

PREPARATION AND PROPERTIES OF NOVEL ASYMMETRIC BPDA BASED THERMOSET POLYIMIDES WITH PHENYLETHYNYL PHTHALIC ANHYDRIDES

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Abstract;

Novel phenylethynyl-terminated, polyimide oligomers consisting of asymmetric 2,3,3',4'-biphenyltetracarboxylic dianhydride (a-BPDA) and oxydianiline (ODA) with 4-phenylethynyl phthalic anhydride (PEPA) were synthesized and were converted to thermoset resins after curing at 370°C for one hour. The melt flow property dramatically decreased above the T_g for the n=1.5 oligomer, resulting in a viscosity as low as 200 Poise at 300°C. For the n=10 oligomer, it was 20000 Poise at 365°C. The glass transition temperatures of these cured oligomers were 341°C and 308°C, respectively. Furthermore, the cured oligomer consisting of a-BPDA/4,4'-ODA and PEPA endcap (n=4.5) exhibited over 13 % flexural elongation in addition to a high T_g of 343°C. Their T-300 carbon fiber composites were also well molded.

1. Introduction

It is well known that the outstanding properties of aromatic polyimides are based not only on their rigid, planar benzoimide structure, but also on the formation of high-order structures even beyond the T_g[1,2]. Generally, the aromatic polyimides do not display high molecular mobility above the T_g, thus requiring extremely severe processing conditions for molding materials[3].

In the past twenty years, many addition type polyimide resins such as bismaleimide and PMR-15 have been developed as high temperature matrix resins for advanced composites. But these composites essentially do not have enough fracture toughness in addition to hard processability because of their rigid structures and high cross-link density[3]. Recently, PETI-5 which exhibits a T_g=270°C and more than 10% elongation-at-break of the film was developed by NASA[4,5]. To improve the fracture toughness, cross-link density must be relatively low. This means that if the addition type, heat resistant resins are to achieve processability, the oligomers must possess a low melt viscosity. Therefore, the main chain structure between the cross-links has to maintain thermoplasticity through flexible structure and low T_g as same as PETI-5. Consequently, the requirement of high thermal stability seems to be in contradiction with processability for the heat resistant polymeric matrix resins[2,4].

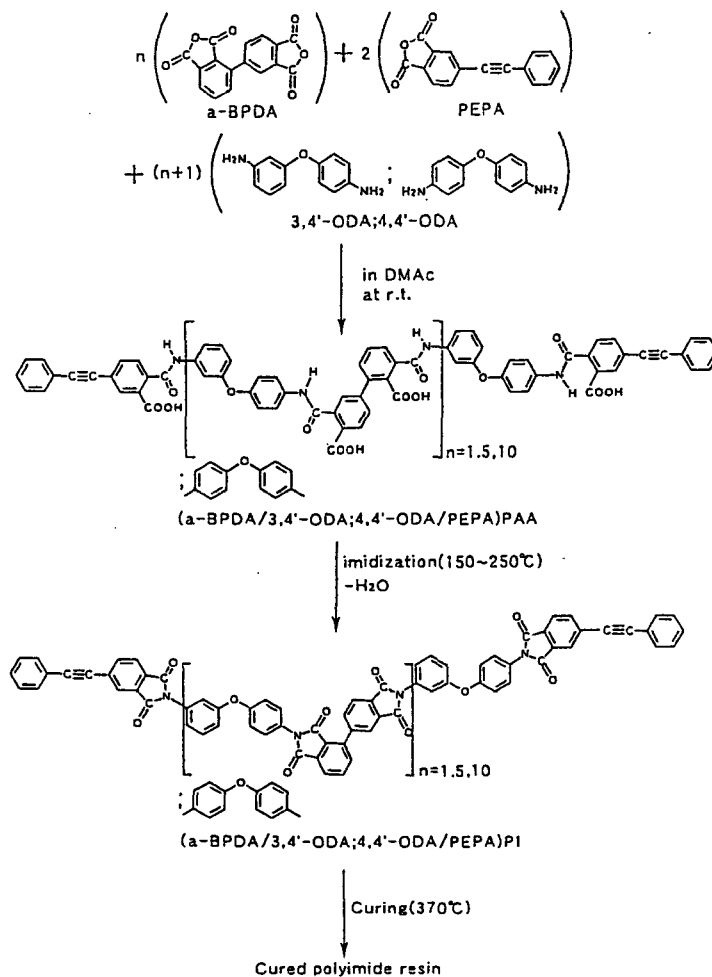


Figure 1. Reactions and curing of a-BPDA with 3,4'-ODA;4,4'-ODA (50:50) endcapped with PEPA.

We recently found that aromatic polyimides derived from asymmetric biphenyl dianhydride(a-BPDA) exhibited higher T_g than that of symmetric s-BPDA and also exhibited a large drop in the storage modulus, E' above the T_g [6]. Based on these thermal and rheological properties of a-BPDA and PEPA, we successfully developed novel a-BPDA based high temperature thermoset polyimide resins with good processability and fracture toughness[3,7]. This paper describes the preparation and properties of novel phenylethynyl-terminated, addition type a-BPDA polyimide matrix resins, and their corresponding composites.

2. Experimental

2.1 Material

2,3,3',4'-biphenyltetracarboxylic dianhydride(a-BPDA, m.p.198-200°C) was supplied by UBE Ind.Ltd. 3,4'-oxydianiline(3,4'-ODA, Mitsui Chemical Co., m.p.84°C) and 4,4'-oxydianiline(4,4'-ODA, Tokyo Kasei Co., m.p.187°C) were used as received. 4-phenylethynyl phthalic anhydride(PEPA, m.p. 151°C) supplied by Manakku Co. was also used as received. T-300 graphite-fiber supplied by Toray was washed in acetone and dried prior to use.

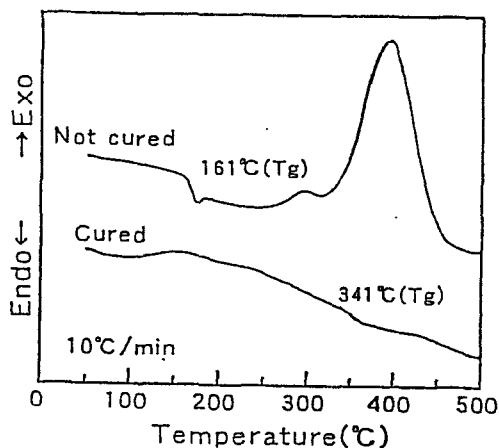


Figure 2. DSC curves of Oligo-1.5 and Oligo-1.5 cured for 2 hours at 370°C in air.

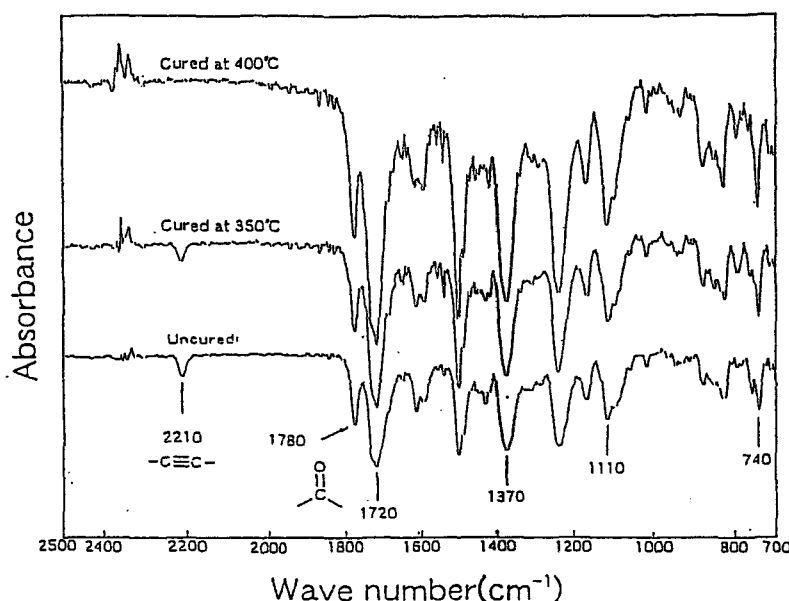


Figure 3. FT-IR spectra of thermally treated Oligo-1.5(a-BPDA and 3,4'-ODA;4,4'-ODA (50:50) endcapped with PEPA).

2.2 Phenylethynyl-Terminated Imide Oligomers(Oligo-1.5 and -10)

a-BPDA based oligomers with a calculated number-average molecular weight(M_n) of 5245 g/mole, $n=10$ and of 1345 g/mole, $n=1.5$ were prepared by reacting a-BPDA with 3,4'-ODA;4,4'-ODA (50:50) and endcapped with PEPA. Figure 1 shows the experimental procedure. The reaction mixture was stirred at room temperature for 3 hours in DMAc under a nitrogen flow. The semi-dried Oligo-PAA obtained from the 30 wt % DMAc solution of poly(amide acid) oligomer was thermally imidized on a glass plate at 150°C for 1 hour, 200°C for 1 hour, and 250°C for 2 hours in an air oven. For resin molding and composites, oligomer $n=4.5$, $M_n=2490$ g/mole which consisted of a-BPDA and 4,4'-ODA with terminal PEPA was also prepared and converted to PI oligomers from an NMP solution for 2 hours at 180°C, and then the soluble Oligo-PIs were recovered by precipitation in water and washing in acetone.

Table 1. Oligomer characterization and properties of polyimides based on a-BPDA/3,4'-ODA;4,4'-ODA(50:50) endcapped with PEPA.

Oligomer	T _g (°C)			Molecular weight Mn(cal.)	Solubility in DMAc Not cured	η inh (DMAc)	Melt flow viscosity (Poise)
	Cure temperature						
n	250°C	350°C	370°C				
Oligo-1.5	161°C	297°C	341°C	1340	○	0.06	200(300°C)
Oligo-10	237°C	281°C	308°C	5240	○	0.15	20000(365°C)
PETI-5	210°C	249°C	270°C	5000	—	0.27	~60000(371°C)

○ ; soluble in DMAc at room temperature

2.3 Characterization and Measurements

The thermal curing process, and thermal and rheological properties of the oligomers were investigated by FT-IR, differential scanning calorimetry, thermogravimetric analysis, dynamic tensile spectroscopy, and dynamic rheometry.

3. Results And Discussion

3.1 Oligomer characterization

Figure 2 shows the DSC curves of Oligo-1.5. The DSC curve of Oligo-1.5(not cured) indicated an endothermic peak at 161°C and a large exothermic peak around 400°C. The endotherm of the oligomer corresponds to the T_g, and the exotherm is the cure reaction of the terminal phenylethynyl groups. After curing, the cured Oligo-1.5 shows only a small endotherm around 341°C which is the T_g of the cured material. Figure 3 shows the FT-IR spectra for Oligo-1.5 with and without thermal curing. Oligo-1.5 shows an absorption of the terminal phenylethynyl C≡C at 2210 cm⁻¹ and the imide carbonyls C=O at 1780 cm⁻¹, 1720 cm⁻¹, and other characteristic imide bands(1370 cm⁻¹, 1110 cm⁻¹, and 740 cm⁻¹). When the sample was cured at 350°C for one hour, the absorption of the C≡C triple bonds slightly decreased. After curing at 400°C for one hour, it had completely vanished, while the absorption of imide groups remained constant during the cure process. While, the T_g of cured Oligo-10 increased to 308°C. Table 1 indicates that when oligomers were cured at 350°C, the T_g of both oligomers did not increase much because the cure reaction was not completed. Therefore, the curing for terminal phenylethynyl groups has been done at 370°C for one hour[8-12].

3.2 Thermal stability and Rheology

The TG curves of the fully cured Oligo-1.5 shows a T_d(the temperature at 5% weight loss)=545°C, with considerably higher residual weight beyond 600°C. Dynamic rheological properties measured by an RDS II dynamic rheometer are shown in Figure 4 and Table 1. Not only Oligo-1.5 but also Oligo-10 displayed low melt viscosity, and exhibited a dynamic melt viscosity of only 200 Poise at 300°C for Oligo-1.5 and 20000 Poise at 365°C for Oligo-10,

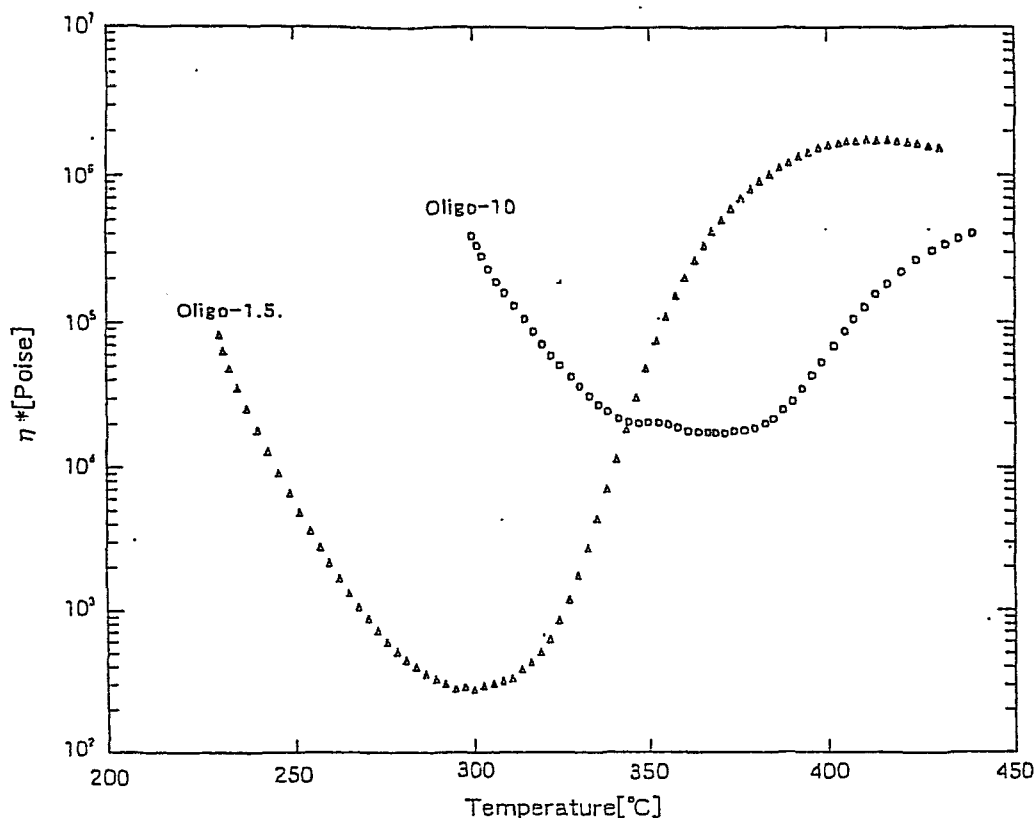


Figure 4. The dynamic rheological behavior of Oligo-1.5 and Oligo-10 by RDS II dynamic rheometer, 3°C /min in air flow.

resulting in significant improvements in processability for neat resin moldings and composites[4,5].

3.3 Neat resin moldings and Composites properties

Because the melted Oligo-1.5 was leaking from the gap in the stainless steel mold at around 320°C during hot press molding, oligomer $n=4.5$, $M_n=2490$ g/mole which consists of a-BPDA/4,4'-ODA with terminal PEPA was synthesized. The moldings were prepared from imidized powder in a stainless steel mold on a plate in a hot press at 320°C for 10 min, and then pressed until the temperature reached 370°C, and held for one hour. T-300 graphite fiber composites of oligomer $n=4.5$ were fabricated from solution coated unidirectional dry prepreps in a stainless steel mold using the same process as used for neat resins.

The molding resins exhibited over 13 % flexural elongation in addition to very high Tg of 343°C as shown in Table 2. Consequently, oligomer($n=4.5$) consisting of a-BPDA/4,4'-ODA and PEPA exhibited significant improvements in processability as well as high thermo-oxidative stability for the composite.

4. Conclusions

Novel phenylethynyl-terminated, heat resistant, thermoset polyimides consisting of a-BPDA

Table 2 . Preliminary properties of 'EPA terminated a-BPDA/4,4'-ODA cured oligomer resins and their T-300 graphite fiber composites.

Properties		Oligomer(n=4.5) neat resin	CFRP T-300 U.D Vf 59.8%
Density	g/cc	1.30	
Mn		2490	
Tg	°C	245	
Tg(cured)	°C	343	
Flexural strength	kg/mm ²	14.9	182
Flexural modulus	kg/mm ²	279	18700
Flexural elongation	%	>13	>2

CFRP; graphite-fiber reinforced plastic

T-300 U.D; unidirectional graphite-fiber supplied by Toray

Vf; fiber volume fraction

and ODA were prepared after curing at 370°C for one hour. The Tg of these cured oligomers(n=1.5, n=10) were 341°C and 308°C, respectively. The oligomer consisting of a-BPDA/4,4'-ODA and PEPA(n=4.5) was well molded and it exhibited over 13 % flexural elongation in addition to a high Tg of 343°C. The considerably irregular a-BPDA structure increased the Tg of the polyimides and decreased the melt viscosity due to the low intermolecular interactions between the polyimide molecules. The excellent properties of these a-BPDA based thermoset polyimides demonstrate a high potential for future aerospace applications.

References

- 1) M.K.Ghosh and K.L.Mittal(Eds.), POLYIMIDES: FUNDAMENTALS AND APPLICATIONS , Marcel Dekker, New York(1996)
- 2) R.Yokota, in Structure and Design of Photosensitive Polyimides, K. Horie and T.Yamashita(Eds.), chap. 3, Technomic, Lancaster, PA (1996)
- 3) T.T.Serafini, in POLYIMIDES; Synthesis, Characterization, and Applications, K.L.Mittal(Ed.), vol.2, p.957, Plenum Press, New York (1984)
- 4) T.H.Hou, B.J.Jensen, and P.M.Hergenrother, J. Composite Mater., 30, 109 (1996)
- 5) R.J.Cano and B.J.Jensen, J. Adhesion, 60, 113 (1997)
- 6) M.Hasegawa, R.Yokota, N. Sensui, and Y. Shindo, Macromolecules, 32, 387 (1999)
- 7) R.Yokota, in Proc. of the 7th Japan Polyimide Conf. T. Takeichi and M.Kochi(Eds.) p.21 Reiteck, Tokyo Japan (1998). R.Yokota, in Proc. of the MST Conf. K.L.Mittal(Ed) (2000) in press
- 8) C.X.Fang, D.F.Rogers, D.A.Scola and M.P.Stevens, J. Polym. Sci., Part A: Polym. Chem, 36, 461 (1998)
- 9) B.J.Jensen and P.M.Hergenrother, Polymer , 34, 630 (1993)
- 10) J.W.Connell, J.G.Smith, Jr., and P.M.Hergenrother, High Perform.Polym., 10, 273 (1998)
- 11) P.M.Hergenrother and J.G.Smith, Jr., Polymer , 35, 4857 (1994)
- 12) G.W.Meyer, B.Tan and J.E.McGrath, High Perform. Polym., 16, 423 (1994)