Synthesis and Characterization of Poly(urethane-imide) Block Copolymers

Yong GUO, Koichi UJIIE, Min ZUO and Tsutomu TAKEICHI
School of Materials Science, Toyohashi University of Technology
Tempaku-cho, 441-8580, Toyohashi, Japan
Tel 0532-44-6815, Fax 0532-48-5833, takeichi@tutms.tut.ac.jp

Introduction

Polyimide (PI) represents one of the most thermally stable polymers, and has been widely used in many applications, ranging from aerospace to microelectronics due to the thermal stability, high mechanical properties and superior chemical resistance. The high temperature properties of PI have become one of the most attractive characteristics, and PI is being utilized in many polymer alloys and blends [1-2]. The introduction of imide group into polyurethane (PU) is one of the effective methods for improving the thermal stability of PU, and thus has been drawing many attentions. We have studied the preparations of poly(urethane-imide) (PUI) from various reactions such as (1) between NCO of PU prepolymer and carboxyl group in poly(amide acid) [3-4] and (2) between NCO of PU prepolymer and the polyimide containing reactive OH group [5]. The previous methods resulted in the formation of PUI with network structures. In this study, we prepared linear block copolymer of PUI from oligoimide and PU prepolymer, and investigated the properties of the PUI films.

Experimental

PU prepolymer used in this study was prepared by endcapping polyester polyol (M_W=1000) with tolylene 2,4-diisocyanate (TDI), followed by protecting NCO group with phenol as shown in **Fig. 1**. To prepare PU prepolymer with various molecular weight, we

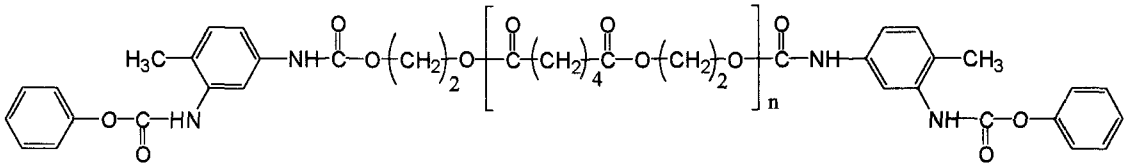

Fig. 1. Structure of phenol-endcapped PU prepolymer

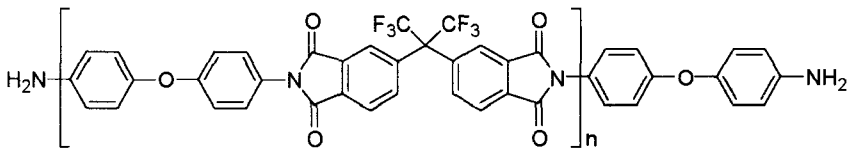

Fig. 2. Amine endcapped oligoimide: n=1, 2, 3, 5 (DP=3, 5, 7, 11)

used the molar ratios of TDI/polyol=2/1 and 3/2, which correspond to the molecular weight of ca. 1000 (PU1000) and 2000 (PU2000), respectively. The amine-terminated olgoimides from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoroisopropane (6FDA) and excess amount of oxydianline, as shown in **Fig. 2**, were prepared using NMP. The degree of polymerization (DP) for the oligoimide was 3, 5, 7, and 11, so the oligoimide was termed as DP-3, 5, 7, and 11, respectively. For the preparation of PUI block copolymer, the oligoimide and PU prepolymer were blended in THF, and cast on glass plates. The cast films were then dried at 50°C for 16 h in a ventilating oven, followed by thermal treatment at 150°C for 2 hrs.

Results and discussion

1. Preparation of PUI block copolymer

The reaction between NCO group in PU prepolymer and amine of the oligoimide was confirmed by IR, from the disappearance of the absorption at 2275 cm^{-1} that is ascribed to NCO characteristics. The obtained PUI block copolymer films were yellow and transparent. The solubility of PUI block copolymer films was given in **Table 1**. The films were soluble in polar solvents like THF and NMP, which suggests the linear structure of the block copolymer.

Table 1 Solubility of PUI block copolymer [a]

Sample code	PU/Imide (wt)	Hexane	Toluene	CH_2Cl_2	Acetone	THF	NMP
PU1000/DP-3	62/38	×	×	○	○	○	◎
PU1000/DP-5	49/51	×	×	○	○	○	◎
PU1000/DP-7	40/60	×	×	△	○	○	◎
PU1000/DP-11	31/69	×	×	×	○	○	◎
PU2000/DP-3	76/24	×	×	○	○	○	◎
PU2000/ DP-5	64/36	×	×	○	○	○	◎
PU2000/ DP-7	54/46	×	×	△	○	○	◎
PU2000/ DP-11	44/56	×	×	×	○	○	◎
Oligoimide [b]	--	×	×	◎	◎	◎	◎
Polyimide [c]	--	×	×	×	○	◎	◎

a: The sample was immersed in the solvent for 72 h. The marks mean, ×: insoluble, △: swelling, ○: partially soluble, ◎: soluble thoroughly.

b: The oligoimide has DP=5.

c: polyimide was synthesized from thermal imidization.

Table 2 Tensile properties of PUI block copolymer

Sample code	PU/imide (wt)	E (MPa)	σ (MPa)	Elongation (%)	Remark
PU1000/DP-3	62/38	1100	22	110	Plastic
PU1000/DP-5	49/51	1300	34	59	Plastic
PU1000/DP-7	40/60	1900	57	16	Plastic
PU1000/DP-11	31/69	1900	68	8	Plastic
PU2000/DP-3	76/24	7.7	4.1	408	Elastomer
PU2000/DP-5	64/36	28	5.4	274	Plastic
PU2000/DP-7	54/46	1800	75.4	174	Plastic
PU2000/DP-11	44/56	1070	11	6	Plastic

2. Mechanical properties of PUI block copolymer

Table 2 shows the tensile properties of PUI block copolymer. It is clear that the molecular weight of PU prepolymer gave effect on the characteristics of the films. In case of PU1000 (TDI/polyol=2/1), all the films exhibited plastic. Since the PUI block copolymer is synthesized by the reaction between NCO group in PU prepolymer and amine in imide oligomer, the weight ratio is defined as shown in **Table 2**. With all of the DP values in case of PU1000, the content of imide unit that acts as hard segment in PUI block copolymer is subsequently more than 30%. As a result, the films exhibited plastic characteristics. On the other hand, in case of PU2000 (TDI/polyol=3/2), the films showed elastic characteristics only with the oligoimides having DP=3. This can also be explained by the weight ratios, because of less than 30% of imide content. These phenomena are similar with those in the network PUI as reported previously [3]. Therefore, it is considered that the ratio of the hard imide segment and the soft PU segment

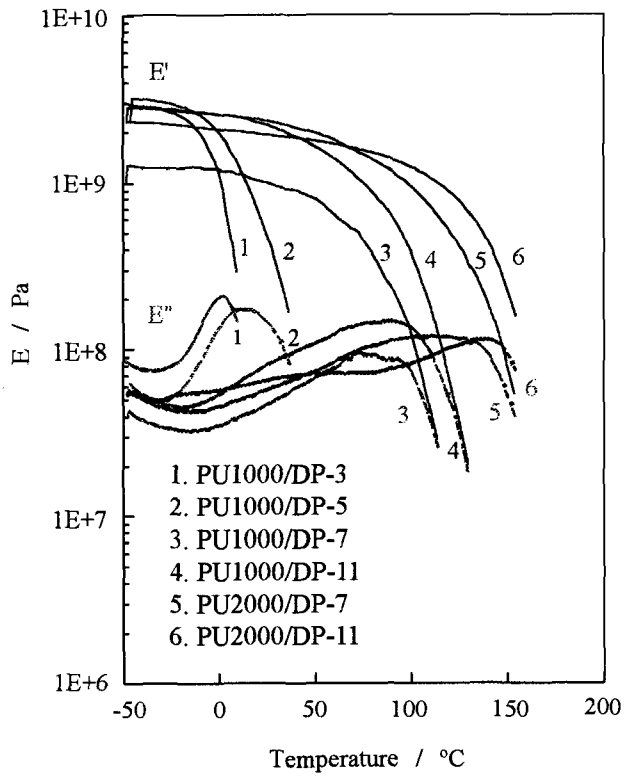

Fig. 3. DMA profiles of PUI block copolymer

is crucial in determining the characteristics of PUI films.

The dynamic mechanical analysis (DMA) of PUI block copolymer, as shown in **Fig. 3**, showed no rubbery plateau region in the E' for all the films from the PU prepolymer based on PU1000. From E", it is observed that all the films have only one Tg, and Tg shifted to high temperature as the imide content increased (**Fig. 4**). Subsequently, the start of the dropdown of E' value was also prolonged to higher temperature, which suggests that the service temperature of PU was improved by the introduction of imide units into the PU backbone.

3. Thermal stability of PUI block copolymer

The thermal properties were investigated by TGA. It is evidently shown in **Fig. 5** that the initial decomposition temperature was about the same around 250°C, regardless of the imide content in this study. In other words, the thermal stability was little improved. This is considered to be due to the linear structure of PUI block copolymer.

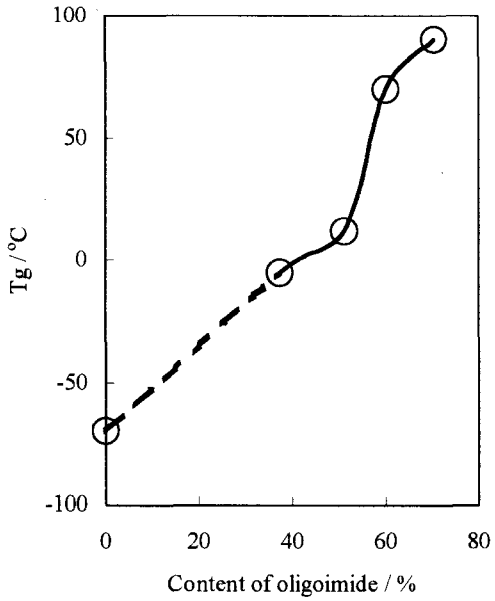

Fig. 4. Effect of oligoimide on Tg of PUI block copolymer.

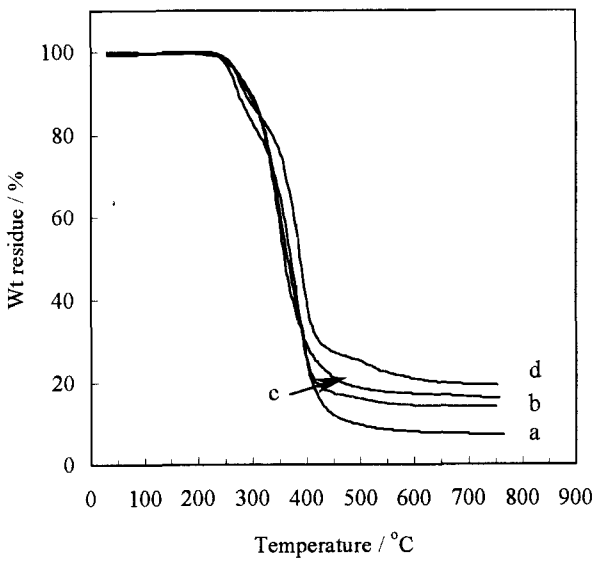

Fig. 5. TGA of (a) PU1000/DP-3, (b) PU1000/ DP-5, (c) PU1000/DP-7 and (d) PU1000/ DP-11

References

[1] Mittal, K. L., *Polyimides 1*, Plenum Press, New York and London, 1984.

[2] Takausu, H., Poriimido Jushi, Gijutsu Johokyokai, Tokyo, 1991.

[3] Zuo, M. and Takeichi, T., *J. Polym. Sci.: Part A: Polym Chem.*, 1997, **35**, 3745.

[4] Zuo, M., Xiang, Q. and Takeichi, T., *Polymer*, 1998, **39**, 6883.

[5] Zuo, M. and Takeichi, T., *Polymer*, 1999, **40**, 5153.