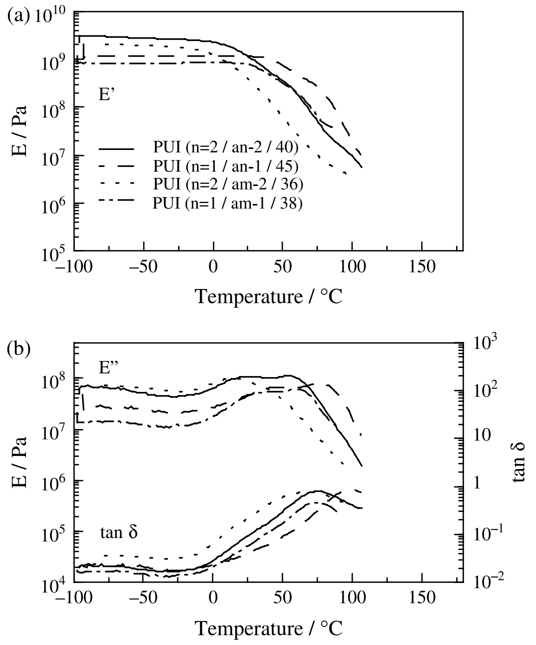


Fig. 7. Viscoelastic analyses of plastic poly(urethane-imide) films.

Fig. 7 shows the viscoelastic results of plastic poly(urethane-imide) films. Storage modulus at room temperature increased with the increase of imide content. It was clearly shown that T_g increased with the increase of the imide content. The increase of T_g was more prominent, as shown in Fig. 8, in the poly(urethane-imide)s from PU prepolymer of $n=1$ than those from PU prepolymer of $n=2$. There was little difference between the am-series and an-series, and also between the molecular weight of oligoimides. The results show that chain length of flexible PU component has strong effect for determining the T_g of poly(urethane-imide) films.

2.5. *Thermal stability of poly(urethane-imide)*

TGA measurements for poly(urethane-imide)s from PU prepolymer of $n=2$ and $n=1$ were performed. The 5 and 10% weight loss temperatures were plotted against the imide content for $n=2$ and $n=1$ in Figs. 9 and 10, respectively. It was clearly observed that the thermal decomposition temperature increased

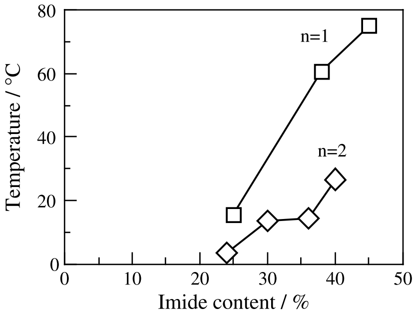


Fig. 8. Shift of T_g (from E'' maximum) of poly(urethane-imide) films against imide content.

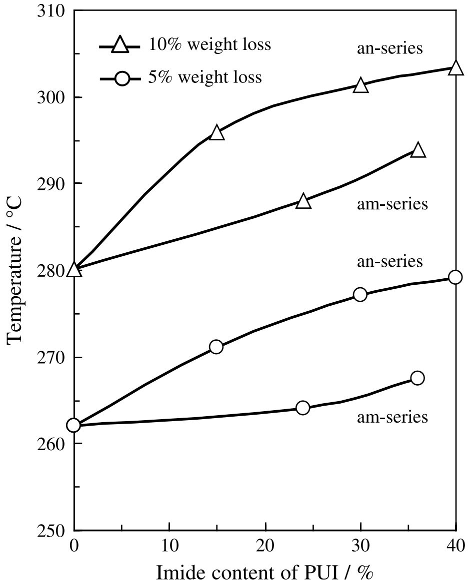


Fig. 9. Five and ten percentage weight loss temperatures of poly(urethane-imide)s from PU prepolymer ($n=2$) against the imide content.

with the increase of the imide content. There is also a clear tendency that anhydride-terminated oligoimides gave poly(urethane-imide)s with higher thermal stability than the amine-terminated oligoimides both for $n=2$ and $n=1$ series. This is because thermal stability of the imide linkages formed from the anhydride-terminated oligoimides is higher than that of the urea linkages formed from the amine-terminated oligoimides.

3. Conclusions

A novel series of linear poly(urethane-imide)s were synthesized by the reaction of PU prepolymer with anhydride- or amine-terminated oligoimide. Elastomer films were obtained with less than 30% of imide content, and plastic films were obtained with more than 36% of imide content. The glass transition temperature and thermal stability increased by introducing the imide component. The increase was more prominent with shorter urethane length. Thermal stability and elongation at break for the poly(urethane-imide) films from an-series were higher than the am-series. On the other hand, tensile modulus and solvent resistance for the poly(urethane-imide) films from am-series were higher than those from the an-series.

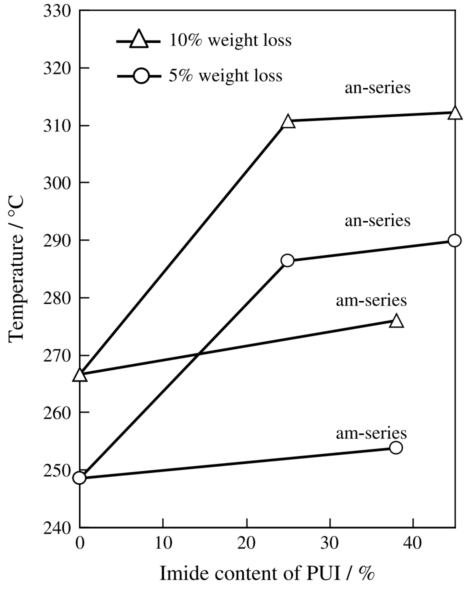


Fig. 10. Five and ten percentage weight loss temperatures of poly(urethane-imide)s from PU prepolymer ($n=1$) against the imide content.

4. Experimental

4.1. Materials

6FDA kindly supplied from Clariant Japan Co. Ltd and ODA obtained from Tokyo Kasei Co. were purified by sublimation. Polyethylene adipatediol (average molecular weight of 1000), obtained from Nippon Polyurethane Ltd, was dried overnight at 70 °C before use. TDI was supplied from the Nippon Polyurethane Ltd, and was used as received. 1,4-Butanediol was dried under reduced pressure overnight. *N*-methyl-2-pyrrolidone (NMP) was distilled at reduced pressure.

4.2. Synthesis of PU prepolymer

Polyol of average molecular weight of 1000 was reacted with TDI at the mole ratio of 1:2 and 2:3, giving PU prepolymer ($n=1$) and PU prepolynmer ($n=2$), respectively.

PU prepolymer ($n=1$) was prepared as follows. Into a dried polyol (28.52 g, 28.52 mmol) in the three neck flask was added TDI (9.93 g, 57.04 mmol), and the mixture was mechanically stirred at 80 °C for 2 h. PU prepolymer ($n=1$) was obtained as a highly viscous colorless transparent liquid. PU prepolymer ($n=2$) was prepared in the same method using polyol (39.61 g, 39.61 mmol) and TDI (10.35 g, 59.42 mmol) in 2:3 molar ratio.

4.3. Synthesis of anhydride- and amine-terminated oligoimide

Two types of oligoimides were prepared: anhydride-terminated oligoimides (an-series) and amine-terminated oligoimides (am-series). General procedure is as follows. In a 50 ml flask ODA was dissolved in NMP. 6FDA was then added, and the solution was stirred at room temperature for ca. 2 h. Toluene was then added, and the solution was refluxed for imidization for ca. 6 h.

4.4. Synthesis of PU elastomer

PU prepolymer and dried 1,4-butanediol were mixed in the equal molar ratio. Typical reaction was performed as follows. Into a solution of 1,4-butanediol (0.090 g, 1.00 mmol) in 4.34 g of NMP was added PU prepolymer ($n=1$) (1.35 g, 1.00 mmol) or PU prepolymer ($n=2$) (2.52 g, 1.00 mmol). After stirring for 2 h, the mixture was cast on a Teflon sheet. The cast films were dried at 50 °C for 16 h, then cured at 100 °C for 1 h in a vacuum oven.

4.5. Synthesis of poly(urethane-imide) films

The poly(urethane-imide)s were synthesized by the reaction of PU prepolymer with equal molar amount of the oligoimide. An example is shown below. Into the solution of anhydride-terminated oligoimide ($n=1$) (1.05 g, 1.00 mmol) in 4.34 g of NMP was added PU prepolymer ($n=2$) (2.62 g, 1.00 mmol), and was stirred for 2 h at room temperature. It was cast on a glass plate, and was dried at 50 °C for 16 h by a vacuum oven, and was then heat treated at 100 and 150 °C for 1 h each to give PUI($n=2$/an-1/30) films.

Other poly(urethane-imide) films were similarly prepared.

4.6. Measurements

Infrared spectra were measured using JASCO spectrophotometer model FT-IR 420. Samples were prepared by coating polymer solution on a KBr pellet followed by heat treatment at various temperatures. Solubility tests were performed by immersing films of 2 mm × 2 mm for one day at room temperature or at elevated temperatures. The tensile properties were measured on Imada Seisaku-sho Model SV-3 at a crosshead speed of 2 mm/min using 15 mm of film length. The tensile properties of each film were determined from an average of at least five tests. Dynamic viscoelastic measurements were conducted on an Orientec automatic dynamic viscoelstomer Rhevibron model DDV-01FP at 35 Hz at a heating rate of 4 °C/min. Differential scanning calorimetry (DSC) was recorded on Rigaku Thermo Plus 2 DSC8230 at a heating rate of 10 °C/min under nitrogen flow of 100 mL/min. Thermogravimetric analyses (TGA) were determined with Rigaku Thermo Plus 2 TG-DTA TG8120 at a heating rate of 5 °C/min under argon flow of 100 mL/min.

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