Synthesis and Characterization of Polyimide-Epoxy Hybrid Films

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Summary: Composites from polyimide and epoxy-amine were prepared aiming for enhancing its thermal and mechanical properties. Polyimide-epoxy-amine hybrid films were prepared by blending of polyimide and epoxy-amine in different ratios whereas, polyimide was prepared by reacting 1,2-di(*p*-aminophenyloxy)ethylene with 3,3′4,4′-benzophenone tetracrboxylic acid dianhydride. The blend systems with Araldite LY564 (1,4-butanedioledigIycidyl ether) (BDDE) and Hardener HY2954 (3,3′-dimethyl-4,4′-diaminodicyclohexyl)methane (MACM) were investigated in term of thermal, mechanical and viscoelastic measurements. Thermal stability was determined using thermogravimetric analysis. The effect of the polyimide content on the glass transition temperature (Tg) and thermal stability was observed. Viscoelastic measurements showed that the glass transition temperature shifted with the increase of polyimide content. The composites showed higher thermal stability in comparison with neat epoxy-amine matrix for higher polyimide concentration. The effect of polyimide content on the mechanical properties was also investigated. The tensile measurements of the films showed that with the increase of polyimide content the tensile modulus of the films was increased.

Introduction

Epoxy resins are widely used for their excellent properties such as chemical resistance, good electrical insulating property, good adhesion to glass and metal and can be easily fabricated. The variety of properties helps the epoxy resins to meet the performance requirements of some demanding applications. These include areas like construction, electronics, adhesives and coatings [1]. The usefulness of epoxy resins for many applications is often limited due to their inherent brittleness arising from their cross linked structure, low modulus and low thermal stability [2]. Different approaches for toughening the epoxy resins without sacrificing modulus and glass transition (Tg) temperature would lead to an increase in the areas of their applications [3-4].The most studied approach to toughen epoxy resin was the use of organic rubbers as toughening additives [5-10] . Such systems have some drawbacks such as a reduction in overall resin modulus and in end use temperatures. Another method of toughening epoxy resins is the incorporation of the thermoplastic toughnening agents such as poly (ethersulfone) [11-13], poly (phenylenether) [14], poly (etherketone) [15], polyester [16], and poly (etherimide) [17-18] has been widely used. Polyimides exhibit an impressive variety of desirable properties such as low dielectric constant, wear resistance, radiation resistance, inertness to solvents, good adhesion properties, good hydrolytic stability, low thermal expansion, long term stability, and excellent mechanical properties [19]. There are many studies in which polyimides have been used in epoxy systems intending mainly to improve the thermal stability and toughness [20]. Almost all the studies are based on physical blending of unreactive linear polyimides. Hay *et al.*, [20] studied the molding of linear unreactive polyimides for toughening of the epoxy resin-diaminodiphenyl-sulfone system. They have achieved increase in fracture toughness with no loss of modulus but there was a little influence on the thermal capabilities across the range of modifying polyimides. They have also used polyimides endcapped with amine in the epoxy system to form protective coatings with high heat and chemical resistance.

In continuation of our previous work [21] here a series of epoxy-polyimide blends are reported along with the effect of blending on thermal and mechanical properties. A diamine 1,2-di (*p*-aminophenyloxy) ethane (DAPE) was prepared and polymerized with 3,3′,4,4′-benzophenone tetra-carboxilic acid dianhydride to prepare polyimide. A series of polyimide-epoxy (LY564) composites were prepared by blending *N*,*N*′-dimethylformamide (DMF) was used as solvent in two step poly(amic acid) synthesis method and epoxy-polyimides hybrid films with different polyimides composition.

Results and Discussion

Preparation of Polyimide-Epoxy-amine Hybrid Films

The structure of the polyimide was confirmed by elemental and FT IR analysis. FT IR

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spectrum of polyimide exhibited the characteristic imide group absorption around 1780 and 1725 cm^{-1} (typical of imide carbonyl asymmetric and symmetric stretching) 1380 cm^{-1} (C–N stretch) and 1100 and 730 cm^{-1} (imide ring deformation). The disappearance of the amide and carboxyl bands indicated the formation of polyimide. The material properties of polyimide -epoxy -amine hybrid films are supposed to be improved by the addition of polyimide in to epoxy-amine network. A series of polyimide-epoxy-amine films BDDE/MACM were prepared by blended with different weigh ratios of polyimide in to the BDDE/MACM system as shown in the Table-1. The polyimide in 10 weight% was found suitable to get homogeneous blends as higher percentage of polyimide resulted in highly viscous mixture leading to non homogeneous blend. The cast films after drying were cured at 100 °C for 2 h and 120 °C for 2 h. The thickness of the resulting hybrid composite films was approximately 0.5 mm. These films were quite transparent for hybrid with polyimide content up to 7.5%. The films, however, become translucent with the increase of PI content up to 10%. The transparency of the hybrid composites comes from the dispersion of PI into epoxy-amine network. The PI particles, at high concentration, could not be completely dispersed into epoxy-amine network which reduces the transparency of the hybrid films.

Thermal Properties of Polyimide-Epoxy-amine Hybrids

The thermal stability of the composites was determined using thermogravimetric analyzer. The TGA curves of the pure epoxy and the composites with different polyimide content are presented in Fig.1. It was shown that the thermal stability has been increased with polyimide loading. The temperature at 5 and 10% weight loss are given in Fig. 2, which indicate that the thermal stability of the hybrid films was enhanced by the incorporation of the polyimide content. For pure epoxy-amine the temperature for 5% decomposition is 200 °C and for 10% polyimide loading is 275 °C. In all the cases the thermal degradation occurs in one step only, which is mainly due to degradation of cross linking [22]. Similarly, for pure epoxy-amine the temperature for 10% decomposition is 290 °C and for 10% polyimide loading 345 °C is observed. Therefore, the incur-poration of polyimide has resulted in pronounced improvement in thermal stability. This can be attributed to the homogenous distribution of polyimide particles in epoxy-amine network and the hindrance in diffusion of the volatile decomposition products in the composites compared to that in pure epoxy-amine network. The improvement in the thermal stability due to the addition of polyimide content has also been reported [22].

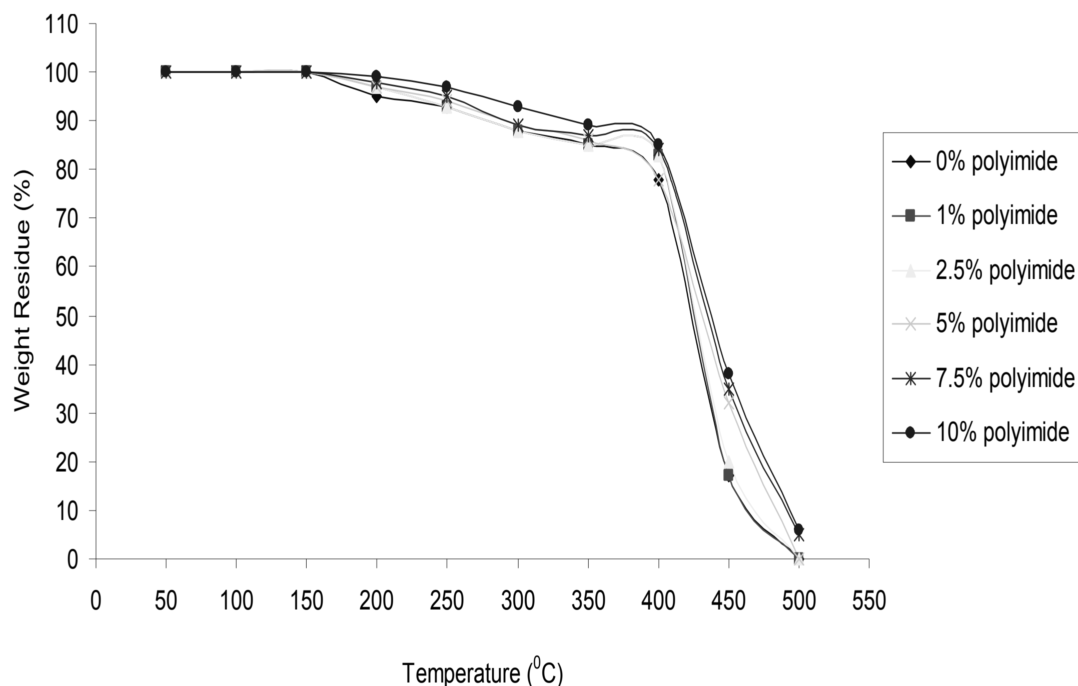


Fig. 1: TGA of polyimide-epoxy composites.

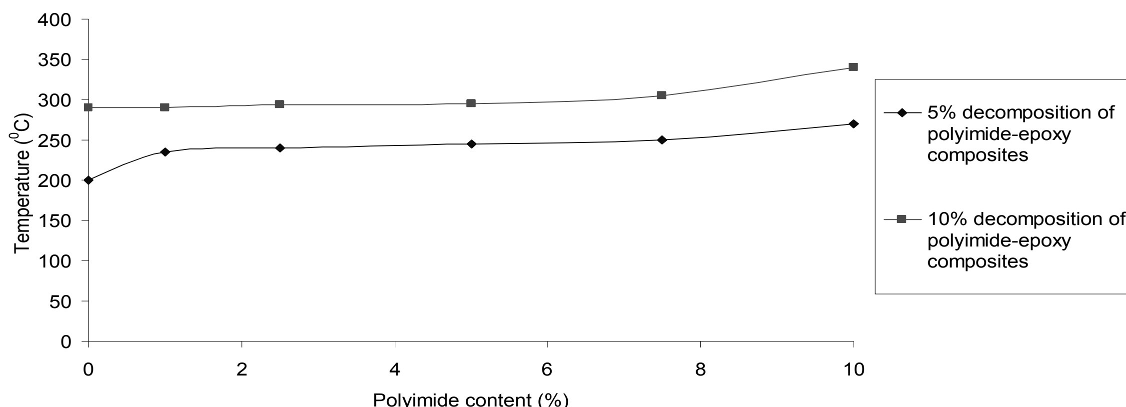


Fig. 2: Effect of Polyimide content on the 5 and 10% decomposition of polyimide-epoxy composites.

Glass Transition Temperature of Polyimide-Epoxy amine Hybrid Composites

The effect of polyimide content in the epoxy-amine network was monitored by differential scanning calorimetry (DSC) as is shown in Table-2. It can also be seen that the glass transition temperature of the epoxy-amine hybrid films has been increased with the incorporation of polyimide up to 7.5% but decreased in case of 10% Fig. 3. In general the increase in Tg is attributed to good adhesion between the polyimide and epoxy-amine because the small size particles can restrict the segmental motion. The other factors that can affect the Tg are degree of particle dispersion and curing conditions. The degrees of particle dispersion include size, homogeneity, orientation and spacing between particles. The improvement in Tg observed in this study may arise from some of these factors.

Table-1: Calculations of Polyimide-Epoxy-amine Films.

Code	Epoxy (g/mmol)	Hardener (g/mmol)	Polyimide (g/wt %)
Epoxy-Amine	3.06(10)	1.19 (10)	0 (0)
Epoxy-Amine -1	3.06(10)	1.19 (10)	0.0425 (1)
Epoxy-Amine -2	3.06(10)	1.19 (10)	0.1062 (2.5)
Epoxy-Amine -3	3.06(10)	1.19 (10)	0.2125 (5.0)
Epoxy-Amine -4	3.06(10)	1.19 (10)	0.31875 (7.5)
Epoxy-Amine -5	3.06(10)	1.19 (10)	0.425 (10.0)

Table-2: Thermal Stability of Polyimide-Epoxy-amine Composites.

Code	Polyimide Content (%)	Temp of 5% Decomposition (°C)	Temp of 10% Decomposition (°C)	Glass Transition Temp (Tg)* (°C)
BDDE-MACM	0	200	290	148
BDDE-MACM	1.0	235	290	155
BDDE-MACM	2.5	240	294	159
BDDE-MACM	5.0	245	295	163
BDDE-MACM	7.5	250	305	168
BDDE-MACM	10.0	275	345	160

* Tg from DSC (Differential Scanning Calorimetry)

Solvent Resistance of Polyimide –Epoxy Hybrid Films

Solvent resistance of the polyimide /epoxy hybrid films after curing at 140 °C was investigated. The films were immersed in various solvents (0.03 g/10 mL) such as DMF, DMAc, NMP, THF and dichloromethane for one week. Table-3 shows the solubility behavior of the polyimide /epoxy hybrid films. The neat epoxy-amine film is partially soluble on heating in NMP, DMF, and DMAc. Films with 1% polyimide content are also partially soluble on heating in DMF and DMAc. Films with 2.5, 5.0, 7.5, and 10.0% polyimide content are insoluble in test solvent even on heating. This shows that the polyimide content rendered the films to have excellent solvent resistance

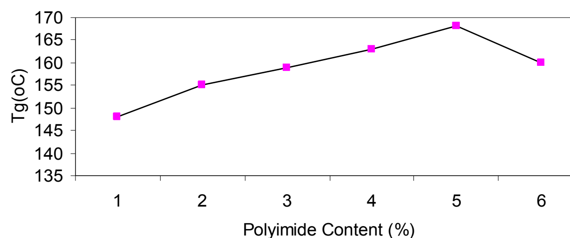


Fig. 3: Effect of Polyimide content on the glass transition (Tg) of the polyimide-epoxy composites.

Table-3: Solubility behavior of the polyimide /epoxy films.

Code	NMP[a]	DMF[a]	DMAc[a]	DCM[b]	THF[a]
Epoxy-Amine	*	*	*	×	×
Epoxy-Amine -1	×	*	*	×	×
Epoxy-Amine -2	×	×	×	×	×
Epoxy-Amine -3	×	×	×	×	×
Epoxy-Amine -4	×	×	×	×	×
Epoxy-Amine -5	×	×	×	×	×

The symbol indicates: b. Dichloromethane, *. Partially soluble on heating: ×. Insoluble

Tensile Properties of Polyimide-Epoxy-amine Hybrid Films

The tensile properties of pure epoxy-amine and reinforced epoxy-amine composites with different wt. % polyimide are summarized in Table-4. This table shows a clear tendency that the tensile modulus increases with increase in the polyimide content and elongation decreases. The variation of tensile modulus with polyimide content is shown in Fig. 4. With the incorporation of 7.5% polyimide, the tensile strength has increased to 85 MPa, which is 16% higher than that of epoxy-amine. This increase in tensile strength was accompanied by 52% decrease in elongation at break. It has been observed that the addition of polyimide content up to 7% in the epoxy-amine matrix increased the tensile strength; however, 10% polyimide concentration decreased the tensile strength. It can be assumed that the increased concentration of the polyimide made the composite more brittle and reduced the elongation at break. The improvement in strength and the modulus can be attributed to the uniform distribution and good interfacial adhesion [22] between the polyimide and epoxy-amine matrix. However, the low strength at high polyimide concentration can be attributed to the inevitable aggregation of the polyimide at high concentration. Therefore, when the composites are under load, the polyimide in the cluster may produce a high stress concentration and cause premature failure. Attempts were also made to calculate the tensile modulus as a function of polyimide content. Tensile modulus is 3.15 GPa up to 7.5% polyimide content but 2.73 GPa in case of 10% polyimide content. The most obvious reason would be the random distribution of polyimide and numerous aggregations instead of good dispersion [23]. The composites consisting of different weight percentages of polyimide and the epoxy-amine matrix were produced. TGA showed that the hybrid films are more stable than neat epoxy-amine matrix. The distinctive increase of the glass transition temperature with increase of polyimide content was observed. The tensile modulus was enhanced by the inclusion of polyimide content accompanied with decrease in the elongation at break. The increase in modulus is due to the reinforcement effect of the dispersed polyimide. The investigation of the thermo-mechanical properties of the composites also resulted in increase of thermal stability through the addition of polyimide in the epoxy-amine matrix by reducing the mobility of the matrix.

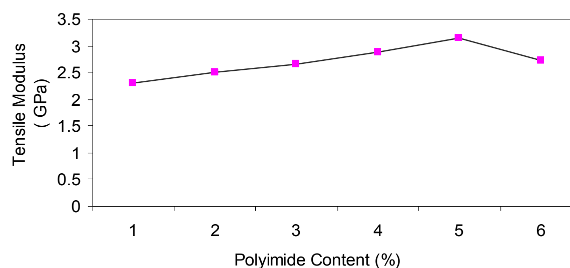


Fig. 4: Effect of Polyimide content on the tensile modulus of the polyimide-epoxy composites.

Table-4: Effect of Polyimide Content on the Tensile Properties of Polyimide- Epoxy-amine Composites.

Code	Polyimide Content (%)	Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
BDDE-MACM	0	2.30	73	5.21
BDDE-MACM	1.0	2.50	75	4.81
BDDE-MACM	2.5	2.65	78	3.55
BDDE-MACM	5.0	2.89	81	2.75
BDDE-MACM	7.5	3.15	85	2.50
BDDE-MACM	10.0	2.73	79	1.43

Experimental

Materials

p-Nitrophenol, 1,2-dichloroethane, hydrazine, Pd-charcoal, Potassium carbonate, ethanol, toluene, 3,3′,4,4′-benzophenonetetra-carboxylic acid dianhydride (BTDA) and DMF were purchased from Fluka / Aldrich Chemical Company and used as received. Araldite LY564 (1,4-butanedioledilgycidyl-ether) (BDDE) and Hardener 2954 (3,3′-dimethyl-4,4′-diaminodicyclohexyl)-methane (MACM) were purchased from Ciba and were used without purification. All other reagents and solvents were of analytical grade.

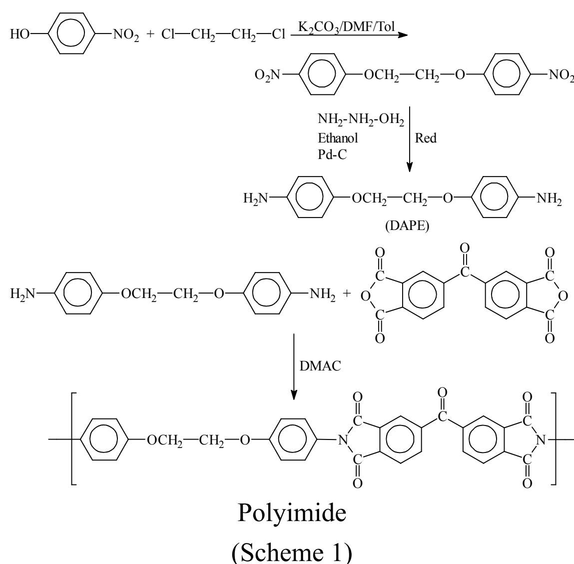
Measurements

^{13}C and ^{1}H-NMR spectra were obtained on instrument Joel 270 Spectrophotometer in DMSO-d_6 using tetramethylsilane as an internal reference. Infrared measurements were recorded within the range of 400-4000 cm^{-1} on Bio-Rad Excalibur FT IR Model FTS3000 MX. Melting points were measured in capillaries from Electrothermal IA 9000 series Digital melting point apparatus. Thermal and DSC analysis were carried out using Perkin Elmer TGA-7 and Perkin Elmer DSC-7. Elemental analysis was conducted using Perkin Elmer CHNS/02400. Average molecular weight of epoxy and hardener was determined by using Alliance GPCV 2000 (Water System 2410) using polybutadiene as

standard and found to be 306 and 238, respectively. Dynamic viscoelastic measurements were calculated on Perkin Elmer Pyris Diamond 115V Japan at 20 Hz and heating rate of 2 °C/min. The tensile properties were recorded with cross head speed of 5 mm/min using Testometric Universal Testing Machine M 350/500 UK. The tensile properties of each sample were determined from an average of at least five tests.

Synthesis of Polyimide

The diamine 1,2-di(*p*-amino-phenyloxy)ethylene (DAPE) was prepared according to reaction Scheme 1 [21]. To a stirred solution of DAPE (0.604g, 2.476 mmol) in 16 ml of DMAc was gradually added 3,3′,4,4′-benzophenone tetra-carboxylic acid dianhydride (BTDA) (0.8 g, 2.476 mmol). The mixture was stirred at room temperature for 24 h under argon atmosphere to form polyamic acid (precursor). The dark brown viscous poly(amic acid) was precipitated in water (500 mL), filtered, washed in the water and dried under vacuum at 60 °C for 15 h. The resulting polyamic acid powder (Yield = 92.8%) was heated in vacuum at 80 °C for 18 h, 150 °C for 2 h, 200 °C for 2 h, 250 °C for 24 h and at 280 °C for 2 h to convert it into polyimide and was confirmed by FT IR and elemental analysis? Elemental analysis for ($C_{31}H_{18}O_7N_2$) (MW = 530) monomer repeat unit in Wt.% Calc. C = 70.18, H = 3.39, N = 5.28 and found to be C = 69.95, H = 3.51, N = 5.15. FT IR (KBr pellet) in cm^{-1} 1780 and 1725 (typical of imide carbonyl asymmetric and symmetric stretching) 1380 cm^{-1} (C–N stretch) and 1100 and 730 cm^{-1} (imide ring deformation). The dis-appearance of the amide and carboxyl bands indicated the formation of polyimide.



Polyimide

(Scheme 1)

Synthesis of Neat Epoxy-amine Network

Neat epoxy-amine system was synthesized by mixing the equimolar concentration of epoxy and amine keeping the ratio of functionalities N = 1. N was defined as number of amine groups/number of epoxy rings. When N = 1, there are equal number of NH_2 groups and epoxy rings in the sample mixture Table-1. Neat epoxy-amine system was synthesized in order to compare its properties with that of polyimide-epoxy-amine composites. For this purpose 10 mmoles of BDDE and 10 mmoles of MACM were mixed in a two necked flask using DMF as a solvent. The mixture was stirred at room temperature for 24 h. The clear solution thus formed was poured into clean dry Teflon coated petridish placed on the leveled surface in the oven at 80 °C for 8 h to bake out the solvent. The dry film obtained was then subjected to stepwise curing *i.e.* 100 °C for 2 h, 120 °C for 2 hand 140 °C for 2 h. The film obtained after curing was transparent and was dried further in vacuum at 60 °C to remove any trapped solvent.

Synthesis of Polyimide-Epoxy-amine Hybrids

BDDE/MACM was blended with polyimide in different weight ratios in DMF solvent. The mixture was stirred at room temperature for 24 h to get the homogeneous solution. The solution was cast on the Teflon coated petridish followed by drying at 80 °C for 8 h. The cast film was then thermally cured 100 °C for 2 h and 120 °C for 2 h. The films were then pealed off from glass substrate and were subjected to further analysis.

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References

1. H. D. Stenzenberger, *Composites Structures*, **24**, 219 (1993).
2. C. Jiwon, H. Jason, F. Albert, Q-Z. Yee, and M. L. Richard, *Journal of the American Chemical Society*, **123**, 11420 (2001).
3. P. T. McGrail, and A. C. Street, *Makromol Chem Makromol Symp.* **64**, 75 (1992).
4. M. I. Fedtke, and H. R. Kricheldorf, Editor Handbook of Polymer Synthesis (Part B), New York: Marcel Dekker, pp. 1489 (1991).

5. S. J. Shaw, E. B. In, Editor Chemistry and Technology of Epoxy Resins, Glasgow: Blackie, pp.131 (1993).
6. C. B. Bucknall, Toughened Plastics, London: Applied Science Publishers (1977).
7. E. M. Yorkgitis, C. Trau, N. S. Eiss, T. Y. Hut, I. Yilgor, G. L. Wilkes, J. E. McGrath, C. K. In: Riew, and J. K. Gillham, Editors Rubber Modified Thermoset Resins, Washington: American Chemical Society (1984).
8. D. F. Bergstrom, G. T. Burns, G. T. Decker, R. L. Durall, D. Fryear, G. A. Gornowiez, M. Tokunoh, and N. Odagiri, *Matererials Research Society Symposium Proceedings*, **274**, 31 (1992).
9. J. Majovic, E. M. Pearce, C. C. Foun, C. K. In: Riew, and J. K. Gillham, Editors Rubber Modified Thermoset Resins, Washington: American Chemical Society (1984).
10. S. L. Kirschenbaum, S. Gazit, J. P. Bell, C. K. In: Riew, and J. K. Gillham, EditorsRubber Modified Thermoset Resins, Washington: American Chemical Society (1984).
11. R.S. Raghava, 28th National SAMPE Symp. pp. 267 (1983).
12. C. B. Bucknall, and I. K. Partridge, *Polymer*, **24**, 639 (1983).
13. R. S. Bauer, H. D. Stenzenberger, and W. Romer, 35th Int. SAMPE Symp. pp.395 (1990).
14. G. S. Bennet, R. J. Farris, and S. A. Thompson, *Polymer*, **32**, 1633 (1991).
15. G. Di Pasquale, O. Matta, A. Recca, J.T. Carter, P. T. McGrail, and D. Acierno, *Polymer*, **17**, 4345 (1997).
16. T. Iigima, T. Tochimoto, M. Tomoi, and H. Kakiuchi, *Journal of Applied Polymer Science*, **43**, 463 (1991).
17. C. B. Bucknall, A. H. Gilbert, *Polymer*, **30**, 213 (1989).
18. N, Biolly, T. Pascal, and B. Sillion, *Polymer*, **35**, 558 (1994).
19. C-P, Yang, S-H, Sciao, and K-H, Chin, *Polymer*, **43**, 5095 (2002).
20. J. N. Hay, B. Woodfine, M. Davies, *High Performance Polymer*, **8**, 35 (1996).
21. M. S. Butt, Z. Akhter, M. Z. Zaman, A. Munir, *European Polymer Journal*, **41**, 1638 (2005).
22. T. Agag, and T. Takeichi, *Polymer*, **40**, 6557 (1999).
23. T. Takeichi, A. Agag, and T. Koga, *Polymer*, **42**, 3399 (2001).