

Novel Asymmetric and Addition-type Imide Resins for High Temperature Composites

Masahiko Miyauchi (宮内雅彦), Yuichi ISHIDA (石田雄一), Rikio Yokota (横田力男)

1 Frontier Material Development Laboratories, Kaneka Corporation

5-1-1 Torikai-nishi, Settsu, Osaka 566-0072, Japan

2 Institute of Aeronautical Technology, Japan Aerospace Exploration Agency (JAXA)

3-1-1 Osawa, Mitaka, Tokyo 274-8510, Japan

Abstract: Novel addition-type phenylethynyl containing imide oligomers (degree of polymerization: $n = 1-10$) were derived from 1,2,4,5-benzenetetracarboxylic dianhydride (PMDA), 2-phenyl-(4,4'-diaminodiphenyl ether) (p-ODA) for use as the matrix resin of highly heat-resistant carbon fiber-reinforced composites. The uncured imide oligomers showed good solubility (more than 30 wt %) in N-methyl-2-pyrrolidone (NMP) and very low melt viscosities. These imide oligomers were converted to cross-linked structures after curing at 370 °C. The glass transition temperature and elongation at break (ϵ_b) of the cured imide resin were found to be excellent (almost 340 °C and >15 %, respectively). Furthermore, imide solution prepregs were prepared from the imide oligomer solution and carbon fibers. A void-less polyimide/carbon fiber composite with high Tg was also achieved for fabrication via the imide solution prepregs.

1. Introduction

Excellent properties of aromatic polyimides such as Kapton® (DuPont) and Apical® (Kaneka Corp.), derived respectively from PMDA and 4,4'-ODA, and Upilex-R® (Ube Industries Ltd.) from 3,3',4',4'-biphenyltetracarboxylic dianhydride (s-BPDA) and 4,4'-oxydianiline (4,4'-ODA) are well known to have high dimensional stability, low thermal expansion, and outstanding thermal and environmental stability [1-3]. These properties are attributed not only to their rigid (planar and symmetric pyromellitimide or biphenylimide) structures, but also to the formation of high-ordered structures beyond Tg. Accordingly, these aromatic polyimides do not exhibit high molecular mobility at temperatures higher than Tg, indicating that processing conditions for molding were extremely severe. Therefore, great effort has been devoted to development of the aromatic imide oligomers with good processability and high Tg after curing for matrix resins of fiber reinforced composites with high temperature resistance ($T_g > 300$ °C).

One well-known high-performance thermosetting polyimides is PMR-15, developed by NASA in the early 1970s for aerospace applications. High-temperature composites from low molecular weight resins endcapped with reactive groups such as PMR-15 are generally fabricated via autoclave processing. PMR-15 cured resin showed high Tg of greater than 300 °C, but it is brittle because of its high cross-link density [4]. Consequently, PMR-15 composites exhibit poor impact resistance or compressive strength after impact.

As secondary generated matrix resins in NASA, phenylethynyl containing imide oligomers have also been developed for various applications including structures for advanced aerospace vehicles such as the once-proposed high-speed civil transport (HSCT). The materials for this vehicle were required to have stable mechanical properties for 60,000 hr at 177 °C. PETI-5 was prepared from the reaction of s-BPDA and two aromatic diamines with PEPA for the reactive end cap at a calculated molecular weight of 5,000 g/mol [5,6,7]. The cured polyimide exhibits a moderate Tg of 270 °C and more than

30 % elongation-at-break (ϵ_b) for a film, indicating that the formation of the converted cured resin was attributed mainly to the chain extension of imide oligomers because of the thermo-additional polymerization of PEPA [8,9]. The phenylethynyl end cap offered important benefits such as a large processing window and good thermo-oxidative stability. PETI-5 imide exhibited excellent processability during the fabrication of neat resin molding, bonded panels, and composites via autoclave processing under pressure 1.4 MPa or less for about 1 hr at 350–370 °C. PETI-5 was evaluated extensively and selected as a candidate of use as the adhesive and composite matrix for the HSCT [10,11,12].

Yokota et al. [13–16] found recently that a polyimide based on 2,3,3',4'-biphenyltetracarboxylic dianhydride (asymmetric-BPDA, a-BPDA) and 4,4'-ODA exhibited a higher T_g than that of s-BPDA based PI and also showed a large drop in the storage modulus, E' at temperatures higher than T_g .

These data are attributed to the decrease in the intermolecular interactions of the polyimides derived from a-BPDA, which have asymmetric and nonplanar structures. Based on the thermal and rheological behavior of a-BPDA based polyimides, Yokota et al. designed a-BPDA based phenylethynyl-terminated, addition-type a-BPDA imide oligomers (TriA-PI) with excellent processability to give rise to cross-linked polyimides with high temperature resistance and more than 20 % ϵ_b after curing at 370 °C / 1 hr [17].

Because TriA-PI exhibits insufficient solubility, the prepregs were manufactured by impregnating carbon fibers with TriA-PI amide acid oligomer solution at high concentrations. However, the water evolution caused by imidization of amide acid oligomers during molding has a tendency to remain as voids in the composites. The preparation of void-less high heat resistant composites can be achieved using prepregs prepared by impregnating fibers with high concentration solution of imide oligomers if imide oligomers with both high solubility and good processability can be synthesized.

As described in this paper, we describe molecular design and the preparation of phenylethynyl-terminated imide oligomer derived from pyromellitic dianhydride (PMDA) with symmetric and planar structures as a diacid and 2-phenyl-4,4'-diaminodiphenyl ether (p-ODA)(Figure 1). p-ODA is an extremely simple diamine with asymmetric and nonplanar structures. The effect of asymmetry, nonplanar structures, and restriction of free rotation of ether linkage of p-ODA on the solubility and processability of addition-type aromatic imide oligomers were investigated.

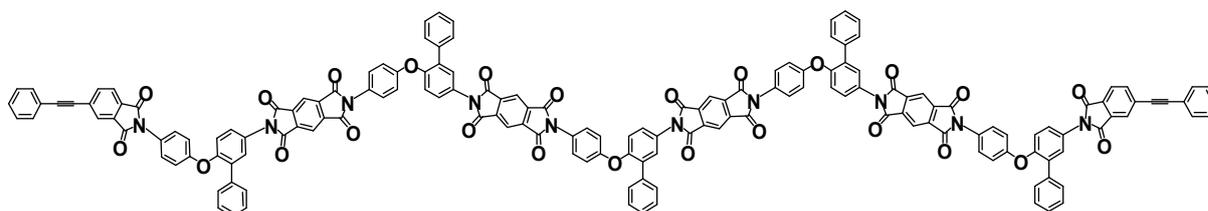


Figure 1. Structures of PMDA/p-ODA/PEPA imide oligomers (n=4)

Based on the thermal and rheological behavior of PI(PMDA/p-ODA) film, we found that the asymmetric and nonplanar structures of p-ODA were able to prevent the intramolecular–intermolecular aggregation of PMDA-based PI chains by DMA measurements. Moreover, the PEPA-terminated aromatic imide oligomers were found to have high solubility in NMP (>33 wt %) and good processability to convert the cross-linked polymers with excellent thermal stabilities ($T_g > 340$ °C) and mechanical properties ($\epsilon_b > 10$ %) with curing at 370 °C / 1 hr.

2. Results and Discussion

2.1 Solubility, Processability and Thermal Properties of Phenylethynyl-terminated Imide Oligomers

PMDA-based imide oligomers derived from p-ODA were obtained from imidization of the solution of corresponding amide acid oligomers at 195 °C for 5 h. After preparing highly concentrated NMP solution of PMDA/p-ODA/PEPA imide oligomer (33 wt %, n=4) at 150 °C, the solution turned into a gel during storage for one day at room temperature. When the gel was heated at 150 °C for 1 hr again, it changed gradually to a solution without precipitation. The sol-gel behavior is conceivably attributed to the intermolecular interaction of the planar and rigid phenyl–pyromellitimide–phenyl structures of tail-to-tail units in oligomer chains [19].

The solubility of the matrix resin probably requires more than 30 wt % in the solution for molding the carbon-fiber reinforced composites via the imide oligomer prepreps (manufactured by dipping carbon fibers in highly concentrated imide oligomer solution) without a gel and precipitations. The phenomenon described above strongly suggests that the PMDA/p-ODA imide oligomer is necessary to put third components for increasing its solubility.

The bulky substituent of polymer side chain is well known to be able to improve solubility with increased solvation. We selected 9,9-bis(4-aminophenyl)fluorene (BAFL) with a side bulky fluorenyl group as a candidate for copolymerization diamine monomer to PMDA/p-ODA imide oligomer (Figure 2).

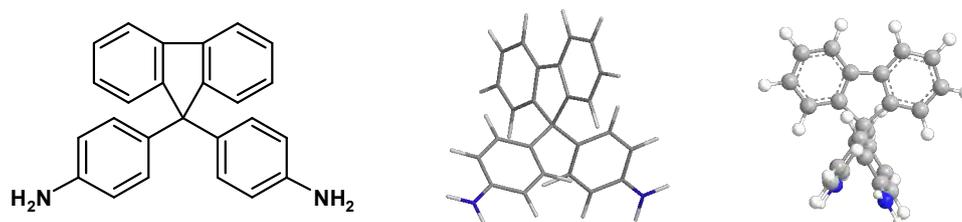


Figure 2. Chemical and stereo structures of BAFL diamine.

Figure 3 shows DMA curves of PI(PMDA/p-ODA;BAFL) as the concentration dependency of BAFL ratio for all diamines. Decrease in drops of E' to the rubbery plateau region above T_g was observed with an increase in the BAFL concentration. Results show that the molecular mobility of PI(PMDA/p-ODA) chains was reduced with an increase in the rigid zigzag structures of phenyl–pyromellitimide–phenyl (PMDA-BAFL-PMDA) units because of the free rotational restriction of quaternary carbon atom by steric hindrance of hydrogen atoms at 2- and 2'-positions of bis(4-aminophenyl) group in BAFL. However, at concentrations up to 25 mol % of BAFL, the large drops of E' were observed sufficiently in the DMA curves. These data strongly suggest that PMDA/p-ODA imide oligomers with an optimal ratio of BAFL (< 25 mol-%) might show sufficient processability to convert the cured resins with high T_g .

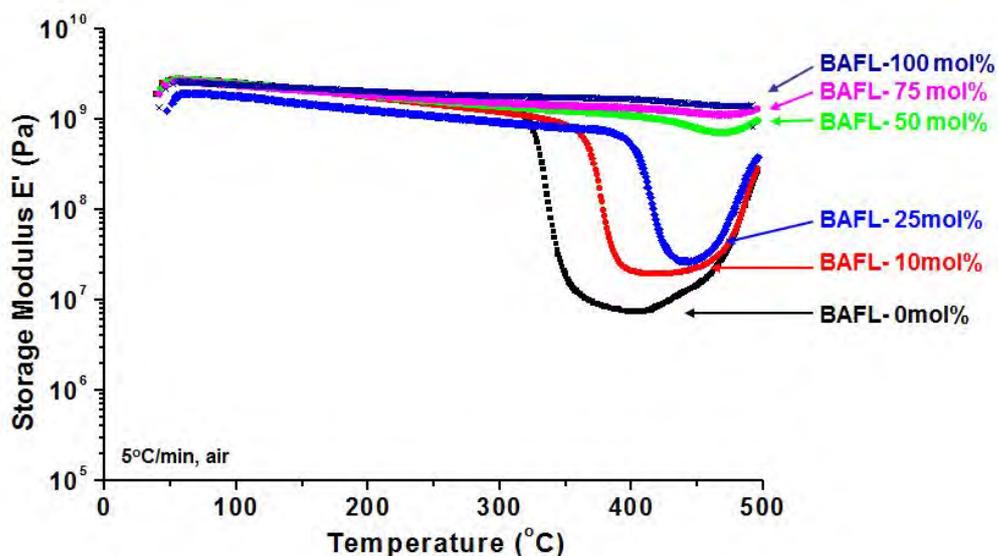


Figure 3. DMA curves of PI(PMDA/p-ODA;BAFL) as the concentration dependency of BAFL ratio for all diamines.

Figure 4 shows a typical DSC curve of PMDA/p-ODA(90);BAFL(10)/PEPA uncured imide oligomer ($n=4$). An endothermic shift (T_g) and a large exothermic peak were observed at 212 °C and at temperatures greater than 400 °C, respectively.

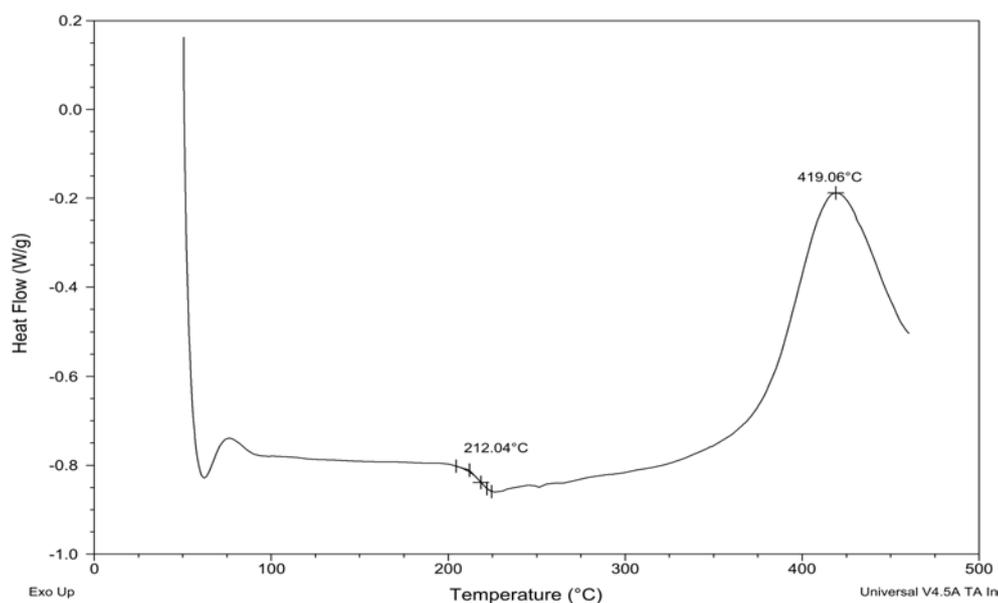


Figure 4. DSC curve of imide oligomer ($n=4$) derived from (PMDA/p-ODA(90);BAFL(10)/PEPA).

Table 1 shows solubility, thermal and rheological properties of (PMDA/p-DA;BAFL/PEPA) imide oligomers with different copolymerized ratio of p-ODA/BAFL. Even an addition of a small amount of BAFL (5 or 10 mol-% for the total diamine) is clearly found to enable the imide oligomers to store as clear solutions for a few months with no sacrifice of their melt viscosity. These data show significant improvements of PMDA-based polyimide resin in processability for molding fiber-reinforced heat-resistant composites.

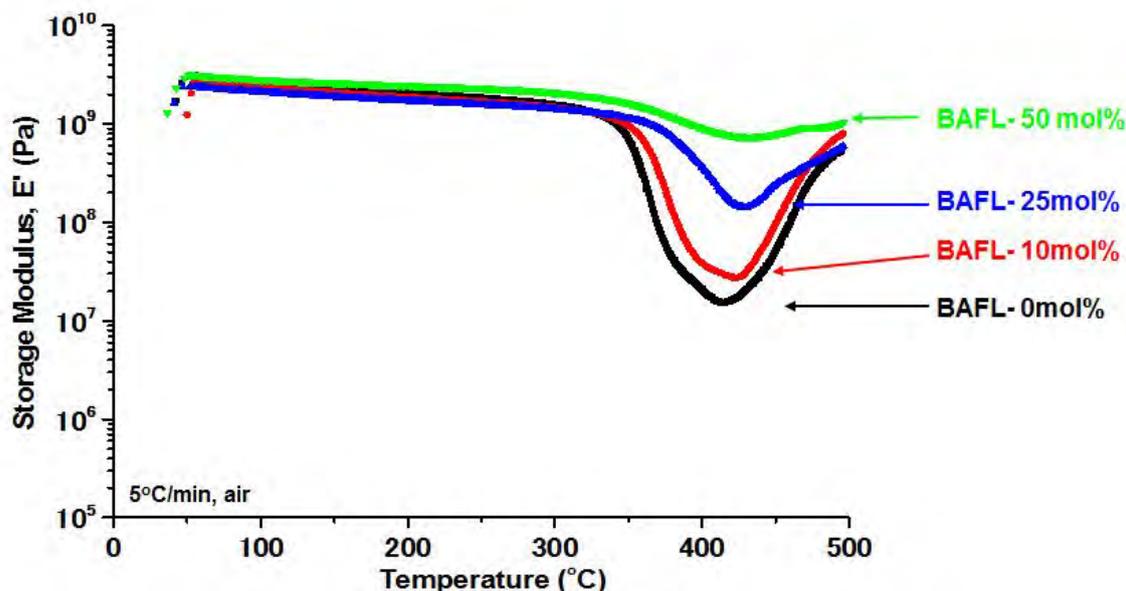


Figure 5. DMA curves of cured resins derived from (PMDA/p-ODA;BAFL/PEPA) as the concentration dependency of BAFL ratio for all diamines.

Table 2 presents the thermal and mechanical properties of their cured resins. These Tg were found to increase with the increase of BAFL in the region of more than 350 °C. In contrast, a decrease in the ϵ_{bs} of the cured resins was observed with an increase of BAFL. Results show that the molecular mobility and flexibility derived from ether linkage of p-ODA in polymer chains decreased concomitantly with the increase of the rigid units of PMDA-BAFL-PMDA. Particularly, even the addition of 5–10 mol % of BAFL enabled the imide oligomer to convert the cured resins with both very high Tg (> 350 °C) and good ϵ_{bs} (>13 %). All cured resins showed high Td5s (>525 °C). Surprisingly, the ϵ_{bs} value of cured polymers were very high (> 9.5 %), indicating that the reaction mechanism of the PEPA was mainly chain extension rather than cyclization or crosslinking [8,9,19].

Table 2. Thermal and mechanical properties of (PMDA/p-ODA;BAFL/PEPA) cured resins.

Mol. ratio of p-ODA/BAFL	Calculated Number-Average Molecular Weight ($M_n \times 10^3$)	Solubility in NMP (wt %)	Tg (°C)	Minimum melt viscosity	
				(Pa·s)	(°C)
100/0	2.6	>33 ^{a)}	209	144	343
95/5	2.6	>33	211	226	340
90/10	2.6	>33	212	154	325
90/10	3.5	>33	258	9036	348
75/25	2.6	>33	231	1323	351
50/50	2.7	>33	- ^{b)}	731	320
25/75	2.8	- ^{c)}	- ^{b)}	- ^{d)}	- ^{d)}

a) Determined by TGA at a heating rate of 5 °C/min under nitrogen. b) Average values of elongation at break. c) Not detected obviously. d) Brittle

3.3 Uni-directional Carbon Fiber/Polyimide Composites

In this study, the uni-directional (UD) composites with cured resin of (PMDA/p-ODA(90);BAFL(10)/PEPA) were fabricated, and mechanical properties were investigated. The imide oligomer/NMP solutions were impregnated into MR-50R carbon fiber (12K, Mitsubishi Rayon). The properties of the UD prepreg tapes and imide oligomers are summarized in Table 3.

Table 3. UD prepreg and UD-composite properties.

Prepreg solids (wt%).	Prepreg volatiles (wt%)	Prepreg areal weight (g/m ²)	Lay-up	Composite fiber fraction (vol. %)
38	15-17	380	[-45/0/45/90] _{2s} ,16Ply	58

Figure 6 shows DMA curves of CF/PI composite. The estimated Tg determined from E' by setting up tangents to the linear portion of the curve before and after the modulus drop off was approximately 370 °C. The PI/CF composite exhibited higher Tg because of Kapton-type rigid backbone structure in comparison with previous TriA-PI(a-BPDA/4,4'-ODA) composite (Tg = 340 °C).

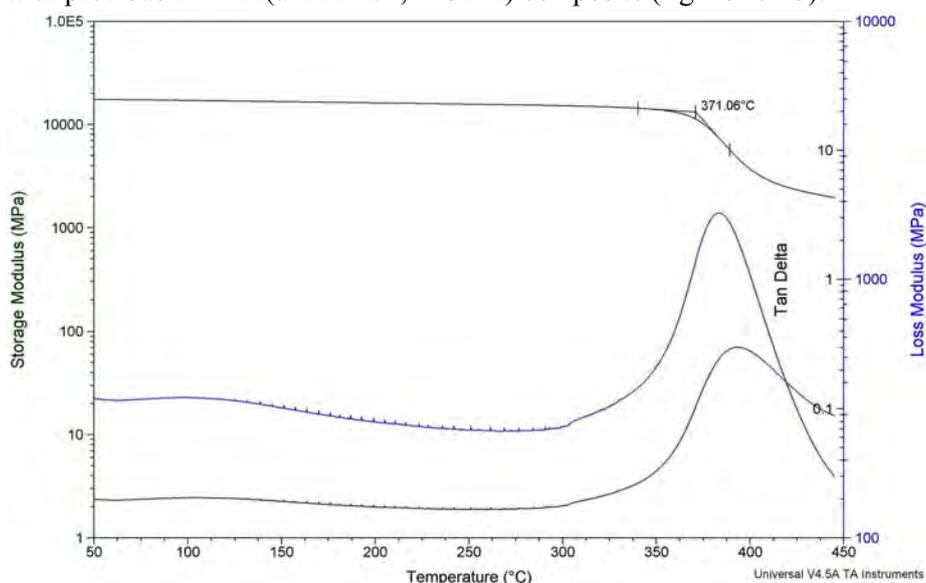


Figure 6. DMA curves of CF/PI composite(Quasi-isotropic, 16Ply).

Mechanical properties of CF/PI composite (Quasi-isotropic,16Ply) are summarized in Table 4. PI/CF composite exhibits excellent SBS, OHC and NHC strengths at high temperature. It is supposed that the irregular and asymmetric structure of polyimide matrix resins contribute to these excellent mechanical properties.

Now, detailed mechanical analyses of the PI/CF composites are under investigation.

Table 4. Mechanical properties of CF/PI composite(Quasi-isotropic,16Ply).

Mechanical Properties	Temperature (°C)	Strength (MPa)	Retention (%)
SBS	30	65	100

	177	47	72
	250	39	60
	300	34	52
NHC	30	494	100
	177	377	76
	250	301	61
	300	276	56
OHC	30	301	100
	177	213	71
	250	162	54
	300	135	45

3. Conclusions

A novel phenylethynyl-terminated, addition-type imide oligomer with a Kapton-type backbone structure was found to have high solubility and good processability. The imide oligomer was converted to cured resin with high T_g at > 345 °C and excellent mechanical properties.

Preliminary studies for processing, thermal and mechanical properties of carbon fiber reinforced TriA-X composite were conducted. The PI/CF composite exhibited excellent processability, T_g (= 370 °C), and mechanical properties at high temperature.

We believe that these excellent properties of PMDA/p-ODA based addition-type aromatic polyimides suggest promising possibilities for application to highly heat-resistant composites prepared by imide wet prepreg.

References

- [1] Polyimides: Fundamental and Application, New York: Marcel Dekker, 1996
- [2] Polyamic Acids and Polyimides: Synthesis, Transformations and Structure Boca Raton: CRC Press, 1993
- [3] Polyimides: Fundamentals and Applications Ghosh, M. K., Mittal, K. L., New York: Marcel Dekker, 1996.
- [4] Serafini, T. T., Delvigs P., & Lightsey, G. R., "Thermally stable polyimides from solutions of monomeric reactants." *Journal of Applied Polym. Sci.* 16 (1972): 905-915.
- [5] Cano, R. J., & Jensen, B. J. "Effect of molecular weight on processing and adhesive properties of the phenylethynyl-terminated polyimide LARC™-PETI-5." *J. Adhesion* 60 (1997): 113-123.
- [6] Hergenrother, P. M., & Smith Jr., J. G. "Chemistry and properties of imide oligomers end-capped with phenylethynylphthalic anhydrides." *Polymer*, 35, (1994): 4857-4864.
- [7] Hergenrother, P. M., Connell, J. W., & Smith Jr., J. G. "Phenylethynyl containing imide oligomers." *Polymer* 41 (2000): 5073-5081.
- [8] Meyer, G. W., Tan, B., & McGrath, J. E. "Solvent-resistant polyetherimide network systems via phenylethynylphthalic anhydride endcapping." *High Perform. Polym.* 6 (1994): 423-435.

- [9] Holland, T. V., Glass, T. E., & McGrath, J. E. "Investigation of the thermal curing chemistry of the phenylethynyl group using a model aryl ether imide." *Polymer* 41 (2000): 4965-4990.
- [10] Jensen, B. J., Bryant, R. G., Smith Jr., J. G., & Hergenrother, P. M. "Adhesive properties of cured phenylethynyl-terminated imide oligomers." *J Adhesion* 54 (1995): 57.
- [11] Hou T., Jensen, B. J. & Hergenrother, P. M., "Processing and properties of IM7/PETI composites." *J. Comp. Matls.* 30 (1996): 109-122.
- [12] Rommel, M., Konopka, L., & Hergenrother, P. M. "Process development and mechanical properties of IM7/LaRC PETI-5 composites" *Proceedings of the 1996 28th International SAMPE Technical Conference, November 4-7, 1996, Seattle, WA, Society for the Advancement of Material and Process Engineering, USA, 1996, Vol. 28, pp 1-13.*
- [13] Hasegawa, M., Sensui, N., Shindo, Y., & Yokota R. "Structure and properties of asymmetric biphenyl type polyimides. Homo and copolymers and blends." *Macromolecules* 32 (1999): 387-396.
- [14] Chen, C., Yokota, R., Hasegawa, M., Kochi, M., Horie, K., & Hergenrother, P. M., "Isomeric biphenyl polyimides. (I) Chemical structure – property relationships," *High Perform. Polym.* 17 (2005), 317-333.
- [15] Kochi, M., Chen, C., Yokota, R., Hasegawa, M., & Hergenrother, P. M. "Isomeric biphenyl polyimides. (II) Glass transitions and secondary relaxation process." *High Perform. Polym.* 17 (2005), 335-347.
- [16] Zhou, H., Chen, C., Kanbara, R., Sakaki, T., & Yokota, R. "Synthesis and properties of copolyimides derived from isometric biphenyltetracarboxylic dianhydrides (a-BPDA and i-BPDA) and oxydiphthalic dianhydride (ODPA) with 4,4'-oxydianiline (4,4'-ODA)." *High Perform. Polym.* 17 (2005): 213-224.
- [17] Yokota, R., Yamamoto S., Yano, S., Sawaguchi, T., Hasegawa, M., & Yamaguchi, H. Ozawa, H., Sato, R. "Molecular design of resistant polyimides having excellent processability and glass transition temperature." *High Perform. Polym.* 13 (2001): S61-S72.
- [18] Miyauchi, M., Kazama, K., Sawaguchi, T., & Yokota, R. "Dynamic tensile properties of a novel Kapton-type asymmetric polyimide derived from 2-phenyl-4,4'-diaminodiphenyl ether." *Polymer Journal* 43 (2011): 866-868.
- [19] Nakamura, K., Ando, S., & Takeichi, T. "Thermal analysis and solid-state ¹³C NMR study of crosslink in polyimides containing acetylene groups in the main chain." *Polymer*, 42 (2001): 4045-4054.