Design and development of sulfonated tetrafunctional epoxy nanocomposites for advanced engineering applications

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ABSTRACT

Attempts were made in the present study to design and develop skeletally modified ether linked tetraglycidyl epoxy resin (TGBAPSB), which is subsequently reinforced with different weight percentages of amine functionalized mullite fiber (F-MF). The F-MF was synthesized by reacting mullite fiber with 3-aminopropyltriethoxysilane (APTES) as coupling agent and the F-MF structure was confirmed by FT-IR. TGBAPSB reinforced with F-MF formulation was cured with 4,4'-diamino diphenyl methane (DDM) to obtain nanocomposite. The surface morphology of TGBAPSB-F-MF epoxy nanocomposites was investigated by XRD, SEM and AFM studies. From the study, it follows that these nanocomposite materials offer enhancement in mechanical, thermal, thermo-mechanical, dielectric properties compared to neat (TGBAPSB) epoxy matrix. Hence we recommend these nanocomposites for a possible use in advanced engineering applications that require both toughness and stiffness.

Keywords: Surface modification; Nanocomposites; Thermo-mechanical properties; Dielectrical properties; Phase separation.

1. Introduction

In modern decades, an increasing research trend in the area of thermosetting polymer like DGEBA epoxy resin widely used as an extensive range of advanced high performance applications such as adhesives, coatings, textiles, civil construction, aircraft, automotive and aerospace components owing to phenomenal performance properties, and low cost. Generally DGEBA epoxy resin is a thermosetting polymer and has been widely used as aerospace, automotive, electronic devices, civil construction, machinery and textiles etc.[1,2] Nevertheless, some drawbacks of DGEBA epoxy resin, namely brittleness and poor impact resistance to crack propagation, restricts its application for high performance materials.[3,4] In order to overcome these problems, modifiers are needed (such as organic fillers, inorganic fillers, metal oxides, carbon nanomaterial, nanofibers and nanorods etc).[5,6] Incorporation of nanofillers into the DGEBA epoxy resin caused significant enhancement of mechanical and thermal properties of DGEBA epoxy nanocomposites.[7,8] Especially silica reinforced epoxy resins have been widely used as an adhesive and encapsulate for electronic industry, for the reason of possessing superior mechanical and electrical properties in addition to the low cost.[9]Additionally, alumina (Al_2O_3) reinforced epoxy nanocomposites demonstrated significant improvement in mechanical properties, even with a low percentage of loading.[10-11]Moreover, the alumina (Al) and silica (Si) combined compounds used as a reinforcement agent into the DGEBA epoxy resin could possess a greater extent mechanical and physical properties. On the other hand, one of the most promising well-known compounds like mullite ($3Al_2O_3$–$2SiO_2$) contains both alumina and silica ceramic material that possesses attractive properties like high chemical, thermal stability, mechanical strength and low thermal expansion coefficient.[12-14] Mullite fibers, which are generally mullite monolithic ceramic materials, exhibit an excellent flexibility at relatively high stress and are commonly used as a reinforcement phase between polymer and oxide ceramic matrix to enhance the composite strength.[15-17] Furthermore, the functional groups introduced into the nanofiller, could either react with polymer molecules and good chemical bonding together between nanofiller and the polymer.[18-19]Therefore, amine functionalized mullite fiber reinforced epoxy matrix system has a great attention to the development of advanced nanocomposites with adequate features of high performance applications. In the present

study amine functionalized mullite fiber (F-MF) was chemically modified by 3-aminopropyltriethoxysilane (APTES) to enhance the properties of the epoxy nanocomposites. In addition, skeletally modified ether linked tetraglycidyl epoxy resin (TGBAPSB) was reinforced with different amounts of F-MF and cured with 4, 4'-diamino diphenyl methane (DDM). The amine functionalized nanocomposite materials possess good chemical bonding with DGEBA epoxy matrix and F-MF leading to simultaneous enhancement of mechanical, thermal, thermo-mechanical, dielectric and water absorption properties for advanced engineering applications.

2. Materials and Methods

2.1 Materials

All chemicals were of reagent grade and were used without further purification except for dimethylformamide (DMF), which was purified by distillation under reduced pressure over calcium hydride. p-Chloronitrobenzene, potassium carbonate (K_2CO_3), 10% palladium on activated carbon (Pd/C), aluminium isopropoxide, aluminium nitrate nonahydrate, o-xylene, absolute ethanol, hydrazine hydrate (80 wt% water solution), epichlorohydrin (EPC), sodium hydroxide, acetone and benzene were obtained from SD fine chemical. The 3-aminopropyltriethoxysilane (APTES), tetraethyl orthosilicate (TEOS) and di-hydroxy diphenylsulphone were purchased from Sigma Aldrich, India. 4,4'-diaminodiphenylmethane (DDM) curing agent, obtained from Huntsman (USA), was used as received.

2.2 Synthesis of TGBAPSB epoxy resin

The synthesis of TGBAPSB epoxy resin was performed in our laboratory as per the literature reported.[20] The TGBAPSB epoxy resin was dissolved in EPC and BAPSB. The solution was stirred and refluxed for 2h. Consequently the addition of 40% NaOH solution was added drop wise into the reaction mixture for 1hr after that the reaction mixture was further reflux period of 5h at 50-55°C. The resultant product a pale brown coloured TGBAPSB epoxy resin obtained (Yield 80%) was percolating and conserved for further use. The reaction sequence is illustrated in **Figure 1.**
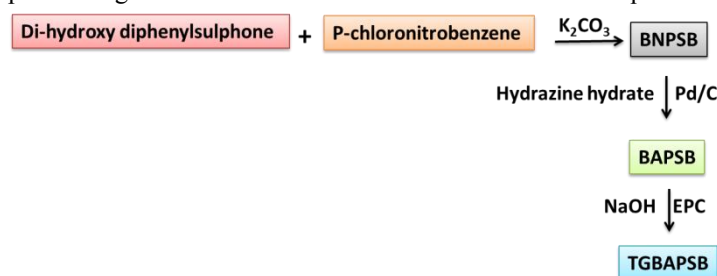

Figure 1; Flow chart representation for the preparation of TGBAPSB epoxy resin

2.3 Synthesis of surface functionalization of mullite

Mullite fiber was synthesized from aluminium isopropoxide, aluminium nitrate nonahydrate and TEOS as per the procedure reported in the literature.[21] 4g of mullite fiber and an appropriate amount of 3-aminopropyltriethoxysilane (4.4g) placed into a 100 ml RB flask equipped with a stirrer and a reflux condenser under nitrogen atmosphere, and 50ml of o-xylene solvent were added into the mixture, the reaction mixture was refluxed for 24 h at 150°C. After the reaction completed, the reaction mixture was filtered and washed several times with acetone to remove the unreacted APTES and dried under vacuum for 24 h. The sequence of reactions involved is illustrated in Scheme 1.
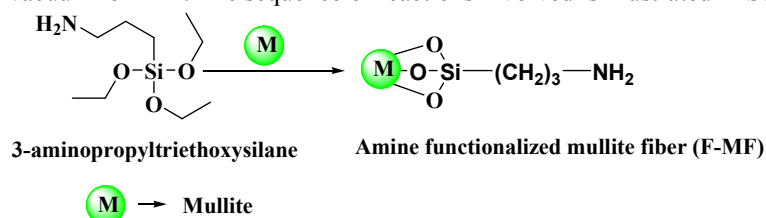
Scheme 1. Surface functionalization of mullite fiber (F-MF)

2.4 Preparation of F-MF reinforced epoxy nanocomposites

In order to prepare the epoxy nanocomposites of TGBAPSB epoxy resins with F-MF (1, 2, and 3 wt%) is placed in mechanically stirred at 70-80°C for 24 h. Subsequently, the stoichiometric amounts of curing agent (DDM) were added

to the mixture and then the reaction mixture was poured into preheated Teflon coated iron mould (Table 1). It was thermally cured firstly at 120 ºC for 2 h and secondly post cured at 180 ºC for 3 h are shown in **Figure 2** and Scheme 2.

System	TGBAPSB	F-MF	Curative
a	100	0	DDM
b	100	1	DDM
c	100	2	DDM
d	100	3	DDM

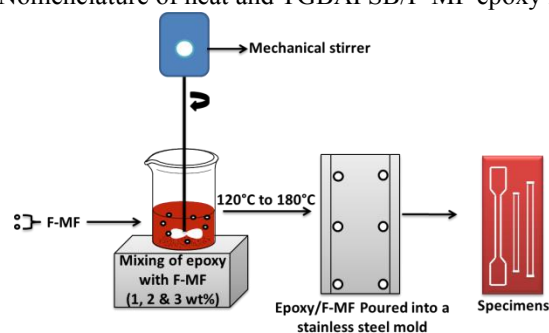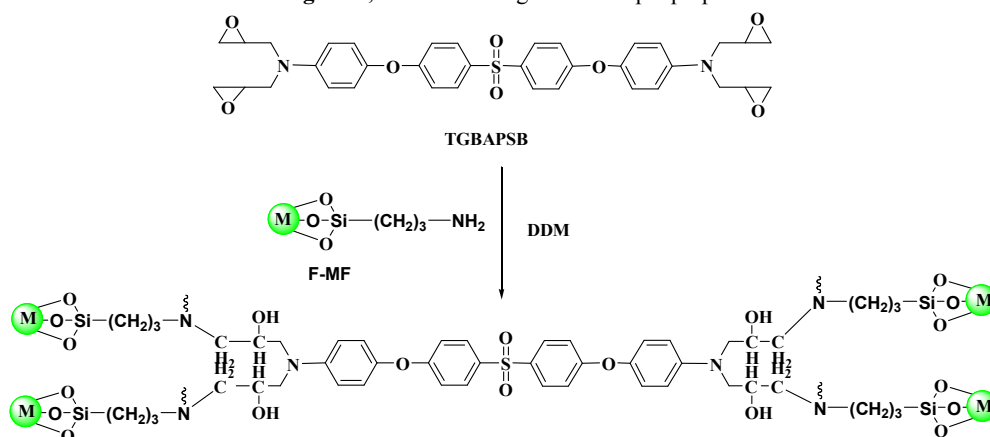**Table 1.** Nomenclature of neat and TGBAPSB/F-MF epoxy nanocomposites

Figure 2; Schematic diagram of sample preparation

Scheme 2. Schematic representation of TGBAPSB epoxy/F-MF nanocomposites

3. Characterization

The FT-IR spectra were recorded on a PerkinElmer 781 FTIR spectrometer to determine the chemical structure of neat TGBAPSB epoxy resin and F-MF/TGBAPSB epoxy nanocomposites cured with DDM. A small portion of the cured epoxy resin and nanocomposites was ground to a fine powder, mixed with KBr powder, and pressed into a pellet which is used to obtain the spectrum. Thermo gravimetric analysis of neat TGBAPSB epoxy matrix and F-MF/TGBAPSB epoxy nanocomposites was carried out using TGA-Thermal Analyst NETZSCH STA 409 PC (TA instruments USA) at a heating rate of 10°C/min from 0°C to 800°C under a continuous flow of N_2 atmosphere to determine thermal degradation temperature, percentage weight loss and char yield formation. About 5mg of samples were taken for each analysis. Dynamic mechanical behavior of the samples was measured using a dynamic mechanical analysis Netzsch 242 at a heating rate of 10°C per minute from 30°C to 300°C. XRD patterns were recorded at room temperature by monitoring the diffraction angle 2θ from 10° to 70° as standard and 0.5° to 10° as low angle on a Rich Seifert (Model 3000) X-ray powder diffractometer. The diffractometer was equipped with a Copper target (λ 1.5405 Å) radiation using Guinier type camera used as focusing geometry and a solid state detector. A curved nickel crystal was used as the monochromator. The step width (scanning speed) was 2θ= 0.04 deg/min. A JEOL JSM-6360 Scanning electron microscope was used for the sample analysis and the fractured samples were prepared by coating, gold on the surface of the samples and analyzed further. The surface topology of the impact fractured surface was investigated using

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AFM Seiko SPI3800N, series SPA-400 (Tokyo, Japan). The dielectric constant measurements were carried out with the help of an impedance analyser (Solartron impedance/gain phase analyzer 1260) at room temperature (RT) using platinum (Pt) electrode at 30°C at a frequency range of 1 MHz. The experiment was repeated for four times at the same conditions. The water absorption measurements of tetraglycidyl epoxy and its nanocomposites were carried out according to ASTM D570-81, The samples were immersed in water for 24 h at 25°C and the percentage of water absorbed by the specimens was calculated using the following equation (1).

% water absorption = (W2-W1) × 100/W1(1)

Where,

W1 is the initial weight of the sample and

W2 is the weight of the sample after immersion in water for 24 h at 25°C.

4. Results and discussion

4.1 FTIR spectra

Figure 3. shows the FT-IR spectra of   amine functionalized mullite fiber (F-MF), TGBAPSB epoxy resin and TGBAPSB epoxy resin cured with DDM. The FT-IR spectrum of F-MF (Figure 3a) shows band at 1565 cm^{-1} corresponding to the N-H bending (scissoring) of the amine functional group of F-MF, this attributed that the chemical bond are formed between mullite fiber with APTES. The appearance of the band at 2929 cm^{-1}, 1418 cm^{-1} due to the symmetric methylene stretch (CH$_2$) and 1014 cm^{-1} to Si-O- stretching vibrations of the mullite fibers respectively. Figure 3(b) shows the band at 912 cm^{-1} assigned to the presence of oxirane ring. The bands appearing at 2984 cm^{-1} and 1630 cm^{-1} correspond to the aromatic rings. The broad peaks at 1499 cm^{-1} (C–O–C) 820 cm^{-1} (C–N) and 750 cm^{-1} (C–S) result of the stretching and bending vibrations of the TGBAPSB epoxy matrix. FT-IR spectra of TGBAPSB epoxy resin cured with DDM showed the absence of oxirane ring peak at 912 cm^{-1}. The appearance of secondary OH group at 3340 cm^{-1} confirming the covalent bonding between TGBAPSB epoxy resin and DDM curing reaction which is depicted in Figure 3(c).
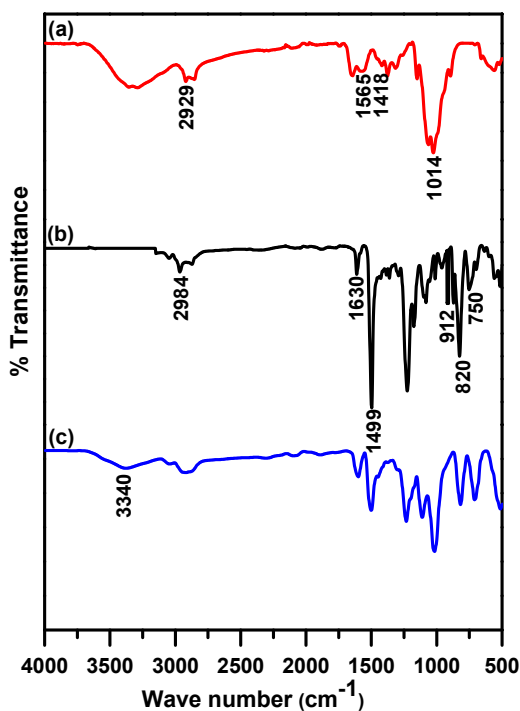

Figure 3. FT-IR spectra of (a) Amine functionalized mullite fiber (F-MF)

(b) TGBAPSB epoxy resin (c) TGBAPSB epoxy resin cured with DDM

4.2 Mechanical properties

The investigations on the mechanical properties were done with tensile strength, flexural strength and impact strength of the neat TGBAPSB epoxy matrix and TGBAPSB epoxy nanocomposites are reported in Table 2. It was found from the data that the incorporation of 1 wt% (system 'b') and 2wt% (system 'c') of F-MF reinforced nanocomposites leads to the increase of tensile strength, flexural strength and impact strength (**Figure 4**). For instance, the values of tensile strength, flexural strength and impact strength of 2wt% (system 'c') are 147.3 MPa, 225.4 MPa and 256.5 J/m^2 respectively, when compared to the neat TGBAPSB epoxy matrix system 'a'. This phenomenon could be attributed to the homogeneous deposition of F-MF, having stronger interfacial interaction between amine functionalized mullite fiber nanocomposites, thereby imparted a covalent bonding F-MF with the TGBAPSB epoxy matrix as reported by Qiang *et al.*[22] However, the mechanical property values decreased in the case of the high percentage loading F-MF (3wt%) reinforced nanocomposites (system 'd') due to filler non-homogeneous in the polymer matrix, which leads to release the stress from the crack tips, thus, enhances the growth of micro voids into the TGBAPSB epoxy nanocomposites was found to be decreasing the values of mechanical performance.[23] Matrix

System	TGBAPSB/%F-MF	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (J/m)
a	100/0	83.5±5	171.1±1	195.8±3
b	100/1	112.4±3	199.5±2	229.5±3
c	100/2	147.3±3	225.4±2	256.5±1
d	100/3	122.5±1	203.5±3	234.3±1

Table 2. Data on mechanical properties of neat and TGBAPSB/F-MF epoxy nanocomposites
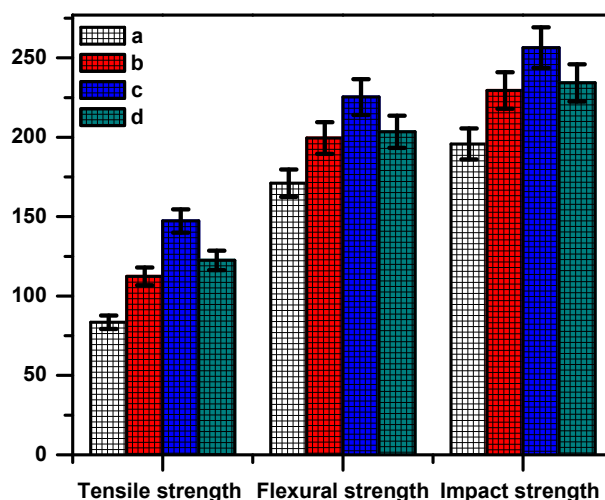

Figure 4; Mechanical properties of (a) neat TGBAPSB epoxy matrix (b) 1 wt% F-MF/TGBAPSB
(c) 2 wt% F-MF/TGBAPSB and (d) 3 wt% F-MF/TGBAPSB epoxy nanocomposites

4.3 Thermogravimetric analysis

The TGA thermograms of the neat TGBAPSB epoxy matrix and F-MF nanocomposites are presented in Table 3 and **Figure 5.** The incorporation of F-MF reinforcement into TGBAPSB epoxy resin improvement the thermal stability and char yield increases up to 2wt% when compared to neat TGBAPSB epoxy matrix system 'a'. For example the initial degradation temperature (IDT) and char yield of a system 'a' was found to be 329°C and 15%, whereas the IDT and char yield of the systems 'b' and 'c' drastically enhanced to 341°C and 347°C, 26% and 33% respectively. This could be attributed to the presence of inorganic moieties like alumina (Al) and silica (Si) in the systems. The

improvement of thermal properties of the TGBAPSB epoxy nanocomposites is owing to its strongly bonded to the -Si-O- groups and better compatibility between F-MF and TGBAPSB epoxy.[24] Nonetheless, the high percentage loading system 'd' (3 wt%) F-MF led to the aggregation of the F-MF in the TGBAPSB epoxy, which results were found to be degradation of the thermal properties. A similar observation was made by Kumar *et al* (2017).[25]

Matrix System	TGBAPSB/%F-MF	Initial Decomposition Temperature (℃)	Char yield (%)
a	100/0	329	15
b	100/1	341	26
c	100/2	347	33
d	100/3	343	31

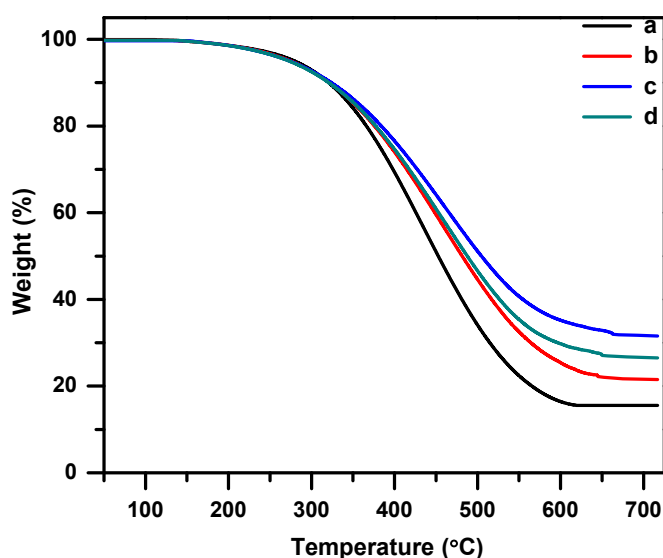**Table 3.** Data on thermal properties of neat and TGBAPSB/F-MF epoxy nanocomposites

Figure 5; TGA of (a) neat TGBAPSB epoxy matrix (b) 1 wt% F-MF/TGBAPSB
(c) 2 wt% F-MF/TGBAPSB and (d) 3 wt% F-MF/TGBAPSB epoxy nanocomposites

4.4 Dynamic mechanical analysis

The values of storage modulus increased as the percentage content of F-MF nanoreinforcement is increased up to 2 wt%. Despite, the values decreased beyond 3 wt% are shown in Table 4. After the incorporation of 1 and 2wt% of F-MF into the TGBAPSB epoxy system 'b' and 'c', the storage modulus value of system 'c' significantly increased, when compared to that of other systems namely 'a ' and 'b ' (Table 4, Figure. 6). The enhancement of the value of storage modulus exhibited by system 'c ' may be due to the presence of crosslinked network between TGBAPSB epoxy and F-MF. Nevertheless,the raise of storage modulus is probably homogenous distribution within the TGBAPSB epoxy which offers the chemical interaction between the inorganic and organic material of F-MF of the resultant TGBAPSB epoxy nanocomposites respectively.[26] However, at higher concentration of F-MF 3wt% (system 'd'), the storage modulus value decreased. This may be due to non-uniformity in the dispersion of the higher loading of F-MF nanoparticles, it was found that the higher loading of 3wt% of F-MF, reduced the storage modulus value (system 'd') and this was complimented by SEM observation and AFM studies (**Figure 9**) As a result of which, there exists a stress concentration regions, which increases the segmental mobility and concomitantly decreased the mechanical properties.[27]

Matrix System	TGBAPSB/%F-MF	Storage modulus (GPa)	Glass transition temperature, T_g (℃)
a	100/0	3.1	146
b	100/1	3.3	178
c	100/2	5.4	188
d	100/3	2.4	173

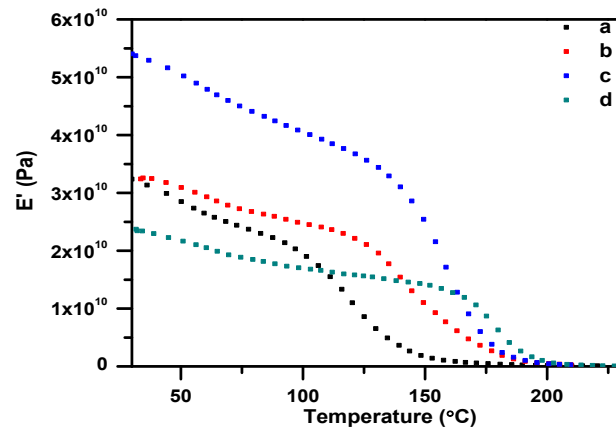**Table 4.** DMA analysis of neat and TGBAPSB/F-MF epoxy nanocomposites

Figure 6; Storage modulus of (a) neat TGBAPSB epoxy matrix (b) 1 wt% F-MF/TGBAPSB
(c) 2 wt% F-MF/TGBAPSB and (d) 3 wt% F-MF/TGBAPSB epoxy nanocomposites

4.5 Damping parameter (tanδ)

The values of glass transition temperature (T_g) of neat TGBAPSB epoxy matrix, F-MF reinforced TGBAPSB epoxy nanocomposites obtained from the damping parameter (tan δ) are presented in Table 4 and **Figure 7.** The T_g values of the neat TGBAPSB epoxy matrix were found at 146°C where as the incorporation of F-MF into the TGBAPSB epoxy systems 'b', 'c' and 'd' slight increase in the T_g values up to 188°C. For example, the systems 'a' and 'b' show the T_g values 146°C and 178°C than that of a system 'a' this should be attributed that the covalent linkage between TGBAPSB epoxy and F-MF that means of uniformly dispersed across the entire surface of the TGBAPSB epoxy matrix, as a result are restricting the segmental mobility of the chain segment.[28] The substantially decreased T_g value of the system 'd' (3 wt%) of F-MF this could be attributed that the aggregation of F-MF in the TGBAPSB epoxy, which was indicated by the deteriorated crosslink of TGBAPSB epoxy, leading to reduced cross-linking density and decreased T_g. A similar observation was made by Colorado *et al* (2013).[29]
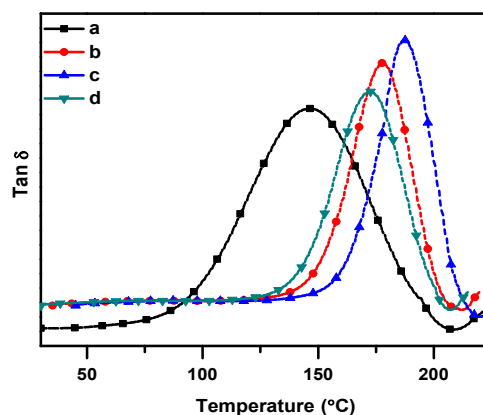

Figure 7; Tan δ of (a) neat TGBAPSB epoxy matrix (b) 1 wt% F-MF/TGBAPSB

(c) 2 wt% F-MF/TGBAPSB and (d) 3 wt% F-MF/TGBAPSB epoxy nanocomposites

4.6 XRD studies

X-ray diffraction spectra were used to analyze the morphology of the neat TGBAPSB epoxy matrix and different weight percentage of F-MF reinforced TGBAPSB epoxy nanocomposites. The results are shown in **Figure 8.** The XRD pattern of TGBAPSB epoxy nanocomposites was found to be exhibiting a peak corresponding to mixed intercalated and exfoliated morphology. However, varying weight percentage of loading F-MF in to the TGBASPB epoxy, the 2θ value shifts towards the lower angle this can be attributed that the mixed intercalated and exfoliated of polymer chain linkages, hence a decrease in the peak intensity from 18.6° to 13.5° was observed (Figure8).[30]
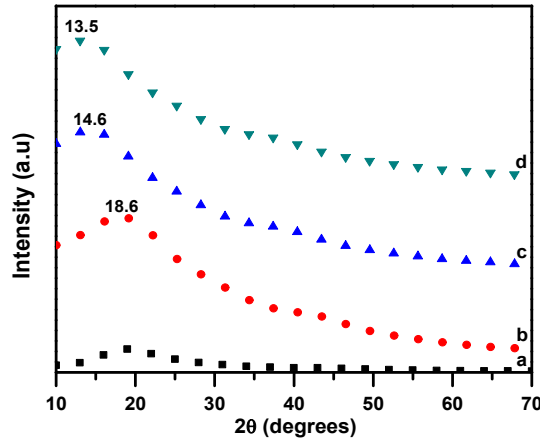

Figure 8; XRD spectra of (a) neat TGBAPSB epoxy matrix (b) 1 wt% F-MF/TGBAPSB

(c) 2 wt% F-MF/TGBAPSB and (d) 3 wt% F-MF/TGBAPSB epoxy nanocomposites

4.7 SEM and AFM analysis

In order to analyze the morphology of the F-MF/TGBAPSB epoxy nanocomposites and neat TGBAPSB epoxy matrix, the SEM and AFM images are represented in Figure 9.Figure 9 (a) shows the smoothsurface of a neat TGBAPSB epoxy matrix when compared than that of F-MF/TGBAPSB epoxy nanocomposites. However, upon loading of varying weight percentage of F-MF, the surface morphology changes for the systems 'b', 'c' and 'd'. It can be assumed that the surface roughness increases with increasing F-MF content. For illustration, the surface roughness of 2 wt% of the system 'c' (Figure 9b) shows good interfacial adhesion between F-MF and TGBAPSB epoxy. This result correlates with the improvement of storage modulus, mechanical properties and thermal properties owing to bonding together between the polymer matrix and organic and inorganic (F-MF) reinforcement respectively.[26, 31] Furthermore, the better dispersion may be due to strong interactions between the F-MF and TGBAPSB epoxy matrix. It was found that highly intercalated and partially exfoliated structure was assumed in XRD studies (Figure 8). On the other hand, the higher content of 3 wt% (system 'd') F-MF TGBAPSB epoxy nanocomposites were found to be heterogeneous morphology along with F-MF and TGBAPSB epoxy (Figure 9c). This indicated that the poor bonding between F-MF and TGBAPSB epoxy, leads to worse mechanical, thermal properties and storage modulus.[32-33]
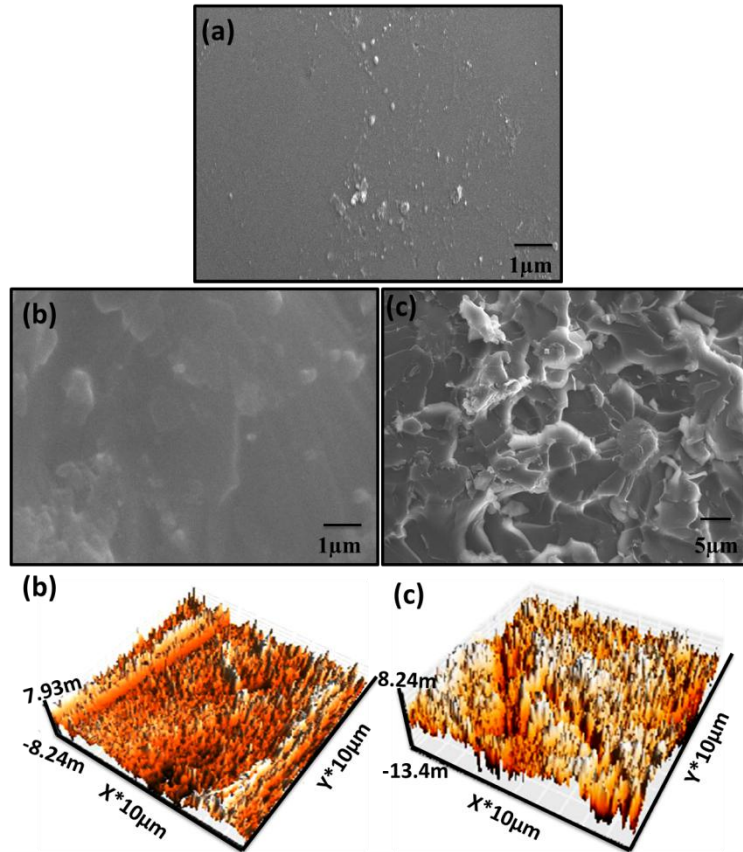
Figure 9; SEM and AFM photographs of systems (a) neat TGBAPSB epoxy matrix
(b) 2 wt% F-MF/TGBAPSB and (c) 3 wt% F-MF/TGBAPSB epoxy nanocomposites

4.8 Dielectric behavior and water absorption properties

The values of dielectric constant of the neat TGBAPSB epoxy matrix and F-MF/TGBAPSB epoxy nanocomposites are represented in Table 5 and **Figure 10.** It was noticed that the loading of F-MF into the TGBAPSB epoxy systems 'b ' (3.55) 'c ' (3.50) and 'd ' (3.45) displays the low dielectric constant values, when compared to neat TGBAPSB epoxy matrix system 'a' (4.10). This could be attributed to the increase in free volume and reducing dipole - dipole interaction between mullite fiber and TGBAPSB epoxy respectively.[34]Figure 11. shows the graphical representation of water absorption of neat TGBAPSB epoxy matrix and F-MF loading in TGBAPSB epoxy nanocomposites. It's indicated that upon the increasing in F-MF content, the water absorption values decrease. This may be due to the low polar content and absorbed less water uptake than that of neat TGBAPSB epoxy matrix.[35] the data is presented in Table 5.

Matrix System	TGBAPSB/%F-MF	Dielectric constants (MHz)	Water absorption
a	100/0	4.10	0.065
b	100/1	3.55	0.060
c	100/2	3.50	0.058
d	100/3	3.45	0.055

Table 5. Dielectric and water absorption properties of neat and TGBAPSB/F-MF epoxy
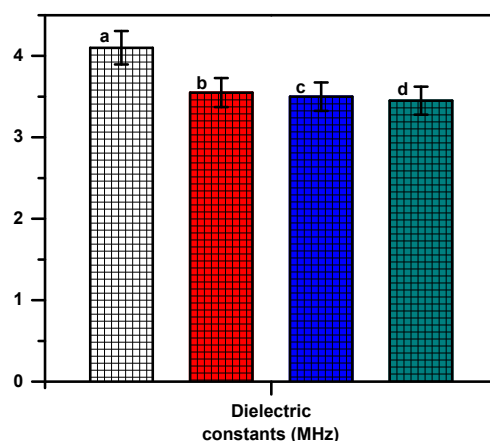
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Figure 10; Dielectric constants of (a) neat TGBAPSB epoxy matrix (b) 1 wt% F-MF/TGBAPSB
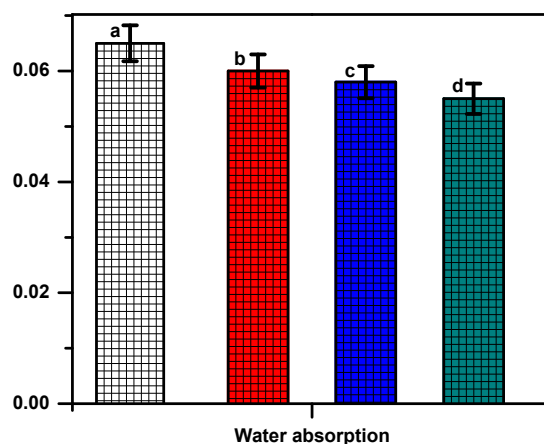(c) 2 wt% F-MF/TGBAPSB and (d) 3 wt% F-MF/TGBAPSB epoxy nanocomposites

Figure 11; Water absorption of (a) neat TGBAPSB epoxy matrix (b) 1 wt% F-MF/TGBAPSB
(c) 2 wt% F-MF/TGBAPSB and (d) 3 wt% F-MF/TGBAPSB epoxy nanocomposites

5. Conclusion

In the present study, the surface modified amine functional groups introduced into mullite fibers (F-MF) prepared by using APTES as a coupling agent. F-MF reinforced with varying weight percentage (1 wt%, 2 wt% and 3 wt%) of the TGBAPSB epoxy nanocomposites were developed and characterized. The incorporation of F-MF leads to the enhancement of mechanical, thermal, thermo-mechanical, dielectric and water absorption properties of the resulting TGBAPSB epoxy nanocomposites. The molecular level dispersion of F-MF in the TGBAPSB epoxy was further confirmed by XRD, SEM and AFM, results which revealed uniform dispersion of F-MF in the TGBAPSB epoxy up to 2wt% nanofiller content. The optimum concentration produced significant improvements in mechanical, thermal, thermo-mechanical of the TGBAPSB epoxy nanocomposites, these materials can be used as advanced nanocomposites in the field of application engineering divisions.

Acknowledgements

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