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Modification of Epoxy Resin with Reactive End-Capped Carboxylic Imide Oligomer for Manufacture of Glass-Fiber Reinforced Composite

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Abstract The present work aims at preparing glass-fiber reinforced epoxy resin composite modified with reactive end-capped carboxylic imide oligomer. The carboxylic imide 2,2-bis[4-(4-aminophenoxy)phenyl propane (CIBAPP) oligomer was synthesized via two-step polycondensation of 2,2-bis[4-(4-aminophenoxy)phenyl propane (BAPP) diamine and trimellitic anhydride (TMA), then the oligomer was characterized by FTIR spectrum and solubility test. The oligomer was used as a blending component for the modification of the epoxy resin system for fabricating glass-fiber reinforced laminate. The resultant composite had good properties such as the dielectric strength of 197kV/cm, volume resistance of $2.1\times10^{15}\Omega\bullet$cm, longitudinal and transverse stress of 686MPa and 631MPa, respectively, water absorption rate of 0.18% and surface energy of 43.6mJ/m^2.

Keywords Polyimide oligomer, Epoxy Resin Modification, Composite, Dielectric strength

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1. Introduction

Thermosets have been historically the principal matrix material for fiber reinforced composites for many applications. [1, 2] Among the thermosetting polymers, epoxy resins are the most widely used for high performance applications including matrices for fiber reinforced composites, coatings, structural adhesives and other engineering applications [3]. Epoxy resins, apart from them being used with fibers for advanced composite applications, they can also be used in both laminating and molding techniques to make fiber reinforcement with better mechanical strength, chemical resistance and electrical insulating properties [4]. Epoxy based composites are preferred insulating materials for several electrical applications such as printed circuit boards, bushings, generator ground wall insulation system and cast resin transformers [5].

In terms of structural applications requiring high impact and fracture strengths like the aerospace, epoxy resins have limited application as resin matrices. This is because their three dimensional cross-linked network structure renders them brittle and this makes it difficult for them to absorb and distribute stress. Due to this limitation, research has focused on developing ways to toughen the epoxy resins without sacrificing modulus and glass transition temperature (T_g) while retaining their relative low cost, which will in turn lead to an increase in their application [6, 7]. One method which is widely used at present is the incorporation of thermoplastic toughening agents [8-10]. These toughening agents improve ductility of the resin matrix via deformation and cavitation in an otherwise linear, brittle polymer by forming a separate phase from the epoxy matrix. Several approaches can be used to combine the versatility of epoxy resins with the high-temperature properties of imide groups [11-14]. This research has applied the method of blending epoxy resins with thermoplastic polyimides or with functionalized polyimides. This is because this method has been found to be successful for polymeric materials used for industrial applications.

In the present work, the multifunctional epoxy resin, modified with end-capped carboxylic imide oligomer (CIBAPP), was applied on a woven glass-fiber to prepare high performance epoxy resin laminate composite.

2. Materials and Experiments

2.1. Materials

All the chemicals used were analytically pure and were used as received. Toluene, N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), acetone, n

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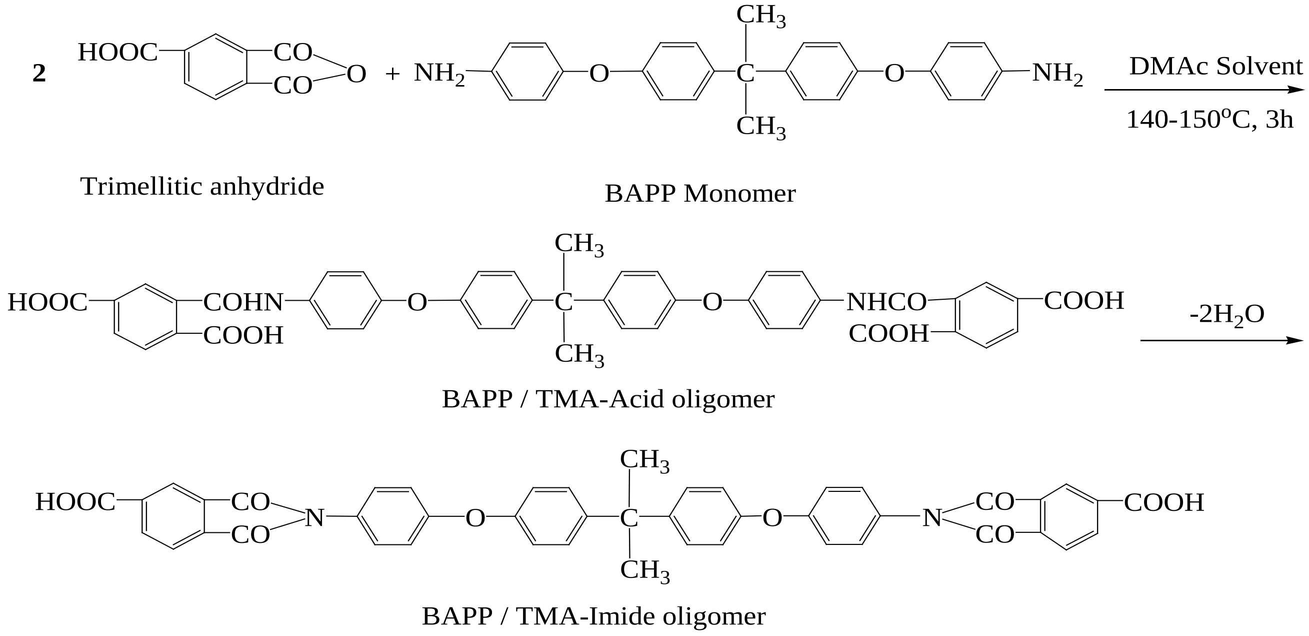
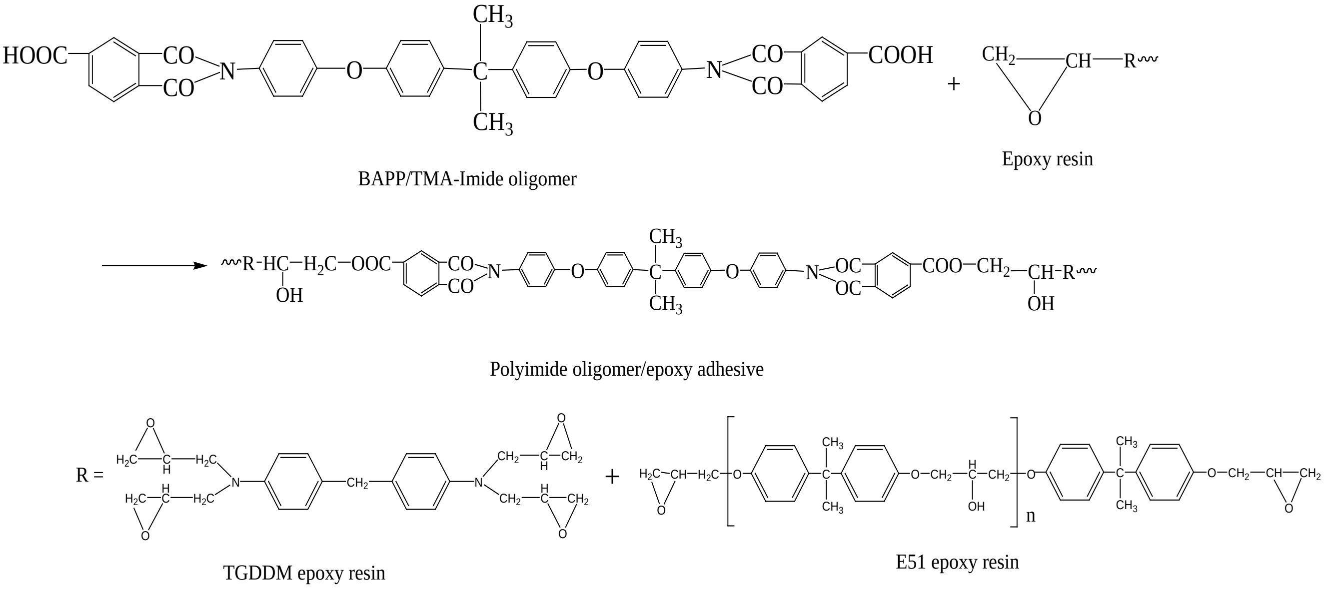
n-Dimethylacetamide (DMAc) and aminopropyltriethoxysilane (KH_{550}) silane coupling agent were obtained from Sinopharm Chemical and Reagents Co., Ltd (China); 2,2-bis[4-(4-aminophenoxy)phenyl propane (BAPP) was obtained from Changzhou Pharmaceutical Co., Ltd (China); trimellitic anhydride (TMA) was supplied by Lancaster Synthesis Inc. (U.S.A.); anhydrous ethyl alcohol (abs.EtOH) was obtained from Shanghai Revitalization Chemical Factory (China); 2-ethyl-4-methylimidazole (2E4MI), DER 331 epoxy resin (E_{51}), N,N,N’,N’-tetraglycidyl-4,4’-diaminophenyl methane (TGDDM) and the plain woven glass-fiber(E grade) were all supplied by Shanghai EMST Electronic Material Co., Ltd (China), Carboxyl-terminated butadieneacrylo nitrile (CTBN) was from Lanzhou Petrochemical Research Center (China).



Scheme 1. Synthetic route of CIBAPP-imide oligomer



Scheme 2. Synthetic route for the modified resin matrix preparation

2.2. Synthesis of the End-Capped Carboxylic Imide Oligomer

In a three-necked round-bottomed flask, 24.63g (0.02mol) of BAPP and 150mL DMAc were added; the mixture was stirred until BAPP was completely dissolved. 23.04g (0.04mol) TMA was then added and stirred until it was completely dissolved. 60mL toluene was then added and the mixture was heated to reflux. The mixture was refluxed at 130-140°C for 3h, and during the reaction time the water was separated. When the reaction was completed, the toluene and 75mL DMAc were removed. The oligomer solution was cooled to room temperature (RT). The synthetic route is shown in Scheme 1. The solid content (ξ) was calculated by use of equation (i):

$$\xi = \frac{W_2 - W}{W_1 - W} \times 100\% \qquad (1)$$

where, W is the weight of the aluminium foil dish; W_1 is the weight of the CIBAPP oligomer and the aluminium foil dish and W_2 is the weight of the aluminum foil dish and the oligomer after heating at 180°C.

2.3. Preparation the Epoxy Resin Matrix

300g epoxy resin (E_{51}: TGDDM=60:40) and 30g CTBN were stirred at 100°C until they were well mixed. The mixture was cooled to below 60°C and 60.1g CIBAPP oligomer solution (20phr) was added, the mixture was stirred at 60°C for 1h, then 4.6g 2E4MI was added while stirring continued at 60°C for 5h to get the epoxy resin matrix. The route is shown in Scheme 2.

2.4. Preparation of the Woven Glass Fabric

The woven glass fabric was cut into 20 equal rectangular shapes with the size of 500 × 300mm and 0.108mm thickness. The total weight of the 20 pieces was 633.12g. Glass fiber has a disadvantage of poor adhesion to polymer matrix resins, therefore to improve their surface adhesion ability; the glass fabric pieces were cleaned by immersing them in a mixture of 3% KH_{550} silane coupling agent (9mL) and 3L cold water for about 4h. They were left in the oven at 80°C until they were well dried.

2.5. Composite Fabrication

The modified epoxy resin matrix was uniformly applied on each side of the woven glass fabric, using a metal blade and hanged vertically for overnight drying at RT so that any excess moisture evaporated. The pre-pregs were pre-cured using the following program: RT→40°C /20min→80°C /20min→ 100°C / 20min→RT. The epoxy composite was prepared at 150°C with the pressure of 5MPa for 5mins, before the pressure was raised to 18-20MPa and the temperature to 170°C. It was kept at this temperature and pressure for 4h and cooled to RT under the same pressure to get the composite.

2.6. Measurements

The FTIR spectrum of the oligomer was scanned on a Varian 640-IR Fourier Transform Infrared spectrometer. The spectral region was 4000~550cm^{-1}. The solubility was done by dissolving the oligomer in various solvents. The gel time test was carried on an ASIDA-NJ11A model gelation times testing instrument manufactured by Zhengye Electronics Company Ltd (China). The viscosity was measured on a CAP2000＋cone and plate viscometer model manufactured by Brookfield Engineering Laboratories (U.S.A). The tensile strength test was carried out on a CZ-8000 tensile strength testing machine manufactured by Zhongzhi Instrumentation Company Ltd (China). The contact angle was determined by using XHKE-CATY type instrument from Chengteh Testing Instruments Co. Ltd (China). The Young-Good-Girifalco-Fowkes (YGGF) formula [15, 16] was used to determine the surface energy (γ). The dielectric properties of the glass-fiber reinforced composite were determined as follows: The Composite material's dielectric breakdown voltage test was done according to GB/T1048.1-2006 standards of China (equivalent to ASTM-D149). The volume resistance test was done according to GB/T 10064-2006 standards of China (equivalent of ASTM-D257). By use of equation (ii), the volume resistance (ohm.cm) was calculated.

$$R = \varphi \frac{L_S}{A_S} \qquad (2)$$

where: φ is the volume resistance (Ω•cm); R is the resistivity (Ω); L_S is the length of the specimen (cm) and A_S is the specimen cross sectional area (cm^2) [17].

The mechanical properties were determined by use of longitudinal (0°) and transverse (90°) three-point bending tests with 15cm length, 1.0cm width and 0.2cm height sample size.

3. Results and Discussions

3.1. CIBAPP Imide Oligomer

The CIBAPP oligomer was synthesized via two-step polycondensation to get the transparent dark red sticky solution which gave a light yellow fine powder in water. From Table 1 the powder was readily soluble in polar solvents such as NMP, DMAc, DMF and DMSO, partially soluble in less polar solvent such as THF and toluene and insoluble in alcohol and acetone. This good solubility in polar solvents could be attributed to the ether linkages in the CIBAPP structure which imparted flexibility.

Table 1. Solubility of the CIBAPP oligomer in different solvents

Solvent	NMP	DMF	DMAC	DMSO	THF	Toluene	Acetone	Alcohol
Solubility	S	S	S	S	PS	PS	IS	IS

S: Soluble; IS: Insoluble; PS: Partially soluble

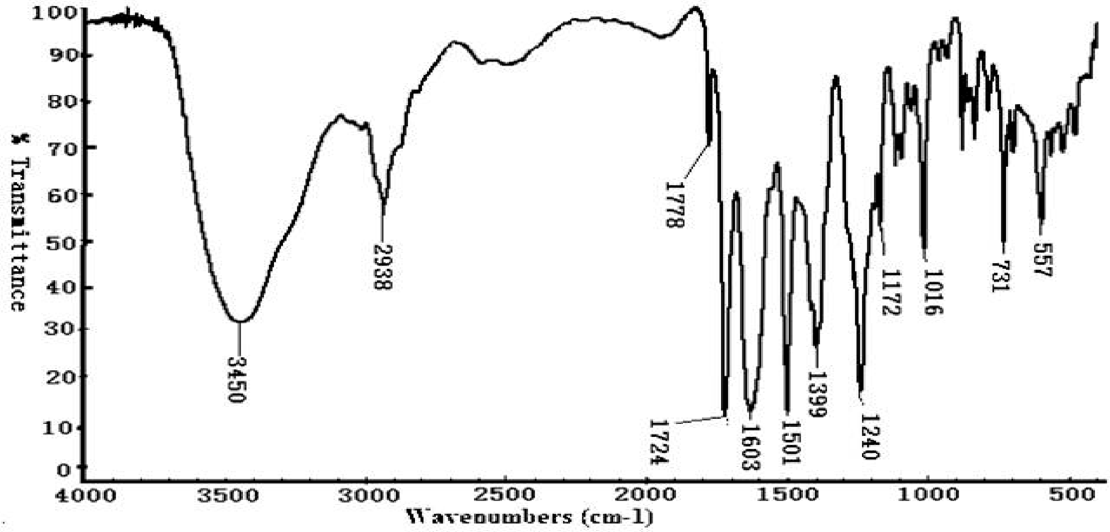


Figure 1. FTIR spectrum for CIBAPP imide oligomer

The FTIR spectrum (Figure 1) had the following characteristic peaks: 1778cm^{-1}, 1724cm^{-1} (C=O asymmetrical and symmetrical stretching); which were the characteristic imide absorption peaks; 1603cm^{-1} and 1501cm^{-1} (aromatic C = C absorption peaks); 1399cm^{-1} (C-N-C stretching of the imide ring) and 2938cm^{-1}, (isopropyl C-H stretching vibration peak). There was also a broad peak at 3450cm^{-1} (O-H stretching) which indicated a carboxylic acid group.

3.2. Characterization of Epoxy Resin Matrix

The viscosity of the epoxy resin matrix

The relationship between viscosity and temperature of the epoxy resin matrix is shown in Table 2. From the table it can be seen that the viscosity decreased with the increase in temperature.

Table 2. The viscosity (η) of the resin matrix at different temperatures (T)

T(°C)	60	65	70	75	80	85	90	95
η (mP•s)	EEE	720	605	441	379	297	259	222

The tensile shear strength of the epoxy resin matrix

The epoxy resin matrix modified with CIBAPP imide oligomer exhibited excellent mechanical properties with tensile shear strength of 42.1MPa as compared to polydimethyl siloxane modified epoxy resin [18] and amine terminated poly(ethylene glycol) benzoate modified epoxy resin [19].

Gel time and the apparent activation energy of the epoxy resin matrix

Table 3 shows the gel time of the resin matrix at different temperatures. From Figure 2 it can be seen that the gel time decreased with the temperature increase. According to the fitting curve equation y = ax + b and in accordance with the Flory gelation theory [20], any resin at gel point must undergo chemical conversion. This chemical conversion has nothing to do with the reaction temperature and the experimental conditions. Therefore, the gelation time can be used to calculate the cure reaction of the apparent activation energy [21, 22]. By use of the K_{slope} gradient of the log t_{gel} verses 1000/T straight line graphs and the equation E_a=2.303RK_{slope}, (where E_a is the activation energy and R is a universal gas constant whose value is 8.314J/mol K), the apparent activation energies of the modified resin matrix was calculated to be 50.6 kJ/mol.

Table 3. Gel time, temperatures (°C and K), log t_{gel}, and 1000/T values of the resin matrix

T(°C)	Gel time (S)	Log t_{gel}	T(K)	1000/T
190	59	1.77	463	2.16
180	70	1.85	453	2.21
170	87	1.94	443	2.26
160	108	2.03	433	2.31
150	153	2.18	423	2.36
140	212	2.33	413	2.42
120	548	2.74	393	2.54
110	825	2.92	383	2.61

3.3. Characterization of Glass-Fiber Reinforced Epoxy Resin Laminate

Contact angle and surface energy

The measured values of the contact angles of the glass-fiber reinforced composite of modified epoxy resin sample were as follows: Water 66.6°; glycerine 70.9°, ethyl glycol 48.2° and 1-bromo naphthalene 17.6°. By use of the YGGF equation, the surface energy was calculated and found to be 43.6mJ/m^2. This value is less than the surface energy of water (72.8mJ/m^2) showing that the composite had good hydrophobicity. Generally epoxy resins are hydrophilic in nature; therefore in this case the modification with the end-capped imide oligomer reduced the hydrophilic nature of the epoxy resin thus increasing its hydrophobicity.

Mechanical property

The data of the bending test are shown in Figure 3 and the results of the bending test were as follows: longitudinal stress that led to breaking was 686MPa, while the transverse stress that led to breaking was 631MPa. The longitudinal stress was higher than the transverse stress. This is because the sample used was of a plain woven structure. During weaving it is the warp yarns at 0° orientation that are under tension, therefore this tension contributes to the higher loading strength in the glass-fiber reinforced composites because during loading both the fibers and matrix carry the load simultaneously. The lower transverse stress could be attributed to the stitch-induced misalignment to the load bearing tows and the fact that weft yarn have crimp therefore before the fibers carry the load, it has to straighten first. The stress values are higher than the values obtained by Reyes and Sharma [23] indicating that the glass-fiber reinforced composite of modified epoxy resin has stronger mechanical properties.

Electrical property

The results of the dielectric strength of the glass-fiber reinforced composite of modified epoxy resin composite are as follows: The average calculated value of dielectric breakdown voltage was 39.4 kV. Dividing this value with the thickness of the sample (0.2cm) gives 197kV/cm. Thus, the dielectric strength of the glass-fiber reinforced composite of epoxy resin was 197kV/cm. This value is higher than the dielectric strength of E-glass fiber itself (104~106kV/cm) [24], and that of the multifunctional glass-fiber reinforced PMMA-BaTiO$_3$ structural/dielectric composite (139kV/cm) [25, 26]. This shows that the glass-fiber reinforced composite of modified epoxy resin had a strong insulating capability because it requires more dielectric breakdown voltage to render failure of its insulating properties. This is of advantage because a breakdown event severely degrades or even destroys the insulating capability of solid materials. Modifying the epoxy resin with CIBAPP imide oligomer solution reduced the volume fraction of polyimide layer within the epoxy resin matrix and this hindered the flow of current between the electrodes resulting in increased dielectric strength of the resulting glass-reinforced composite.

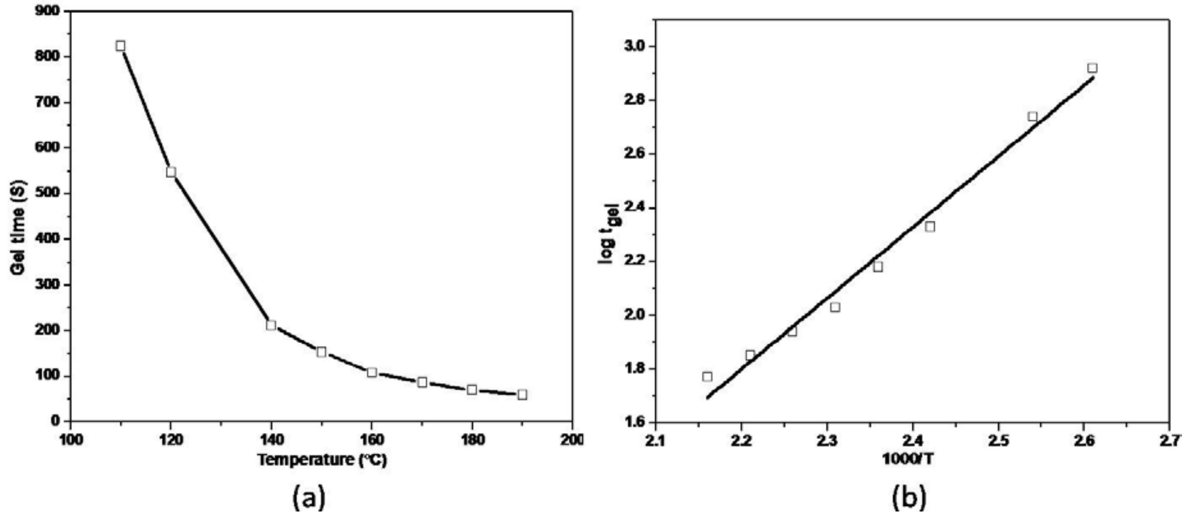


Figure 2. (a) Gel time verses temperature and (b) log t$_{gel}$ verses 1000-T relationship graphs for the modified resin matrix

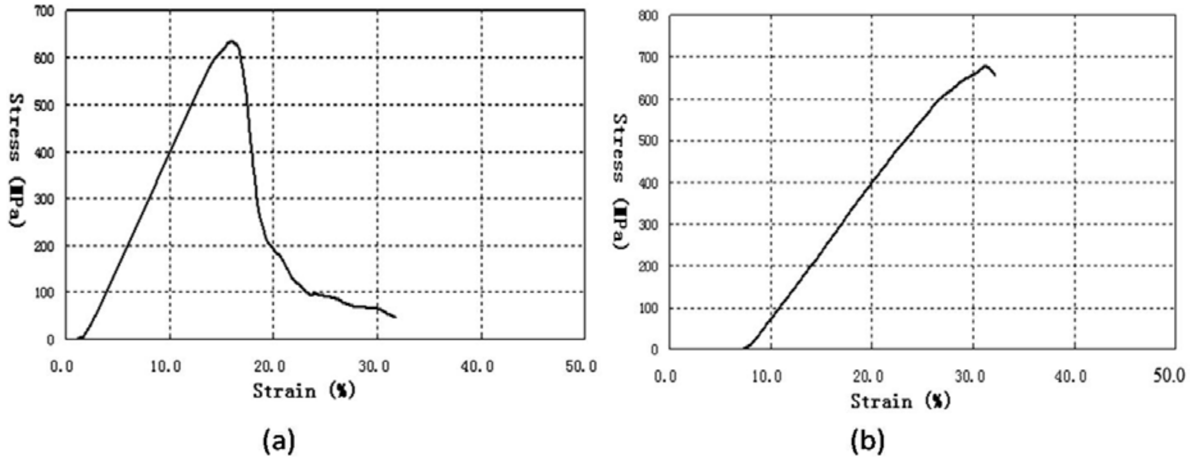


Figure 3. Three-point bending test results; (a) Transverse and (b) Longitudinal directions

Volume resistance is the electrical resistance of a body to current passing through its bodily substance irrespective of any surface leakage. The higher the resistance, in ohms, the harder it is for current to flow through the material. The RT resistivity of the glass-fiber reinforced composite of modified epoxy resin composite, as read from the ohmmeter, was $15.8\times10^{15}\Omega$. From formula (2), the calculated volume resistance was $2.1 \times 10^{15}\Omega$•cm. This value is higher than the volume resistance of E-glass fiber, glass-fiber reinforced composite of nylon and glass-fiber reinforced composite of polystyrene. This shows that the glass-fiber reinforced composite of modified epoxy resin has a high resistance to flow of current within it, because of its better volume resistance ability, than the mentioned composites. The CIBAPP oligomer solution that was used to modify the epoxy resin might have acted as filler and reduced the free charges in the epoxy resin system which in turn affected the conductivity of the resultant fiber reinforced composite leading to higher volume resistivity.

Water absorption

The water absorption of the glass-fiber reinforced epoxy resin composite was 0.18% which showed excellent resistance to moisture absorption. Water, when absorbed into any composite material has a very strong effect, in that, it leads to the degradation of the fiber matrix interface region creating poor stress transfer efficiencies resulting in a reduction of the mechanical and dimensional properties. Thus, it is essential to manufacture composites with very low water absorption rate. The water absorption rate of the glass-fiber reinforced composite of modified epoxy resin (0.18%) showed that the glass-fiber reinforced composite of modified epoxy resin had very good resistance to water absorption, which is an advantage for their use in microelectronic industries.

4. Conclusions

The modification of a two-component epoxy resin system with an end-capped carboxylic imide oligomer resulted in a resin matrix with excellent mechanical properties, good hydrophobicity and excellent resistance to moisture absorption. When this modified resin matrix was used to fabricate the glass-fiber reinforced laminates, the resultant composite had good insulation capability due to its higher dielectric breakdown voltage (197kV/cm); higher volume resistivity (2.1×10^{15} Ω•cm) than glass-fiber reinforced composites of nylon and polystyrene; it was also stronger than other fiber reinforced polymer composites due to its high flexural stress values both in the longitudinal and transverse direction. In addition to the above properties, the composite also had good hydrophobicity (43.6mJ/m^2), very good resistance to water absorption (0.18%). This composite has better application as an insulating material in microelectronic industries.

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