

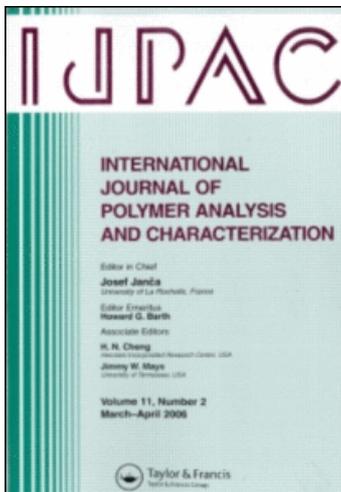
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Thermomechanical and Electrical Studies on Epoxy/Hyperbranched Polyester Blends

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Abstract: Hyperbranched polyesters (HBPE) have been synthesized using 2, 2-bis (hydroxymethyl) propionic acid (bis-MPA) as monomer and triethanol amine as core via condensation reaction. Different polymers like first-generation (G_1), second-generation (G_2), and third-generation (G_3) have been synthesized and characterized. Synthesized G_3 HBPE having weight-average molecular weight of 2828 has been considered for this study. An aliphatic amine (diethylenetriamine) cured epoxy resin has been modified by the addition of 1, 2, and 5 wt.% G_3 HBPE to form epoxy/HBPE blends. Thermal, electrical, and mechanical studies of the epoxy/HBPE blends were carried out and the results were compared with cured epoxy resin. Incorporation of 1, 2, and 5 wt.% G_3 HBPE in epoxy resin has negligible effect on thermal and electrical properties but shows an increase in mechanical properties, i.e., tensile strength, Barcol hardness, and impact strength, indicating the toughening of the epoxy resin.

Keywords: Electrical properties; Epoxy resin; Hyperbranched polyesters; Thermomechanical; Toughness

INTRODUCTION

In the past decade, new classes of branched architectural polymers, such as dendrimers and hyperbranched polymers, have attracted much

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attention because of the expectation that their unique structures might offer unusual properties and lead to novel applications.^[1,2] Dendrimers can be synthesized through convergent or divergent growth in a repetitive multistep synthetic strategy. This makes dendritic polymers expensive and difficult to produce on a large scale. In contrast, hyperbranched polymers are prepared in one step, which results in a mixture of linear and dendritic branched units, and the products exhibit properties similar to those of dendrimers. Due to compact three-dimensional structure and lack of restrictive interchain entanglements, hyperbranched polymers show low melt and solution viscosity even at high molecular weights.^[3,4]

The most important properties of hyperbranched polymers are high solubility, good reactivity, low viscosity in solution and melt, absence of entanglement, and good compatibility with other materials. These polymers have been used in several applications such as additives,^[5] coatings,^[6] blends,^[7] nonlinear optics,^[8] molecular imprinting,^[9] and catalysis.^[10]

Epoxy resins are thermosets having attractive properties such as high strength and stiffness and excellent dimensional, thermal, and environmental stabilities. However, the major drawback that can limit the use of epoxy resins as matrices for composites is their brittleness. Traditionally, carboxyl-terminated butadiene acrylonitrile (CTBN) rubber materials are used as tougheners, but this affects the processability of the resin system. The addition of thermoplastics into the thermoset has widely been recognized as an alternative to rubber toughening in order to improve the brittleness of epoxy networks while maintaining, or in some cases decreasing, the thermal properties of the original resins. Hyperbranched polymers due to their compact structure have a lower melt point and solution viscosity than their linear analogue polymers. Also, due to their high density of tailorable end groups on the shell, they can effectively function as blends with other polymers.

Literature survey indicated epoxy functionalized hyperbranched polyesters (HBPE) have been used as tougheners^[11,12] in epoxy systems. Mezzenga and Manson^[13] studied the thermal and mechanical properties of blends of the hydroxyl functionalized hyperbranched polymer of fifth generation (G_5), supplied by Perstorp, hyperbranched polyols with epoxy resin. Cicala and coworkers^[14] studied third-generation hyperbranched polyesters (Boltorn H30) having 32 primary hydroxyl end groups as tougheners for epoxy resins. Ratna and Simon^[15] studied the catalytic effect of the hydroxyl group of hyperbranched polyester in epoxy-amine curing reaction. Literature survey also indicated that no significant amount of work has been reported on the effect of electrical properties on addition of HBPE in epoxy/HBPE blends.

The present study involves the use of third-generation hydroxyl functionalized hyperbranched polyesters having 24 terminal hydroxyl end groups as tougheners for epoxy resins. These hyperbranched polyesters were synthesized with triethanolamine as core and 2, 2-bis(hydroxymethyl) propionic acid as AB₂ monomer. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the synthesized product were 2381 and 2828 respectively. Mechanical, thermal, and electrical properties of cured epoxy/HBPE blends were studied.

EXPERIMENTAL SECTION

Materials

2, 2-Bis(hydroxymethyl) propionic acid (bis-MPA) of purity > 99% (Aldrich), p-toluene sulphonic acid (p-TSA) (Thomas Baker), and triethanolamine (TEA) (Merck) of purity > 98% were used as received. Analytical grade acetone and hexane obtained from Merck were used without any further purification. The epoxy resin used was liquid diglycidyl ether of bisphenol A (DGEBA) (Araldite GY 257 of Ciba Specialty Chemicals) with the epoxy value 0.520–0.550 eq/100 g. The curing agent, diethylenetriamine, was used as hardener. Figure 1 shows the chemical structures of epoxy resin, hardener, and HBPE.

Synthesis of Generation 3 Hyperbranched Aliphatic Polyester (G₃)

Hyperbranched polyesters with triethanolamine as core were prepared by a procedure described by Viswanath and Guhanathan.^[16] This reaction is an acid-catalyzed polyesterification, performed in bulk at a reaction temperature (140°C) below the melting point of bis-MPA (190°C). The reaction mixture was initially a two-phase system where bis-MPA slowly dissolves in a low-viscosity melt instead of melting by itself. Bis-MPA (132.16 g, 985.3 mmol), TEA (7 g, 46.92 mmol), and p-TSA (0.66 g, 3.48 mmol) were mixed in a three-necked round-bottom flask equipped with argon gas inlet and a drying tube. The three-necked flask was placed in an oil bath, which was preheated and maintained at 140°C. The reaction was continued for 6 h (optimized) with stirring under a stream of argon, which removed water formed during the reaction. Complete consumption of monomer was confirmed through Fourier transform-infrared (FT-IR) spectroscopy (acid carbonyl to ester carbonyl). The product obtained was purified by dissolving in acetone and precipitated

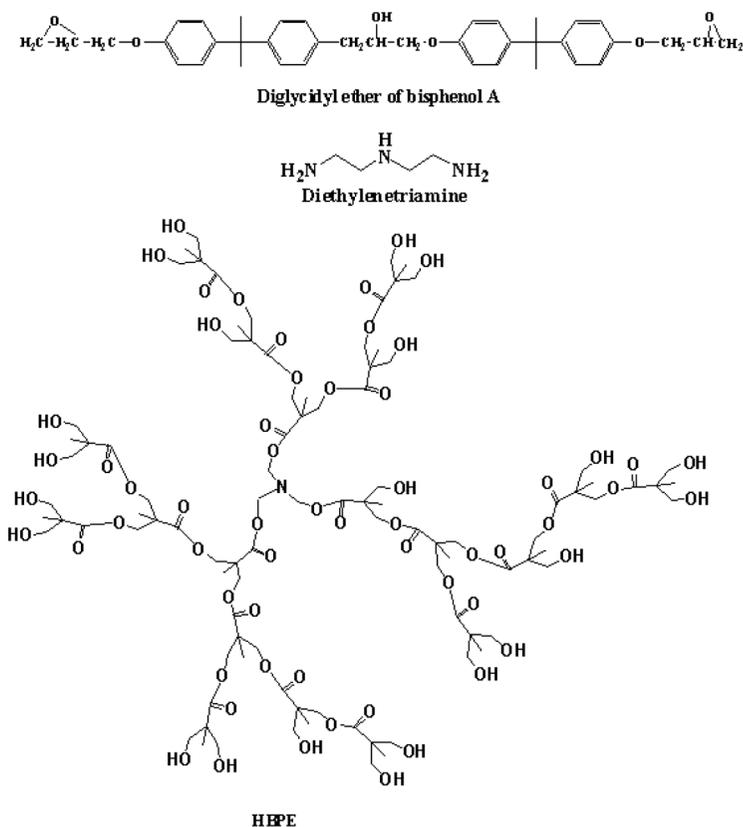


Figure 1. Structures of epoxy resin, hardener, and HBPE.

by hexane. The product was kept at reduced pressure at 50°C for a day to remove the traces of moisture present.

Preparation of Epoxy/HBPE Blends

The solution casting method was adopted to prepare neat epoxy as well as epoxy/HBPE blends. The synthesized hyperbranched aliphatic polyester was dissolved in acetone and the solution was added to epoxy resin. The mixture was stirred until a homogeneous solution was observed. The resultant solution was kept in a vacuum oven to remove the acetone and air bubbles formed during mixing. A stoichiometric amount of curing agent (HY 951) was added with constant stirring for 5 min and immediately poured into a Teflon-coated mold. The curing was done for 24 h at 40°C and post-curing at 80°C for 3 h and 120°C

for 3 h. Synthesized HBPE in the ratio of 1, 2, and 5 wt.% was added to epoxy resin to make the sheet.

Characterization

FT-IR

The samples were mixed with KBr and pelletized. The spectrum from wave number 370 to 4000 cm^{-1} was recorded by a Perkin-Elmer FT-IR spectrophotometer at the Central Power Research Institute (CPRI), Bangalore, India.

^{13}C NMR

An AMX 400 high-resolution multi-nuclear spectrometer at the Indian Institute of Science, Bangalore, India was used to record ^{13}C nuclear magnetic resonance (NMR).

MALDI

Molecular weight of hyperbranched polyesters was determined by matrix-assisted laser desorption/ionization (MALDI) using the instrument Voyager-DE PRO Biospectrometry at IIT Madras, Chennai, using alpha cyano-4-hydroxy cinnamic acid as matrix and accelerating voltage of 20 kV; wavelength of laser beam used was 337 nm.

Thermal Studies

Thermomechanical Analyzer (TMA). A Universal V4.3A model TA instrument at Central Power Research Institute (CPRI), Bangalore, India, was used for this study.

Thermogravimetric Analysis (TGA). A Universal V4.3A model TA instrument was used. About 4 mg of sample was heated to 900°C at a heating rate of 10°C/min under nitrogen atmosphere maintained at a flow rate of 60 mL/min. Measurements were carried out at CPRI, Bangalore, India.

Mechanical Properties

Tensile Strength. Tensile strength is the stress at which a material breaks or permanently deforms. Tensile strength is an intensive property, hence it does not depend on the size of the test specimen. This test was carried

out at Central Institute of Plastics Engineering and Technology (CIPET), Chennai. Tensile strength tests were carried out as per ISO-527-5 standard.

Charpy Impact Strength. Charpy impact strength, also known as the Charpy V-notch test, is a standardized high strain rate test that determines the amount of energy absorbed by a material during fracture. The absorbed energy is a measure of a given material's toughness. This test was carried out at CIPET, Chennai. Charpy impact strength tests were carried out as per ISO-179 standard.

Barcol Hardness. Barcol hardness was determined as per ASTM D-2583 standard. Barcol hardness is used to determine the hardness of both reinforced and nonreinforced rigid plastics. The specimen is placed under the indenter of the Barcol hardness tester and uniform pressure is applied to the specimen until the dial indication reaches a maximum. The depth of the penetration is converted into absolute Barcol numbers. This test was carried out at CIPET, Chennai. The data reported were the average of the five readings.

Electrical Studies

Capacitance, dielectric dissipation factor, and dielectric constant of epoxy/HBPE blends were measured according to ASTM D 150-1998 standard using tan delta and C bridge of Tettex Instruments. Volume resistivity and surface resistivity of epoxy/HBPE blends were measured by DTR-3K model tan delta and resistivity bridge of Eltel Instruments at CPRI, Bangalore, India, according to ASTM D257-1999 standard. The data reported are the average of four readings taken during the measurements.

Morphology Studies

Scanning electron microscopy (SEM) micrographs were obtained using a Hitachi model S-415A model at CPRI, Bangalore. The fractured surface of the epoxy/HBPE blend was cleaned and gold-coated before the SEM analysis.

RESULTS AND DISCUSSION

Generation 3 (G_3) hyperbranched aliphatic polyester was synthesized as per the literature procedure.^[16] It was characterized by FT-IR, ^{13}C NMR, and MALDI techniques. FT-IR spectrum indicated carbonyl group of ester at 1736cm^{-1} . Absence of absorbance of

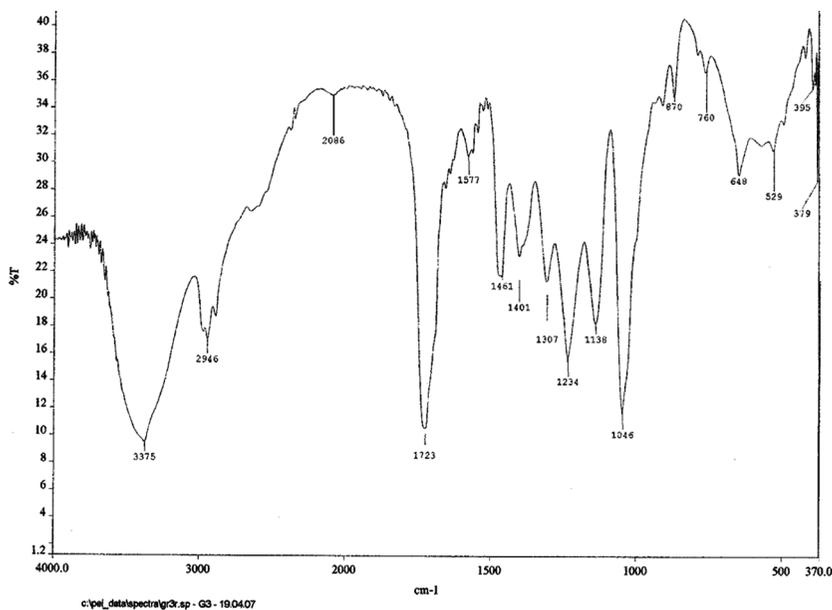


Figure 2. FT-IR spectra of hyperbranched aliphatic polyesters G₃ HBPE.

carbonyl group of carboxylic acid at 1696cm^{-1} confirmed the total consumption of bis-MPA monomer in the reaction. Further, FT-IR spectra presented in Figure 2 indicated broad absorbance at 3400cm^{-1} , confirming the presence of terminal hydroxyl groups. ^{13}C -NMR of hyperbranched polyesters indicated the presence the dendritic, terminal, and linear units of hyperbranched polyesters at 48.6, 49.6, and 50.4 ppm respectively.^[16] The carbonyl peaks observed at 174.39, 175.49, 177.25, and 178.03 ppm confirm the formation of hyperbranching. The number-average molecular weight 2381 and weight-average molecular weight 2828 g/mole were calculated by the MALDI technique. Figure 3 shows the FT-IR spectra of cured epoxy sheets. There was no absorbance at 911cm^{-1} , indicating the absence of an epoxy peak, which confirms the complete curing of epoxy resin.

Thermal Studies

TMA

Differential scanning calorimetry (DSC) is not the best technique to determine the glass transition temperature (T_g) of the complex blends, hence the T_g of cured epoxy/HBPE blends was measured by the TMA

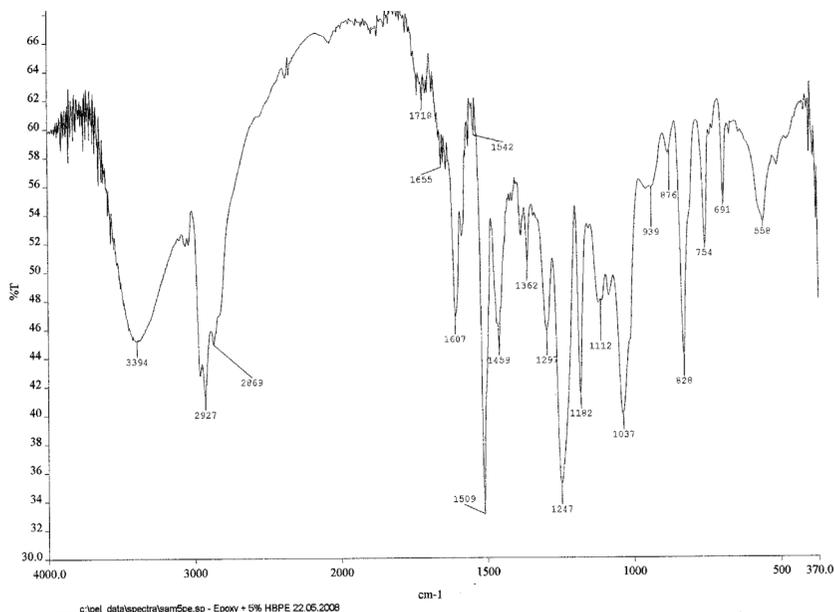


Figure 3. FT-IR spectra of 5 wt.% HBPE in epoxy/HBPE blends.

technique. The results in Table I indicate that for increasing contents of the hyperbranched toughener, the T_g remained constant or decreased marginally. The addition of low molecular weight aliphatic hyperbranched polyesters had negligible effect on the T_g . These results are in agreement with earlier findings.^[17]

TGA

The overlaid TGA thermograms of epoxy and epoxy/HBPE blends are shown in Figure 4. From the results, it can be concluded that epoxy and 1, 2, and 5 wt.% of HBPE with epoxy shows maximum weight loss at around 358°C. There was not much difference in weight loss. Hence, it

Table I. Glass transition temperature obtained from TMA

Sample no.	Identification	T_g (°C)
1	Neat	86.9
2	1 wt.% HBPE	86.9
3	2 wt.% HBPE	86.7
4	5 wt.% HBPE	86.1

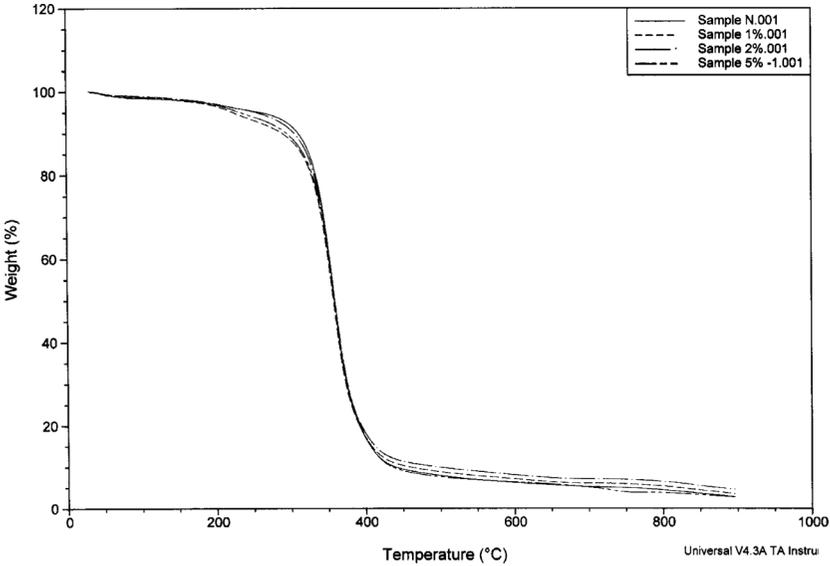


Figure 4. Thermograms of cured epoxy resin and epoxy blends.

may be concluded that the addition of HBPE has negligible effect on thermal stability of epoxy resins.

Mechanical Studies

Results of tensile strength are indicated in Table II. From the results it is observed that tensile strength of epoxy sheets increases with addition of HBPE as toughener from 1, 2, and 5 wt.%. The tensile strength of 5 wt.% HBPE/epoxy blends was 67.3 MPa and 27.7, 38.4, and 44.0 MPa for pure epoxy resin, 1%, and 2% HBPE/epoxy respectively.

Table II. Mechanical properties of epoxy/HBPE blends

Sample no.	Identification	Tensile strength MPa	Charpy impact strength KJ/m ²	Barcol hardness
1	Neat	27.7	6.85	40.9
2	1 wt.% HBPE	38.4	6.39	42.0
3	2 wt.% HBPE	44.0	7.15	48.7
4	5 wt.% HBPE	67.3	22.9	51.0

Results of Charpy impact strength test are shown in Table II. From the results it is clearly seen that Charpy impact strength of epoxy/HBPE blends increases with addition of HBPE. The HBPE addition led to a small improvement in impact strength up to 2 wt.% HBPE (7.15 KJ/m²) and significant improvement in impact strength for 5 wt.% HBPE (22.9 KJ/m²), which is approximately three times more than that of the neat sample, 6.85 KJ/m². This may be due to the perfect interfacial bonding between epoxy and HBPE by the contribution of hydrogen bonding.

Results of Barcol hardness, indicated in Table II, demonstrate that Barcol hardness of epoxy sheets increases gradually with addition of HBPE. The increase in Barcol hardness was 2.69%, 19.07%, and 24.69% on addition of 1 wt.% HBPE, 2 wt.% HBPE, and 5 wt.% HBPE respectively when compared with the baseline of neat resin (40.9). The large number of surface hydroxyl groups of HBPE was expected to form strong hydrogen bond with DGEBA matrix, which was necessary for HBPE to function as an effective toughener. Harani et al. have observed similar phenomena.^[18]

Electrical Studies

Electrical studies were carried out on epoxy/HBPE blends by measurement of dielectric dissipation factor, capacitance, dielectric constant, and volume resistivity at 50°C and surface resistivity at 27°C. Results of volume resistivity and surface resistivity and dielectric dissipation factor, capacitance, and dielectric constant are given in Tables III and IV respectively.

From the results of dielectric dissipation factor (DDF) at 35°C (Table IV), it was observed that an addition of HBPE increases the DDF value. Nakamura and Arima^[19] have concluded that epoxy resins without hydroxyl groups are expected to have high electric resistance,

Table III. Volume resistivity and surface resistivity of epoxy/HBPE blends

Sample no.	Identification	Volume resistivity, Ω-cm, 50°C	Surface resistivity, Ω, 27°C
1	Neat	6.333×10^{14}	2.79
2	1 wt.% HBPE	5.867×10^{14}	2.20
3	2 wt.% HBPE	5.000×10^{14}	2.12
4	5 wt.% HBPE	5.033×10^{14}	1.49

Table IV. Electrical properties of epoxy/HBPE blends

Sample no.	Identification	Dielectric dissipation factor		Capacitance pf		Dielectric constant	
		35°C	50°C	35°C	50°C	35°C	50°C
1	Neat	0.0050	0.0061	21.11	22.14	3.76	3.94
2	1 wt.% HBPE	0.0084	0.0131	18.93	21.08	3.71	4.13
3	2 wt.% HBPE	0.0099	0.0167	20.80	22.28	3.79	4.06
4	5 wt.% HBPE	0.0094	0.0196	18.20	20.13	3.25	3.60

low dielectric constant, and low hygroscopic properties. Hence, the increase in dielectric dissipation factor values of the epoxy/HBPE blends may be attributed to the presence of free hydroxyl groups present in epoxy/HBPE blends. DDF increases with increase in temperature, hence the results taken at 50°C are higher than the results at 35°C. The effect of various concentrations of HBPE in epoxy/HBPE blends was insignificant with respect to dielectric constant values measured at 35°C and 50°C.

An addition of HBPE in epoxy/HBPE blends increases the concentration of the hydroxyl group, which is polar in nature and hence increases conductivity of the samples. From Table III, it is noted that volume resistivity decreases by 20.5% on addition of 5 wt.% HBPE. Similarly, surface resistivity also decreased by 46.6% for 5 wt.% HBPE.

Morphology Studies

The fractured behavior of the cured epoxy resin and epoxy/HBPE blends can be explained in terms of morphology observed by SEM micrographs. The SEM micrographs of epoxy resin and epoxy/HBPE blends are shown in Figures 5–8.

A smooth glass fractured surface with cracks in different planes in the pure epoxy network can be observed in Figure 5. This indicates the brittle fracture of the unmodified epoxy network, which accounts for poor impact strength.

As shown in Figure 8, the SEM micrographs of fracture surfaces of 5% HBPE in epoxy/HBPE blends reveal particulate morphology with spherical domains rich in HBPE dispersed in the continuous epoxy matrix. SEM micrographs of 1% HBPE and 2% HBPE in epoxy/HBPE blends, shown in Figures 6 and 7 respectively, indicate homogeneous morphology. Therefore, it was concluded that HBPE at low concentration (i.e., 1% and 2% HBPE) is fully miscible in the epoxy resins, and at higher concentration (i.e., 5% HBPE) it is dispersed as two phases in

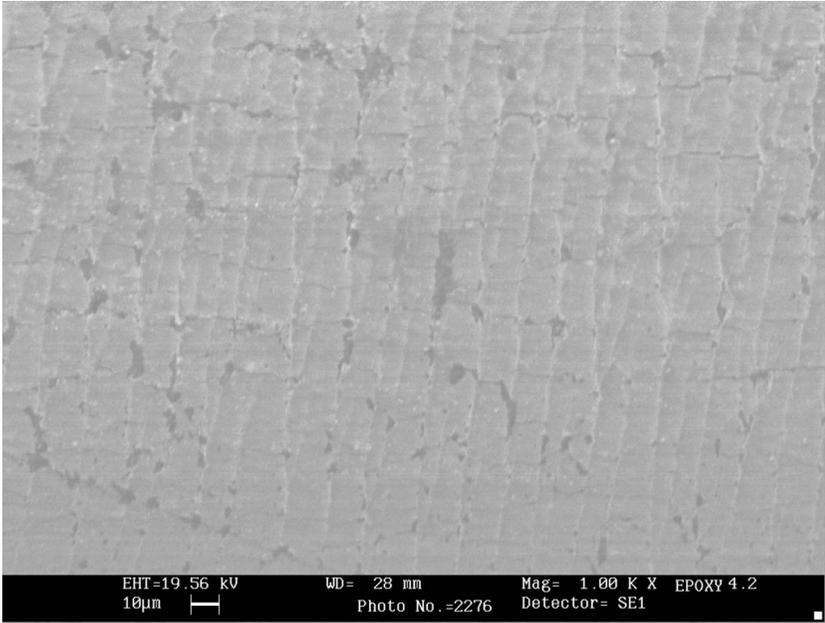


Figure 5. SEM micrographs of epoxy resin.

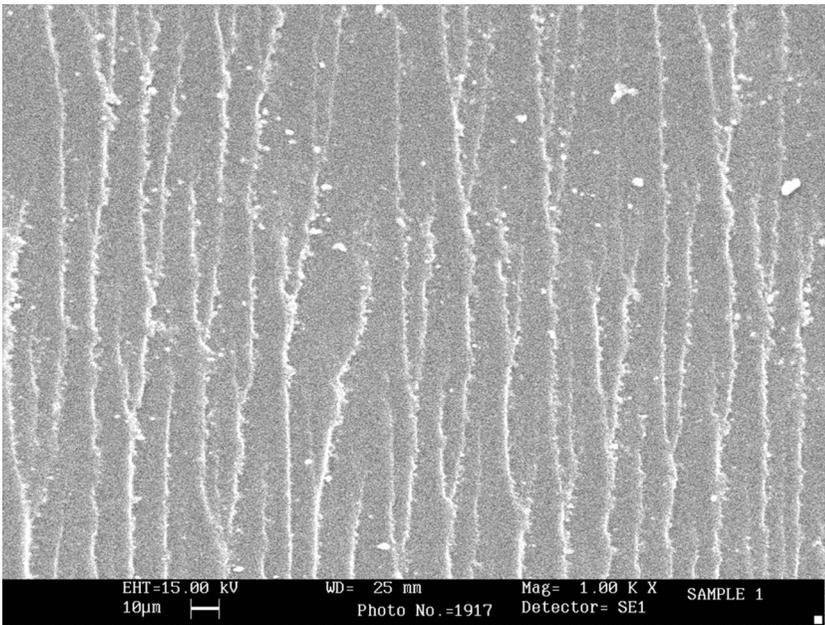


Figure 6. SEM micrographs of 1% HBPE in epoxy/HBPE blends.

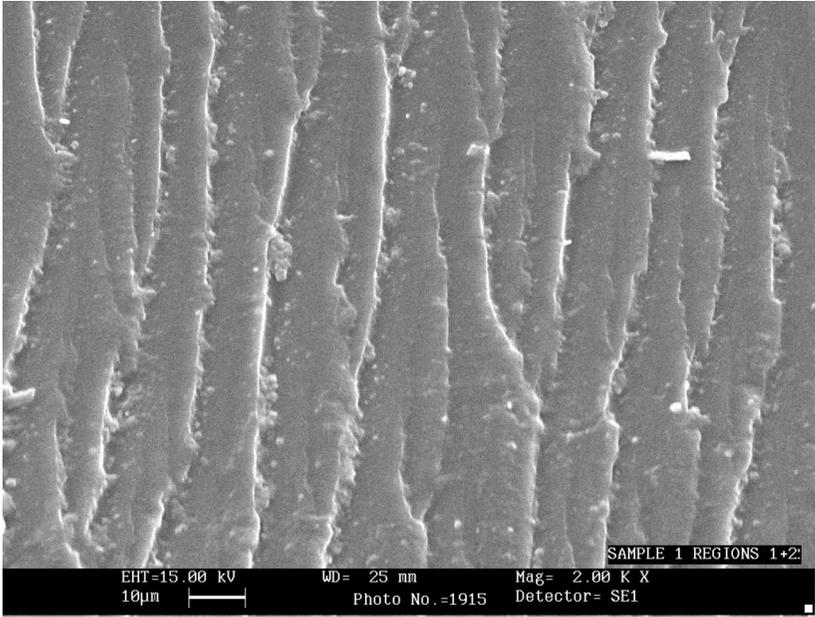


Figure 7. SEM micrographs of 2% HBPE in epoxy/HBPE blends.

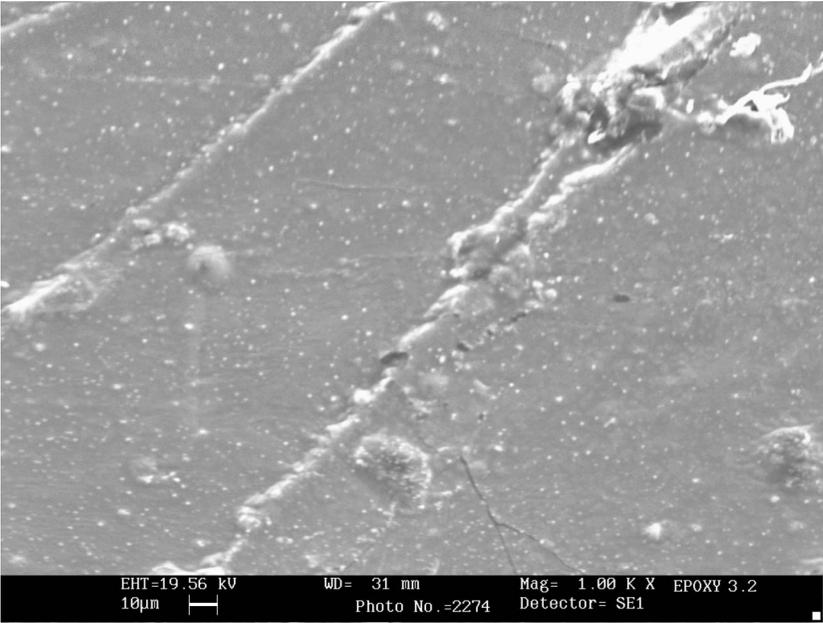


Figure 8. SEM micrographs of 5% HBPE in epoxy/HBPE blends.

the epoxy/HBPE blends. These results are in agreement with the earlier findings of Cicala et al.^[20]

CONCLUSIONS

The presence of a large number of surface hydroxyl groups of hyperbranched polyester forms strong hydrogen bond with DGEBA matrix and hence increases the toughness property. This was confirmed by increase in tensile strength, impact strength, and Barcol hardness properties on addition of 1, 2, and 5 wt.% of hyperbranched polyesters (HBPE). Also, the addition of hyperbranched polyesters as tougheners did not significantly alter the electrical properties like dielectric dissipation factor, dielectric constant, capacitance, volume resistivity, and surface resistivity. Glass transition temperature and thermal stability did not vary significantly on addition of HBPE as tougheners. The effect of increased mechanical properties on addition of low concentration of low molecular weight hyperbranched polyester was significant. SEM micrographs confirmed that HBPE at low concentrations is fully miscible in epoxy resins and shows two-phase separation at higher concentrations.

REFERENCES

- [1] Seiler, M. (2002). *Chem. Eng. Technol.* **25**, 237.
- [2] Jikei, M., and M. Kakimoto. (2001). Hyperbranched polymers: A promising new class of materials. *Prog. Polym. Sci.* **26**, 1233.
- [3] Nunez, C. M., B.-S. Chiou, A. L. Andraday, and S. A. Khan. (2000). Solution rheology of hyperbranched polyesters and linear polymers. *Macromolecules* **33**(5), 1720–1726.
- [4] Magnusson, H., E. Malstrom, A. Hult, and M. Johansson. (2002). The effect of degree of branching on the rheological and thermal properties of hyperbranched aliphatic polyethers. *Polymer* **43**, 301–306.
- [5] Kim, Y. H., and O. W. Webster. (1992). Hyperbranched polyphenylenes. *Macromolecules* **25**, 5561.
- [6] Tomalia, D. A., A. M. Taylor, and W. A. Goddard III. (1990). Starburst dendrimers: Molecular-level control of size, shape, surface chemistry, topology, and flexibility from atoms to macroscopic matter. *Angew. Chem. Int. Ed.* **29**(2), 138–175.
- [7] Pettersson, B., and K. Sörensen. (1994). *Proceedings of the 21st International Waterborne, High-Solids, and Powder Coatings Symposium*. Hattiesburg, Miss.: University of Southern Mississippi, Dept. of Polymer Science. p. 753.
- [8] Massa, D. J., K. A. Shriner, S. R. Turner, and B. I. Voit. (1995). Novel blends of hyperbranched polyesters and linear polymers. *Macromolecules* **28**, 3214–3220.

- [9] Zhang, Y., L. Wang, T. Wada, and H. Sasabe. (1996). One-pot synthesis of a new hyperbranched polyester containing 3,6-di-acceptor-substituted carbazole chromophores for nonlinear optics. *Macromol. Chem. Phys.* **197**, 667–676.
- [10] Griebel, T., and G. Maier. (2000). Core shell hyperbranched polymers for molecular imprinting. *Polym. Preprints* **41**(1), 89–90.
- [11] Persigehl, P., N. West, B. Zimmermann, and O. Nuyken. (2000). Paper presented at the Freiburger Makromolekularem Kolloquium, Freiburg.
- [12] Boogh, L., B. Pettersson, and J.-A. E. Månson. (1999). Dendritic hyperbranched polymers as tougheners for epoxy resins. *Polymer* **40**(9), 2249–2261.
- [13] Mezzenga, R., and J. A. E. Manson. (2000). Thermo-mechanical properties of hyperbranched polymer modified epoxies. *J. Mater. Sci.* **36**, 4883–4891.
- [14] Blanco, I., G. Cicala, C. Lo Faro, O. Motta, and G. Recca. (2006). Thermo-mechanical and morphological properties of epoxy resins modified with functionalized hyperbranched polyester. *Polym. Eng. Sci.* **46**(11), 1502–1511.
- [15] Ratna, D., and G. P. Simon. (2001). Thermomechanical properties and morphology of blends of a hydroxy-functionalized hyperbranched polymer and epoxy resin. *Polymer* **42**(21), 8833–8839.
- [16] Viswanath, G. R., and S. Guhanathan. (2007). Synthesis and characterization of nitrogen containing aliphatic hyperbranched polyesters. *Bull. Pure Appl. Sci.* **26C**, 71–83.
- [17] Cicala, G., and G. Recca. (2008). Studies on epoxy blends modified with a hyperbranched polyester. *Polym. Eng. Sci.* **48**(12), 2382–2388.
- [18] Harani, H., S. Fellahi, and M. Bakar. (1999). Toughening of epoxy resin using hydroxyl-terminated polyesters. *J. Appl. Polym. Sci.* **71**, 29–38.
- [19] Nakamura, S., and M. Arima. (1995). Characterization of the network structure of epoxy resins cured with active esters. *Int. J. Polym. Anal. Charact.* **1**, 75–86.
- [20] Cicala, G., A. Recca, and C. Restuccia. (2005). Influence of hydroxy-functionalized hyperbranched polymers on the thermomechanical and morphological properties of epoxy resins. *Polym. Eng. Sci.* **45**(2), 225–237.