New Concept on Heat Resistant, Addition-type Polyimides; Developing Amorphous Aromatic Asymmetric Polyimides, TriA-PI

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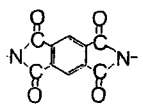
Abstract

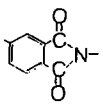
For developing heat resistant addition type polyimide with high toughness, the relationships between the imide structures and morphology are discussed. According to the study, addition type imide oligomers derived from asymmetric 2,3,3', 4'-biphenyltetracarboxylic dianhydride (a-BPDA) and oxydianiline(ODA) with 4-phenylethynyl phthalic anhydride (PEPA) were evaluated. It is understood that a-BPDA imparted a low melt viscosity to the oligomers and high glass transition temperatures to the cured resins. The cured oligomers exhibited good room temperature mechanical properties and high thermo-oxidative stability. The cured imide oligomer consisting of a-BPDA and 4,4'-ODA with PEPA (Oligo-4.5) at a calculated number average molecular weight of 2490g/mole provided over 13 % flexural elongation and a Tg of 343°C. Preliminary composite work using T-300 carbon fiber composites was done with good consolidation. The molecular design for new heat resistant polyimides with a unique combination of attractive properties are presented. It is noted that amorphous, aromatic asymmetric imide structures without any weak linkages such as alkyl and methylene groups are very attractive in the molecular design of heat resistant, addition type polyimides.

pyromerilitimide



rigid and planar structure
strong intermolecular interaction
charge transfer complex, high-order structure

phthalimide



➡➡ excellent thermal stability, low C.T.E
➡➡ outstanding environmental stability

Figure 1 Aromatic polyimide: structure and property

1. *Chemical Structures/Tensile Mechanical Properties Relationships of Polyimides*

Aromatic polyimides were known to have excellent properties such as high dimensional stability, low thermal expansion and outstanding thermal and environmental stability [1-5]. It is noted that the attractive properties of aromatic polyimides are based not only on their rigid, planar pyromelltimide (PMDI) or symmetric biphenylimide (s-BPDI) structures, but also on the formation of high-order structures even beyond the Tg [2,4] as shown in Figure 1. Accordingly, these aromatic polyimides do not display high molecular mobility above the Tg, thus, in general, requiring extremely severe processing conditions for molding [3,4,6].

In the past thirty years, many addition type polyimides have been developed for advanced composites in aerospace applications.

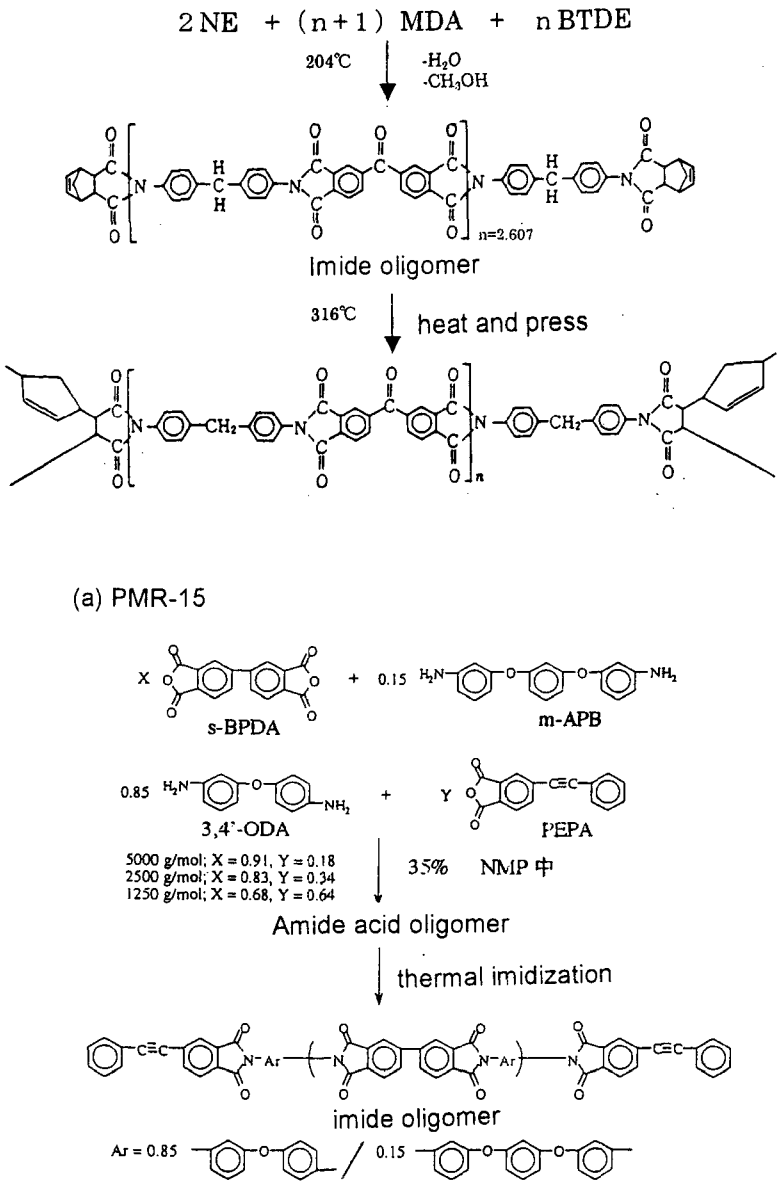


Figure 2 Addition type polyimide resins; (a) PMR-15 and (b) PETI-5

Figure 2 shows the chemical structures of typical addition type polyimides developed from NASA: PMR-15 and PETI-5. PMR-15 prepared from the reacting of 3,3', 4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-methylene dianiline (MDA) with nadic acid derivative for reactive endcap is a resin for using composites at 300°C. However, the cured resin is brittle due originally to the high cross-link density, as shown in Figure 2[3]. As a result, composites exhibit poor impact resistance or compressive strength after impact. Currently, the phenylethynyl endcap is the preferred group on structures for use as high temperature composite matrices resins in the United States high speed civil transport (HSCT) program [6]. A phenylethynyl terminated imide oligomer designed PETI-5 was prepared from the reaction of s-BPDA and two aromatic diamines with phenylethynyl endcap (PEPA) at a calculated molecular weight of 5.000 g/mole [7,8]. The cured lightly crosslinked PETI-5 exhibits a Tg of 270°C and more than 30% RT elongation-at-break for the film. The properties of cured PETI-5 are very similar to those of a thermoplastic and not a thermoset. Furthermore, it was also noted that this endcap offer distinct advantages such as a large processing window and when cured, good thermo-oxidative stability compared with other reactive endcaps such as nadic acid derivative of PMR-15 and maleic acid of BMI [3,6]. For improving processability, the oligomers must generally show a low melt viscosity. As a result, the imide oligomer(structure) between the endcaps has to indicate thermoplasticity through flexible structure and relatively low Tg. Furthermore, the cured resin must exhibit a high Tg. It may appear to be in contradiction with processability for the heat resistant polymeric matrix resins [4,11].

Table 1 is the list of the key parameters for developing the heat resistant polyimides without sacrificing good processability and thermo-oxidative stability. In respect to the main chain imide structures in Table 1, PMDI or s-BPDI and BTDI (of PMR-15) structures would not expect to give good processability for molding resin, because of high intermolecular interactions in addition to the essentially rigid chemical structures, as reported already [2-4]. It means that if there are some imide structures without a strong intermolecular interaction and with high thermal stability, the corresponding oligomers may lead to thermo-stable polyimide matrix resins.

Table 1 List of the parameters on heat resistant addition type polyimide for advanced composites

Subject		Effect	Problem
main chain	increasing rigidity	physical thermo-stability, Tg	melt flow
	fluoro comp.	thermal stability, flowability	cost
	increasing Mw	toughness	melt flow
	narrow Mw	flowability	process
side chain	--CH_3	increasing Tg & solubility	thermal stability
	--CF_3	increasing Tg & solubility	cost
	benzene ring	increasing Tg & solubility	process
end cap	maleic, MA	common	thermal stability
	nadic, NE	common	reaction control
	vinyl aniline, V-CAP	thermal stability	reaction control
	acetylene, APA	thermal stability	melt flow
	phenyl ethynyl, PEPA	thermo-oxidative stability	cost
additive	functional aromatics	flowability	thermal stability

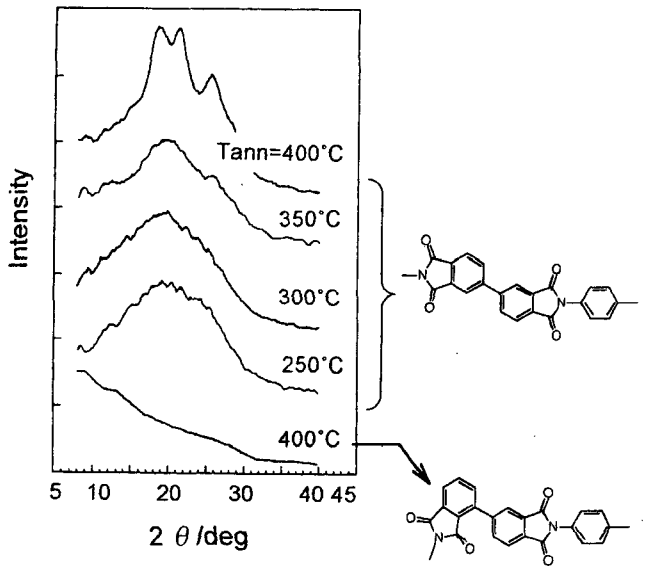


Figure 3 Effect of curing temperature on order-structures (WAXD)

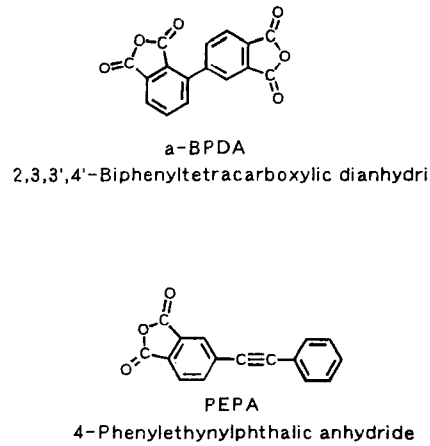


Figure 5
Chemical structures of a-BPDA and PEPA

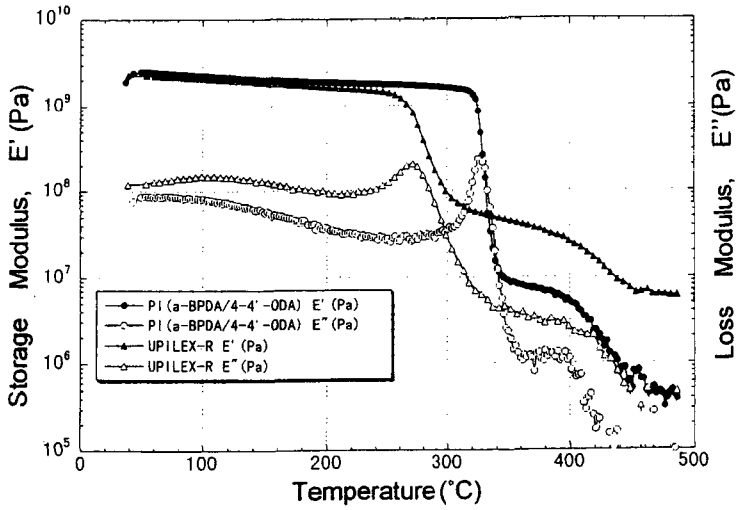


Figure 4 Temperature dependence of DMA curves of PI (a-BPDA/4,4'-ODA) and UPILEX-R: PI (s-BPDA/4,4'-ODA)

Recently, a new asymmetric aromatic dianhydride, 2,3,3', 4'-biphenyltetracarboxylic dianhydride (a-BPDA) was used to make polyimide with Tgs higher than the analogous polyimide from the symmetric aromatic dianhydride, 3,3', 4,4'-biphnyltetracarboxylic dianhydride (s-BPDA). In addition, a-BPDA based polyimide exhibited a large drop in the storage modulus, E' above the Tg [12]. It is understood that these properties is attributed to the decrease in the intermolecular interactions of the geometrically irregular a-BPDA based polyimide molecules as discussed for the main chain structure of polyimide in Table 1.

Figure 3 shows the differences of WAXD patterns of s-BPDA and a-BPDA based polyimides on thermal imidization condition (Tann. °C: annealing temperature), respectively. a-BPDA/PDA showed a typical amorphous pattern, independent of the annealing temperature, while s-BPDA/PDA proceeded the order-structure at high temperature annealing. Figure 4 shows DMA curves of PI(a-BPDA/4,4'-0DA) and PI(s-BPDA/4,4'-0DA)(UPILEX-R of UBE). The difference in temperature dependence of dynamic tensile properties (DMA curves) of PI(a-BPDA/4,4'-ODA) and Upilex-R indicates the difference in their molecular mobility beyond the Tg, resulting n low melt viscosity for a-BPDA/4,4'-ODA polyimide.

2. a-BPDA Based Imide Oligomers

Based on these unique behaviors of a-BPDA polyimides, we designed and developed a-BPDA based high temperature addition type polyimides [5,16]. Figure 5 shows the chemical structures of a-BPDA and PEPA.

Figure 6 shows the preparation of terminal phenylethynyl imide oligomer. The reaction mixture of a-BPDA and PEPA with ODA in DMAc solvent was stirred at room temperature for 3 hours under a nitrogen flow. After that, the mixture was cooled in a refrigerator. The 30 wt % solution of amide acid oligomer was cast onto a glass plate and then dried at 60°C to produce a semi-dried material. The semi-dried 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. a-BPDA based imide oligomers a-BPDA/ODA/PEPA obtained from the thermal imidization of the above mentioned, corresponding amide acid oligomers following to the molding.

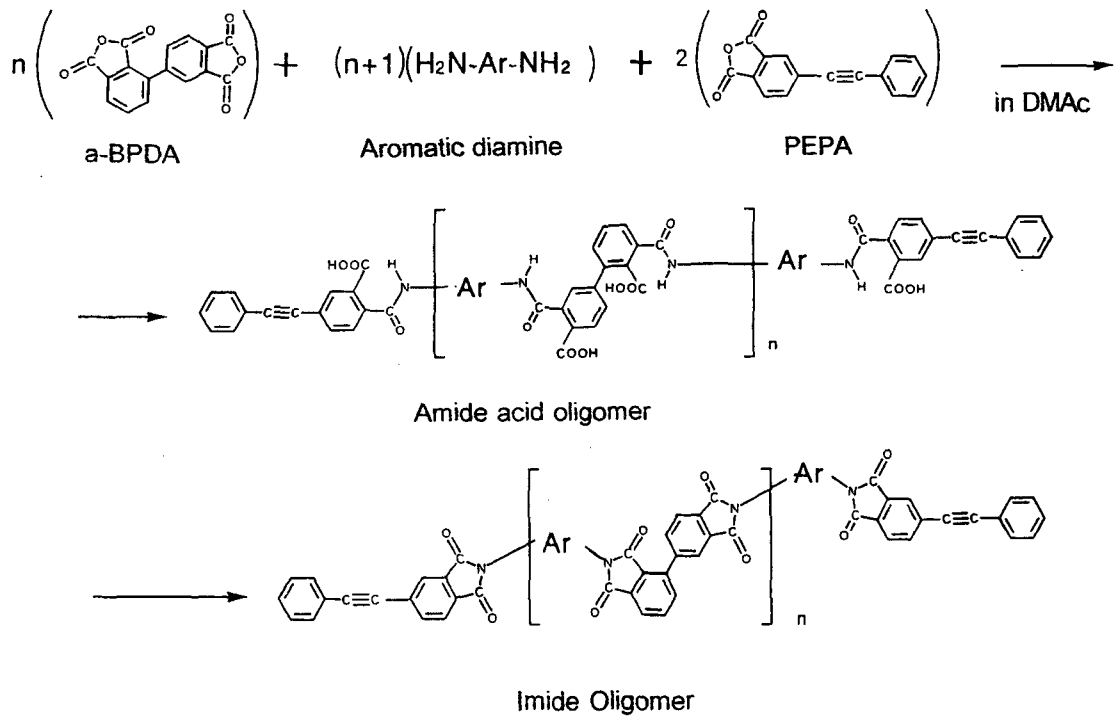


Figure 6 Scheme-Synthetic routes to addition type polyimide: Tri-A-PI

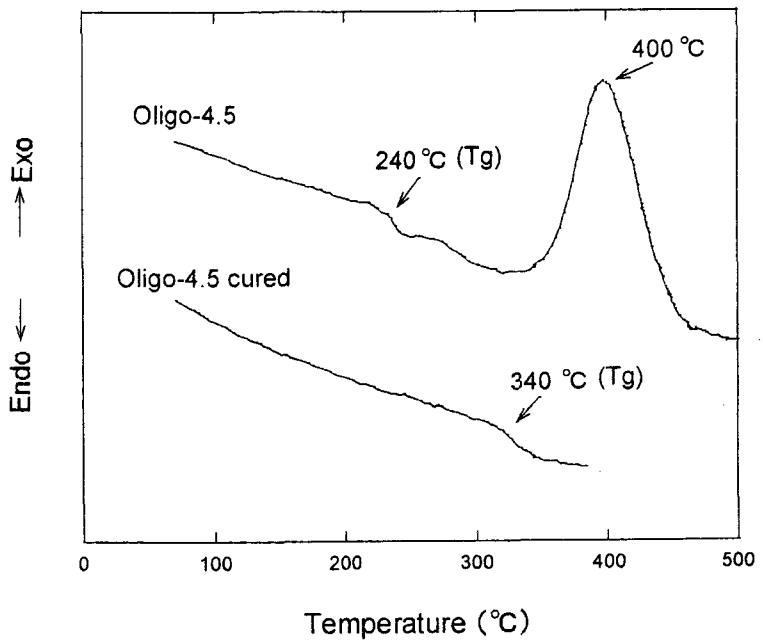


Figure 7 DSC curves of imide oligomer: Oligo-4.5 and Oligo-4.5 cured

Figure 7 shows the DSC curves of imide oligomer: Oligo-4.5 and cured for 2 hours at 370°C in air. The DSC curve of Oligo-4.5 (not cured) showed an endothermic shift at around 240°C and a large exothermic peak around 400°C. Endotherm of the oligomer corresponds to the Tg, and the exotherm is the cure reaction of the terminal phenylethynyl groups. After curing, the cured resin shows only a small baseline deflection around 340C that is the Tg of the cured oligomer. The Tg of the thermally cured phenylethynyl containing oligomer increases significantly relative to the uncured oligomer [11,16]. It was identified by FT-IR that when imide oligomer n=1.5 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.
Table 2 are summarized the characterization and properties of the imide oligomers. The Tg of cured Oligo-10 increased to 308°C. Onset of exothermic reaction increased from 385°C for Oligo-1.5 to 427°C for Oligo-10, suggesting the restriction of the cure reaction imposed on the terminal phenylethynyl groups by the longer spacer and the high Tg of Oligo-10 (not cured). This table also indicates that the oligomers were not fully cured at 350°C. The Tgs of both oligomers increased further when cured at 370°C The curing of PETI-5 at 370°C for one hour is also shown in Table 2[11,16].

3. Rheology, Resin Molding and Composite Properties

Dynamic rheological properties were measured by an RDS II dynamic rheometer at a ramp rate of 3°C /min in a nitrogen flow. These data are also shown in Table2. The imide oligomers gave low melt viscosity, resulting in significant improvements in processability for neat resin moldings and composites [11,16]. Here again, it is clearly distinct that a-BPDA imparts a low melt viscosity to the imide oligomer. Because the melted Oligo-1.5 was leaking from the gap in the stainless steel mold, imide oligomer a-BPDA/4.4'-ODA/PEPA (Oligo-4.5) at a number average molecular weight of 2490

g/mole was used for resin molding and composites (Table 2). The resin was molded from imidized powder in a stainless steel mold in a hot press at 320°C for 10 min, and then followed at 370°C for one hour. T-300 graphite fiber composites of Oligo-4.5 were fabricated from solution coated unidirectional dry prepreg in a stainless steel mold using the same process as used for neat resin moldings. Figure 8 shows the DMA curves of the fully cured imide oligomer. In comparison with the DMA curves of a-BPDA/4,4'-ODA polyimide in Figure 4, the cured molding resin of imide oligomer: Oligo-10 did not exhibit a large drop in the storage modulus, E' above the Tg. Furthermore, the increasing of the storage modulus, E' beyond 400°C suggests further crosslink reaction due to PEPA moiety. While DMA curve of PETI-5 resin

Table 2 Characterization and properties of imide oligomers and PETI-5

Oligomer	Tg (℃)			η_{inh}	Molecular	Solubility	Melt flow
	Cure temperature			(DMAc)	weight	in DMAc	viscosity
n	250℃	350℃	370℃		Mn(cal.)	Not cured	(Poise)
Oligo-1.5	161	297	341	0.07	1340	◎	200(300℃)
Oligo-4.5	245		343		2490	○	2000(310℃)
Oligo-10	237	281	308	0.15	5240	◎	20000(365℃)
PETI-5	210	249	270	0.27	5000	X	60000(371℃)

Oligo-4.5; a-BPDA/4,4'-ODA/PEPA, X; insoluble, ○; soluble, ◎; highly soluble
PETI-5; Ref.[16]

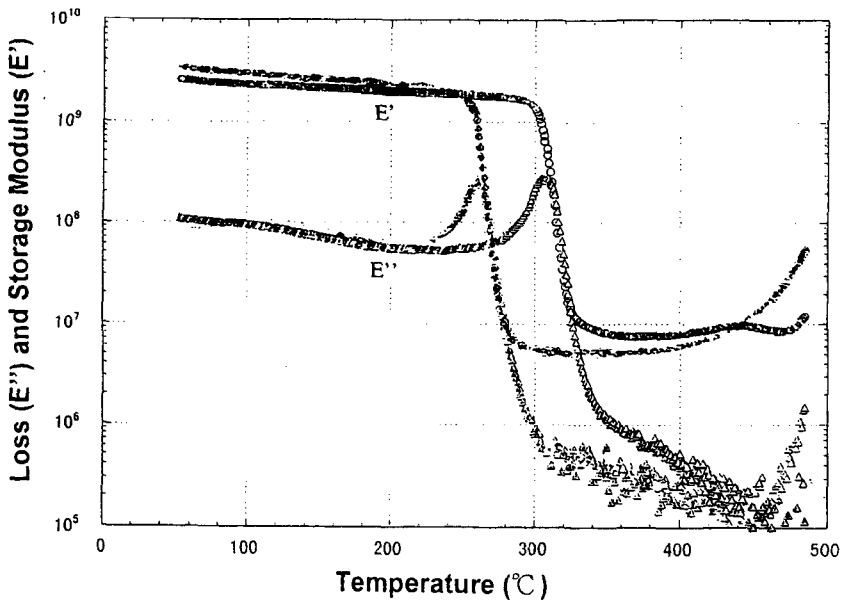


Figure 8 Temperature dependence of dynamic tensile properties (DMA) of cured Oligo-4.5(○, △) and PETI-5 (●, ▲) (supplied from NASA and molded by us)

Table 3 Physical and mechanical properties of various heat resistant addition type polyimides

	「TriA−PI」 (n＝4.5)	「PETI−5」	「PMR−15」
Tg(℃)	343	270	340
Density (g/cc)	1.30	1.3	1.32
T. strength (MPa)	115	130	39
E. at break (%)	＞14	32	1.1

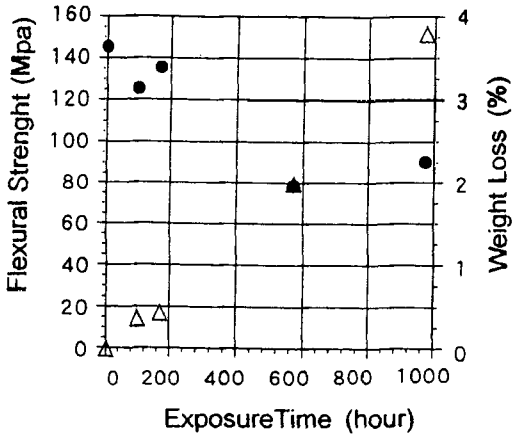


Figure 9. Thermo-oxidative stability of the fully cured Oligo-4.5 neat resin in a air oven at 300°C

Table 3 shows the physical and mechanical properties of the fully cured Oligo-4.5, PMR-15, and PETI-5. The molded resins were easily obtained and exhibited excellent mechanical performance with flexural elongation of 13% and a Tg of 343°C.
Figure 9 shows the thermo-oxidative stability for fully cured Oligo-4.5 neat resin. Flexural strength of the cured Oligo-4.5 neat resins decrease gradually 144 MPa to 90 MPa during exposure for 1000 hours, while the weight loss increases linearly with exposure time, resulting in 3.8% of weight loss for 1.000 hours at 300℃ in a forced air oven. These results indicate excellent thermo-oxidative stability for a-BPDA based, addition type polyimides. Consequently, it is concluded that imide oligomers consisting of a-BPDA and ODA with PEPA exhibited significant improvements in processability without sacrificing high thermo-oxidative stability for the resins and their composite.

4. Conclusions

Molecularly designed phenylethynyl-terminated, a new asymmetric aromatic dianhydride, 2,3,3', 4'-biphenyltetracarboxylic dianhydride a-BPDA imide oligomer with PEPA were prepared. Imide oligomer with 3,4'ODA; 4,4, -ODA/PEPA of n=1.5

indicated a melt viscosity; 200 Poise during the cure process, while the melt viscosity for Oligo-10 was 20,000 Poise. Imide oligomer, in particular, from the reaction of a-BPDA with 4,4'-ODA and endcapped with PEPA at a calculated number average molecular weight (Mn) of 2500 g/mole was of special interest because the cured polymer was tough and had a Tg of 343°C. Because of the catenation from the dianhydride, the oligomers have highly irregular structures resulting in relatively low melt viscosity that suggests the fabrication of composites and bonded parts could be performed under relatively low pressures. 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 molecules above the Tg without a loss in good thermo-oxidative stability. It is shown that amorphous, aromatic asymmetric imide structures without any weak linkages such as alkyl and methylene groups are very promising for molecular design of heat resistant, addition type polyimides. Furthermore, amorphous, aromatic, asymmetric polymers (TriA-PI: Polymeric material) are expected to be the next generation high performance organic materials.

References

1) J.P.Critchley, G.J.Knight, and W.W.Wright (Eds.), HEAT-RESISTANT POLYMERS Technologically Useful Materials, Plenum Press, New York (1983)
2) M.K.Ghosh and K.L.Mittal (Eds.), POLYIMIDES: FUNDAMENTALS AND APPLICATIONS, Marcel Dekker, New York (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) R.Yokota, in Structure and Design of Photosensitive Polyimides, K. Horie and T.Yamashita (Eds.), chap. 3, Technomic, Lancaster, PA (1996)
5) R.Yokota, Proc. of the 7th Int. Conf. on Materials in a Space Environment, p.293 SP-399 ISBN 92-9092-279-6, European Space Agency Publication Division, Noordwijk, The Netherlands (1997)
6) J.W.Connell, J.G.Smith, Jr., and P.M.Hergenrother, J. Macromolecular Sci., -REV. MACROML. CHEM., C40 (2&3), 207-230(2000)
7) T.H.Hou, B.J.Jensen, and P.M.Hergenrother, J. Composite Mater. 30, 109 (1996)
8) R.J.Cano and B.J.Jensen, J. Adhesion, 60, 113 (1997)
9) P.M.Hergenrother and J.G.Smith, Jr., Polymer, 35, 4857 (1994)
10) G.W.Meyer, B.Tan and J.E.McGrath, High Perform. Polym. 16, 423 (1994)
11) R.Yokota, in Proc. of the 7th Japan Polyimide Conf. T. Takeichi and M.Kochi (Eds.) p.21 Reiteck, Tokyo Japan (1998)
12) M.Hasegawa, R Yokota, N. Sensui, and Y. Shindo, Macromolecules, 32, 387 (1999)
13) C.X.Fang, D.F.Rogers, D.A.Scola and M.P.Stevens, J. Polym. Sci., Part A: Polym. Chem, 36, 461 (1998)
14) B.J.Jensen and P.M.Hergenrother, Polymer, 34, 630 (1993)
15) J.W.Connell, J.G.Smith, Jr., and P.M.Hergenrother, High Perform.Polym., 10, 273 (1998)
16) R.Yokota, S, Yamamoto, S, Yano, T, Sawaguchi, M.Hasegawa, Y.Yamaguchi, H.Ozawa, and R.Sato: High Perf. Polymers, vol.13, S61 (2001)