Development of Thermoplastic-Thermosetting Polyimides with Pendent Phenylethynyl Group

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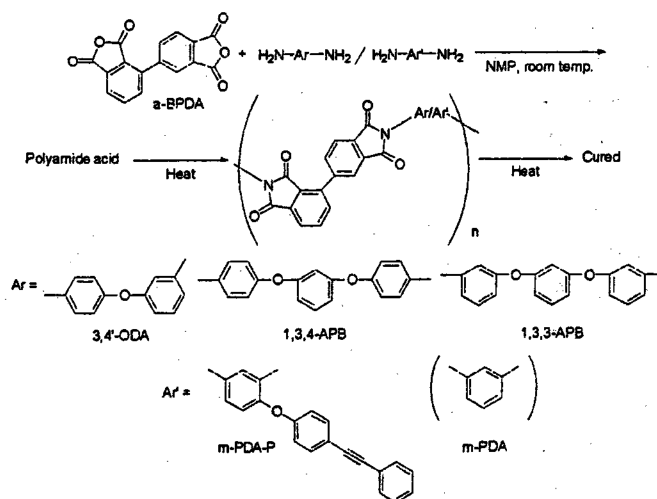
ABSTRACT

In order to obtain thermoplastic (before curing) and thermosetting (after curing) polyimides, we prepared novel polyimides having phenylethynyl group in the side chain from a-BPDA, 3,4'-ODA or 1,3,4-APB or 1,3,3-APB, and m-PDA-P. All uncured polyimide films with pale yellow color had toughness and appropriate Tg (223°C-279°C, DMA), and DMA analyses revealed that the films showed good thermo thermoplasticity. After curing, Tgs increased dramatically due to curing reaction (290°C-379°C, DMA), although the cured film were slightly brittle. Especially, the polyimide films synthesized from a-BPDA/1,3,4-APB;m-PDA-P and a-BPDA/3,4'-ODA;m-PDA-P were found to have wide process window between uncured and cured Tg (approximately 100°C). These properties indicated that the films had promising potential for thermoplastic-thermosetting adhesive film.

1. INTRODUCTION

Aromatic polyimides have been investigated for aerospace applications (high-speed aircraft and reusable vehicles, etc) due to their outstanding combinations of mechanical and thermal properties. Polyimide has rigid and intermolecular ordered structure for involving aromatic imide rings, having high heat resistance and ordered structure even after glass transition temperature (Tg). Therefore, it is difficult to consolidate directly in the fully imide forms.

It has been reported that the disordered and amorphous polyimide having a-BPDA showed excellent thermal and mechanical properties, being ascribable to its bent structure derive from a-BPDA.[1] Moreover, we had reported a phenylethynyl-terminated addition-type imide oligomer based on 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA)/4,4'-oxydianiline (4,4'-ODA) (Asymmetric, Aromatic, and Amorphous type imide oligomer; TriA-PI) demonstrated good processability before curing, and outstanding heat resistance and toughness after curing.[2] We have been conducting a NEDO (New Energy and Industrial Technology Development Organization) project to develop and evaluate the fiber-reinforced composite for reusable space vehicle and jet engine application by use of TriA-PI since 2002, and the development of film adhesive is also involved in the project, which is required for honeycomb sandwiches, etc. It is necessary for preparing adhesive film as the basic study to be thermoplasticity before curing and thermosetting with high Tg after curing; the adhesive film was softened, and materials (composites, metals, etc) was joined with the adhesive film at over uncured Tg before curing, and the shape of the joined materials was retained tightly after curing.



We selected a-BPDA as dianhydride monomer and 3,4'-oxydianiline

(3,4'-ODA) or 1,3-bis(3-aminophenoxy)benzene (1,3,3-APB) or 1,3-bis(4-aminophenoxy)benzene (1,3,4-APB) as easily obtainable diamine monomers, whose producing polyimides are expected to show thermoplasticity. In this study, 2,4-diamino-1-(4-phenylethynylphenoxy)benzene (m-PDA-P), which has phenylethynyl group as curing group, was introduced as the pendant in the polyimide, whose Tgs after curing increase drastically due to curing reaction, to accommodate the aforementioned requirement. This paper deals with the development of thermoplastic (before curing) and thermosetting with high Tg (after curing) polyimides, introducing phenylethynyl group as the pendant in the polyimide chain.

2. EXPERIMENTAL

2.1 General Procedure for the Synthesis of Polyimide

m-PDA-P (mp=164°C) was kindly supplied by Wakayama seika Co, and used as received. m-PDA-P (0.91 g, 3.02 mmol) and NMP (11 ml, 25 wt%) were placed into a 100 ml of flask equipped with a magnetic stirrer. After dissolution of m-PDA-P, a-BPDA (2.01 g, 6.82 mmol) was added into the flask. The reaction mixture was stirred at room temperature for 1 h, and 3,4'-ODA (0.76 g, 3.78 mmol) was added and the mixture was stirred at ambient temperature for 3 h. The resulting polyamide acid solution was stored in the refrigerator. The polyimides were obtained by the following procedure: the polyamide acid was doctored on a glass plate, dried at 60°C for 4 h in an air oven and the glass plate attached with the polyamide was put into a glass tube equipped with a thermocouple, and then imidized at 150°C/0.5 h, 200°C/0.5 h, 250 °C/1 h and 300 °C/10 min *in vacuo*.

2.2 General Procedure for the making cured film

The polyimide film obtained was put into a glass tube equipped with a thermocouple, and then heated at 370°C for 1 h and further heated under inert atmosphere.

3. RESULTS AND DISCUSSION

In this study, we chose 3,4'-ODA, 1,3,4-APB, and 1,3,3-APB as diamine monomers, which are easy to obtain, and the polyimides prepared from these diamines, having ether linkages at meta and para positions, should be high Tg and produce flexible and tough film. We synthesized polyamic acids with the monomer ratios of a-BPDA/3,4'-ODA or 1,3,4-APB or 1,3,3-APB/m-PDA-P = 9/5/4 (m-PDA-P = 44%), which is consistent with the concentration of phenylethnyl group of TriA-PI, and subsequently heated the films for imidization. In order to compare the various properties with and without phenylethyl group, polyimides derived from *m*-phenylene diamine (m-PDA), which has no phenylethynyl group as the pendant, were also prepared (Table 1. Run no 4-6).

The imide reaction was monitored by IR spectroscopy by the disappearance of the carbonyl absorption (amide acid) at 1660 cm^{-1} and thermogravimetric analyses (TGA) by the disappearance of the water produced during imidization. Uncured Tgs of polyimides without phenylethyl group was found to be higher than those with phenylethyl group, ascribable to forming ordered structure between intermolecules due to no steric hindrance. Moreover, uncured polyimide prepared from 3,4'-ODA has higher Tg (285°C) than other polyimides (223°C and 270°C), which is attributed to molecular mobility restricted due to molecular rigidity (less ether linkage unit). Polyimide from 1,3,4-APB possessed higher Tg (270°C) than that from 1,3,3-APB (223°C) due to higher rigidity of 1,3,4-APB with ether linkage at para position and higher molecular packing.

We conducted to monitor the disappearance of exothermic reaction of phenylethynyl group by means of DSC (Figure 1-3). To prepare the cured films, the polyimide films were heated at 370°C for 1 h using vacuum oven, which is curing condition of TriA-PI, and further heated depending on the results of DSC. The curing reaction of the polyimide derived from 1,3,3-APB was accomplished by heating at 400°C for 10 min (Figure 3), while the polyimides derived from 3,4'-ODA and 1,3,4-APB required 430°C for 10 min (Figure 1 and 2). This suggest that the molecule of polyimide prepared from 1,3,3-APB, which is lower uncured Tg than other two polyimides, cure easily at lower temperature.

Some cured sample did not indicate well-defined Tg, and we carried out DMA to detect detailed mechanical and thermal behavior.

Figure 4-6 showed the DMA profiles of polyimide films with (uncured and cured) and without phenylethnyl group. In the DMA profiles of uncured polyimide films, there are observed Tgs in the range of 223-279°C and steep drops of storage modulus (E') (10^9 to 10^6) over the Tg, suggesting that the films have good thermoplasticity. At over approximately 300°C, E' of the polyimide films without phenylethnyl group (dashed lines in Figure 4-6) decreased with increasing temperature, while E' of the uncured film derived from 3,4'-ODA and 1,3,4-APB with phenylethnyl group (thin and solid lines in Figure 4 and 5) gradually increased with increasing temperature, which indicate that the curing reaction take place. The film derived from 1,3,3-APB with phenylethnyl group did not show increase on E' at around 300°C (thin and solid lines in Figure 6) and had lower process window between uncured and cured Tg (approximately 60°C), suggesting that the molecules exhibit mobility even after curing due to ether linkage at meta position of 1,3,3-APB. DMA profiles of cured polyimide films (thick and solid lines in Figure 4 and 5) derived from 3,4'-ODA and 1,3,4-APB showed ideal Tgs (over 320°C), having wide process window (approximately 100°C).

Cured TriA-PI showed flexible and tough film.[2] On the other hand, these cured films with brown color were slightly brittle, although the polyimides are evaluated and synthesized by the same phenylethynyl concentration as TriA-PI. This phenomenon can be speculated as follows: flexible films from TriA-PI, having phenylethyl group at the molecular ends, were obtained after curing due to occurring chain extension together with branching and cross linking, while polyimide films, having phenylethyl group in the polymer side chain, made network structure after curing, showing brittle film with no flexibility. We touch on the synthesis of polyimide with the monomer ratios of a-BPDA/1,3,4-APB/m-PDA-P = 5/4/1(m-PDA-P = 20%), showing that the uncured and cured Tg are 260° and 290°C, respectively. There are observed improvement of toughness, indicating that the elongation at break exhibited 12%.

We also investigated melt fluidity of uncured film prepared from 1,3,4-APB by using optical microscope attached with a temperature controlled heater, indicating that the film turned soft at 300°C showing minimum value for storage modulus E' (Figure 5), however, retained film shape. It might be needed for practical use to synthesize polyimide film having highly melt fluidity, and this project is under way.

Table 1. Polymerization and thermal properties of polyimides

Run	Ar	Conc. for polym. (wt%)	η_{inh} (dL/g)	MW[a]	Tg (°C) DSC	Tg (°C) DMA	Tg (°C) DMA
		Polyamic acid			Uncured	Uncured	Cured
1	3,4'-ODA/m-PDA-P	25	0.38	13900	285[b]	279[b]	379[e]
2	1,3,4-APB/m-PDA-P	25	0.61	25100	270[b]	265[b]	364[e]
3	1,3,3-APB/m-PDA-P	25	0.45	16900	223[c]	223[c]	290[f]
4	3,4'-ODA/m-PDA	20	0.84	37200	313[d]	302[d]	-
5	1,3,4-APB/m-PDA	20	1.07	50400	289[d]	281[d]	-
6	1,3,3-APB/m-PDA	20	0.69	29100	250[d]	243[d]	-

a: Molecular weights were calculated by use of the inherent viscosity. b: 300°C/10 min. c: 250°C/1 h. d: 300°C/1h. e: 370°C/1h and 430°C/10 min. f: 370°C/1 h and 400°C/10 min.

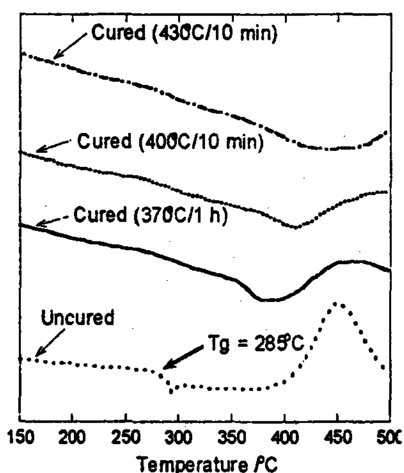


Fig 1. DSC profiles of uncured and cured polyimide prepared from a-BPDA, 3,4'-ODA and m-PDA-P. Heating temp. and time were shown in parentheses to prepare cured film.

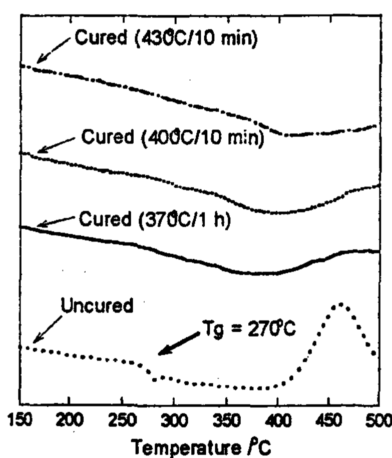


Fig 2. DSC profiles of uncured and cured polyimide prepared from a-BPDA, 1,3,4-APB and m-PDA-P. Heating temp. and time were shown in parentheses to prepare cured film.

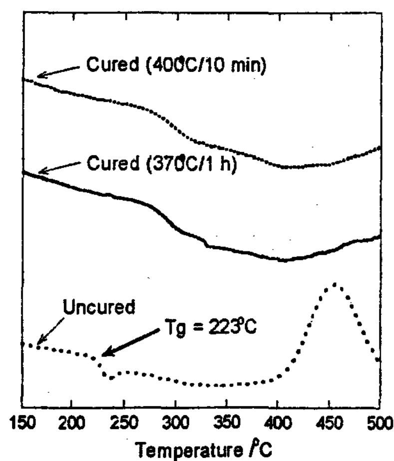


Fig 3. DSC profiles of uncured and cured polyimide prepared from a-BPDA, 1,3,3-APB and m-PDA-P. Heating temp. and time were shown in parentheses to prepare cured film.

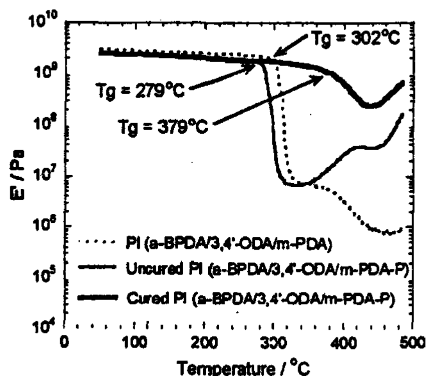


Fig 4. DMA profiles of uncured and cured polyimide prepared from a-BPDA/3,4'-ODA;m-PDA-P and a-BPDA/3,4'-ODA;m-PDA.

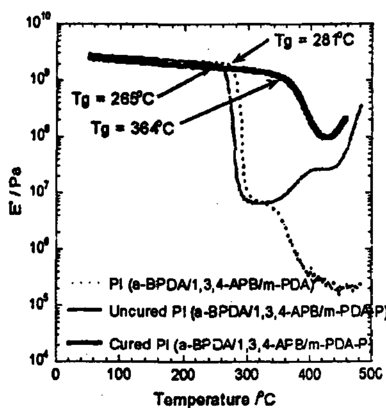


Fig 5. DMA profiles of uncured and cured polyimide prepared from a-BPDA/1,3,4-APB;m-PDA-P and a-BPDA/1,3,4-APB;m-PDA.

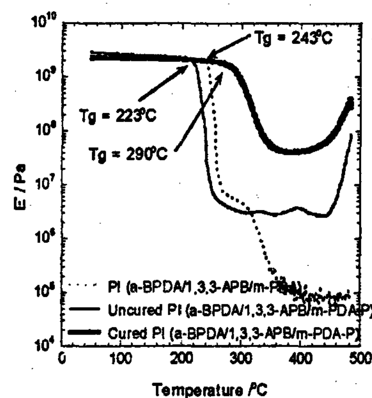


Fig 6. DMA profiles of uncured and cured polyimide prepared from a-BPDA/1,3,3-APB;m-PDA-P and a-BPDA/1,3,3-APB;m-PDA.

4. CONCLUSIONS

We prepared three kinds of polyimide having phenylethynyl group as the pendant in the polymer in order to obtain thermoplastic (before curing) and thermosetting (after curing) polyimide films: a-BPDA/3,4'-ODA;m-PDA-P, a-BPDA/1,3,4-APB;m-PDA-P, and a-BPDA/1,3,3-APB;m-PDA-P. All uncured films had appropriate Tgs and thermoplasticity (E' drop over Tg = 10^9 to 10^6). Cured films obtained were found to have high Tg (290°C-379°C) due to curing reaction and be slightly brittle, although uncured films possessed an excellent toughness. The polyimide films synthesized from a-BPDA/1,3,4-APB;m-PDA-P and a-BPDA/3,4'-ODA;m-PDA-P were found to have wide process window between uncured and cured Tg, which is approximately 100°C. The changing the composition ratio of monomers or introducing other monomers into the polyimide might be necessary to improve the toughness of cured film without sacrificing high Tg. Detailed investigation of adhesive properties including mutually adhering and melt fluidity are under way.

5. REFERENCES

1. M. Hasegawa et al., *Macromolecules*, **32**, 387-396 (1999).
2. R. Yokota et al., *High Perform. Polym.*, **13**, S61-S72 (2001).