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Glass fiber reinforced bismaleimide/epoxy BaTiO₃ nano composites for high voltage applications

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ABSTRACT

BaTiO₃/bismaleimide/epoxy/glass fiber reinforced composites were prepared using E-glass fiber (E-GF) and silane coated E-glass fiber (SC-EGF) separately as reinforcement. BaTiO₃ nanoparticles were prepared by hydrothermal method. Results show that the addition of BaTiO₃ nanoparticles has significant effects on the mechanical and dielectric properties of the composite. Both E-GF and SC-EGF reinforced BaTiO₃/bismaleimide/epoxy composites with 2 wt percentages of BaTiO₃ nanoparticles showed improved tensile strength, flexural strength and dielectric constant and those with 3% showed high dielectric strength indicating this composition is more adaptable for high voltage insulating applications. Dielectric constants and dielectric loss of the fabricated nanocomposites have been obtained at higher frequencies (in GHz) by using Vector Network Analyser at room temperature and was found to be highest for the BMI-Epoxy nanocomposite with 1% weight nanofiller.

1. Introduction

Bismaleimide(BMI) is a high performance thermosetting polyimide and find applications in radar, spacewarecomposites, stealth areas, super capacitors, PCB etc. [1,2]. Unmodified BMI composites owing to high crosslinking density during curing are brittle in nature [3,4]. In order to overcome its brittleness, structural modifications, co-reactions, blending with suitable compounds, glass fiber or carbon fiber reinforcement are adopted. Epoxy resins are widely used as matrix materials for high performance composites. In order to enhance both the temperature performance and the processing ease, BMI is blended with epoxy resins [3,5–10]. High dielectric permittivity is highly desired for the dielectric materials used in the embedded capacitors and energy storage device [11–13]. In order to enhance the dielectric properties of BMI composites suitable nanofillers with high dielectric constants are added.

Dielectric properties of BaTiO₃ ceramics depend on the grain size. The BaTiO₃ with grain size 10 μ m exhibits dielectric constant in the range of 1500–2000 at room temperature and those with grain size approximately 1 μ m are capable of exhibiting dielectric constant in the range of 3500–6000 at room temperature, values as high as 15000 are possible for BaTiO₃ with nanosize [14]. To improve the mechanical properties of nanocomposite, glass fibers are reinforced into

bismaleimide resin matrix via hand layup method and tested for dielectric properties and mechanical properties like tensile strength and flexular strength [15].

Morphological studies of the synthesized composite have been performed using SEM and structural studies using XRD-EDX, FT-IR. Dielectric constant, dielectric strength, dielectric loss factor and tan δ using LCR Meter, dielectric breakdown voltage (BDV) through I-V characteristics using Keithley high resistance meter, thermal stability using TGA and DSC [16,17].

This article focused on the effect of the influence of BaTiO₃ nanoparticles on the dielectric, mechanical and thermal properties of Bismaleimide – epoxy composites reinforced with glass fiber. BaTiO₃ nanoparticles were synthesized by hydrothermal method and characterized using Scanning Electron Microscopy (SEM) and Powder X-ray Diffraction (XRD). The synthesized BaTiO₃ nanoparticles were incorporated to Bismaleimide – epoxy matrix in varying percentages and the parameters were investigated.

2. Experimental

2.1. Materials

Bismaleimide powder resin was obtained from ABR Organics Ltd.,

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Table 1

Weight percentages of Bismaleimide-Epoxy- BaTiO₃ nanoparticles for composite preparation.

Code	Weight Ratio
BMI -Epoxy	15:1.5
BMI –Epoxy-BT-1	15:1.5: 0.165
BMI –Epoxy- BT-2	15:1.5: 0.33
BMI –Epoxy- BT-3	15:1.5: 0.66
BMI –Epoxy- BT-4	15:1.5: 1.32
BMI –Epoxy- BT-5	15:1.5:2.64



Fig. 1. TGA curves of (a) BMI resin (b) BMI Epoxy nanocomposite with 2% BT nanofiller(c) BMI Epoxy composite.

Table 2						
Weight loss	percentages	of sampl	es obtained	from T	GA (curve

Sample	Stage	Temperature in ⁰ C	Weight loss %	Total weight loss in %
BMI Resin	I	Up to 302	3	68
	11	3/5-46/	23	
	III	470–575	20	
	IV	588–725	22	
BMI Epoxy Composite	I	Up to 301	No considerable weight loss	44
Without BT filler	II	302-398	5	
	III	400–563	17	
	IV	564–711	22	
BMI Epoxy Composite with	Ι	Up to 320	No considerable weight loss	20
(2%) BT nanofiller	II	332-423	5	
	III	424-570	10	
	IV	571-725	5	

Hyderabad. Epofine-1564 was purchased from Fine Finish Organics Pvt. Ltd., Taloja. E Glass fibres (E-GF) and Silane coated E Glass fibres (SC-EGF) from Urja Products Pvt. Ltd. India. Tetrabutyltitanate Ti (C_4H_9O)₄, Barium hydroxide octahydrate Ba(OH)₂.8H₂O, Nitric acid were purchased from Sigma Aldrich, India and were used as such without any further purification.

2.2. Preparation of BaTiO₃ (BT) nanoparticles

 $BaTiO_3$ nanoparticles was synthesized by hydrothermal method from $Ti(C_4H_9O)_4$ and $Ba(OH)_2.8H_2O$ precursors [18–24]. Typically 1 ml of Ti

(b) 0 (c) Derivative Weight % -2 -4 -6 (a) -8 -10 100 200 300 400 500 600 700 800 Ċ Temperature ⁰C

Fig. 2. DTG curves of (a) BMI resin(b) BMI Epoxy composite (c) BMI Epoxy nanocomposite with 2% BT nanofiller.



Fig. 3. DSC curves of (a) BMI resin powder (b) BMI Epoxy composite (c) BMI Epoxy nanocomposite with 2% BT nanofiller.

 $(C_4H_9O)_4$ was added to18 ml ethanol solution in drops with continuous stirring. Slow addition of 0.06 ml HNO₃ and 3 ml distilled water was then followed. 10 ml of this freshly prepared solution was added dropwise into aqueous Ba(OH)₂ solution whose concentration was maintained at the range of 1.0 M, with continuous stirring. This mixture was transferred into a Teflon lined autoclave maintained at 200 °C and kept for 16 h. The autoclave was cooled to room temperature, products were filtered, washed with distilled water – ethanol mixture and dried at 60 °C under vacuum for 24 h [25].

2.3. Preparation of BMI-Epoxy composites

The conventional solvent method was inappropriate for the preparation of composites because the solvent DMF will not be able to evaporate completely and during evaporation blisters appear on the surface of composite. BMI and Epoxy resin containing $BaTiO_3$ nanoparticles in the ratio 15:1.5were mixed and ground well. Unidirectional E glass fiber is used as reinforcement. First glass fiber sheet is placed above resin nanoparticle matrix, uniformly pressed using Teflon rollers. It is repeated up to four layers. The different samples of glass reinforced



Fig. 4. SEM image (A) and EDAX (B) of BaTiO₃nanoparticles.



Fig. 5. SEM images of A) BMI epoxy composite B) BMI Resin.



Fig. 6. Cross sectional SEM images of BMI epoxy nanocomposites with (A)1% (B)2% (C) 3% weights of BT nanoparticles.

Table 3

Weight and atomic percentages of various elements present in ${\rm BaTiO}_3$ nanoparticles obtained from EDAX.

Element	Weight %	Atomic %
ОК	17.46	55.05
Ti K	21.31	22.45
Ba L	61.23	22.50
Total	100	

BMI/Epoxy/BaTiO₃ nanocomposites were prepared by mixing the resin mixture with varying percentages of BaTiO₃ nanoparticles as mentioned in Table 1. Thus simple hand lay up method is used for the fabrication of glass fibre reinforced composites followed by compression moulding at 200 psi. The composite was kept in press at 100 °C for 10 min then raised to 120 °C for further 10 min, again raised to 140 °C for 10 min and finally for half hour at 180 °C [26–30]. The same procedure is adopted for the preparation of glass reinforced BMI-Epoxy composites without BaTiO₃ nanoparticles.

2.4. Measurements

Scanning Electron Microscopy (SEM) –EDAX of BMI, BaTiO₃, BMI/ Epoxy composite and BMI/Epoxy/BaTiO₃ nanocomposite were obtained on ESEM Quanta 200 FEI from IISC Bangalore. Powder X-ray Diffraction (XRD) were recorded on Bruker AXS D8 Advance from CUSAT, Kochi to determine the morphology and composition of the synthesized BaTiO₃ [30–32]. FTIR spectra were recorded on IR Affinity-1S, Shimadzu from MES Keveeyem College, Valanchery. TGA and DTA measurements were carried out on PerkinElmer Diamond and DSC using Mettler Toledo DSC 822E from CUSAT, Kochi. Mechanical properties such as tensile strength and flexural strength of BMI-Epoxy composites were studied on 50 KN UTM-1205 from CBPST (CIPET), Kochi.

3. Results and discussion

3.1. Thermogravimetric analysis

TGA curves of cured BMI, BMI-Epoxy and BMI-Epoxy composite with 2% weight of BT nanofiller composites without glass fiber were obtained by thermogravimetric analyser apparatus at a heating rate of 20°C/min



Fig. 7. SEM and EDX of BMI-Epoxy containing 2 wt % BT nanocomposite.



Fig. 8. X-ray Diffraction pattern of the (A) synthesized $BaTiO_3$ nanoparticles (B) (a) BMI-Epoxy 3%BT (b) BMI-Epoxy 2% BT.

from 40°C to 730°C. All sample weights remained less than 10 mg.(see Fig. 1)

From the TGA curves it is clear that BMI Epoxy composite with 2% BTis having higher thermal stability compared to BMI resin and BMI-Epoxy matrix that may be due to the interaction of the dispersed BT nanofiller with adjacent polymer matrix layers. The addition of thermally stable fillers can ensure not only good compatibility but also will improve the nano composite thermal stability due to their low migration characteristics [33].(see Table 2)

Curing is observed as a large exothermic peak. The exothermic peak temperature reflects the maximum rate of curing of the resin. By analyzing the DTG curves of cured BMI, BMI-Epoxy and BMI-Epoxy composite with 2% weight of BT nanofiller composites without glass fiber (Fig. 2), it is clear that exothermic peak temperature decrease from 446.83 C to 440.52 C in cured BMI Epoxy and to 421.60 C in the case of



Fig. 9. X ray Diffraction pattern of (A) unmodified uncured neat BMI resin(B) BMI Epoxy composite.

BMI Epoxy composite with 2% weight of BT nanofiller composites indicating that maximum rate of curing of resin decreases during the fabrication of BMI Epoxy composite with 2% weight of BT nanofiller composites without glass fibers.

Comparative analysis of the DSC curves of cured BMI (Fig. 3(a)), BMI Epoxy and BMI Epoxy composite with 2% weight of BT nanofiller we are getting peaks in negative direction for both BMI Epoxy and BMI Epoxy composite with 2% weight of BT nanofiller reveals they are undergoing crosslinking (Fig. 3(b) and (c). Among the above two BMI Epoxy composite with 2% weight of BT nanofiller has undergone more crosslinking. The DSC curve also confirms the Tg of Bismaleimide resin is at 288.85°C. Tg of BMI resin and BMI-Epoxycomposite with 2% weight of BT nanofiller were increased by the modification and addition of BT nanofiller [34]. In DSC broadened Tg is associated with an enhancement of tensile strength [35].



Fig. 10. FTIR Analysis of the synthesized BaTiO₃.



Fig. 11. FTIR Analysis of unmodified uncured BMI Resin.

3.2. Morphology of BMI epoxy nanocomposite

The morphology of $BaTiO_3$ nanoparticles Fig. 4(A), BMI epoxy composite (Fig. 5) and BMI epoxy nanocomposites(Fig. 6) has been studied by SEM.

Elemental Dispersive X-ray (EDAX) spectrum of the synthesized $BaTiO_3$ nanoparticles (Fig. 4B) confirms the formation of $BaTiO_3$ with compositions as Barium 55.05%, Titanium 22.45% and Oxygen 22.5% in the sample (Table 3).

From the SEM images of BMI-Epoxy BT composites BT nanoparticles (Fig. 7)are homogeneously dispersed throughout the polymer matrix and no agglomeration or voids are observed (see Fig. 5). Epoxy moiety can induce interaction with BMI resin via ring opening reaction. As a result, the distribution of nanofiller in the polymer matrix is enhanced which is important to obtain desired dielectric and thermal properties.

The highest tensile strength is observed in composite with 2% weight of the BT nanoparticles may be due to the uniform distribution of nanofiller in the Bismaleimide-epoxy matrix and less agglomeration of the nanofiller that facilitated the good interaction between the polymer matrix and nanofiller and are evident from SEM images (Fig. 7).

From EDX of BMI-Epoxy nanocomposite with 2% BT,we can see

overlapped regions in the initial stage which indicates the presence of C (0.277),N(0.392),O(0.525)and Ti(0.39,0.452,0.5 & 4.51,4.5,4.9). We can see two small peaks between 4.5 and 5.0 which indicates the presence of both Ti and Ba. From this it is evident that the BT nanofillers are effectively dispersed in the polymer matrix.

3.3. X ray diffraction analysis

(a) X ray Diffraction analysis of BaTiO₃ nanoparticles

The analysis of XRD pattern matched with JCPDS No#892475. The most intense peak (110) is found at $2\theta = 31.57$. The peaks at $2\theta = 22.19$ (100), 31.57(110), 38.92(111), 45.27(200), 50.96(210), 56.18(211), 65.87(220), 70.39(300), 74.82(310) and 79.17(311) confirm the formation of perovskite structure of the synthesized BaTiO3 nanoparticles. Using Scherrer's formula, the average crystallite size of the BaTiO₃ nanoparticles is calculated and found to be 32.64 nm.

By comparing Fig. 8B (a) and 8B (b) with 9B, it is clear that the narrow diffraction peaks between 2θ ranges from 19 to 22 is retained at XRD patterns of both BMI Epoxy composites with and without BT nanofiller. Further analysis of Fig. 8(B) (a) and (b) reveals that 2θ values of most intense peak (110) is not that much changed and peaks at 110,111,200,210,211,220 and 310 are also seen in both BMI Epoxy composites with 2% and 3% BT nanofiller confirming the effective dispersion of BT nanofiller.

(b) X-ray Diffraction analysis of BMI Resin

The X-ray diffraction pattern of the unmodified uncured neat BMI resin (Fig. 9A) shown below exhibits its characteristic peaks at $2\theta = 12.86$, 13.76, 15.86, 21.96, 26.29 and 27.75. The sharp narrow diffraction peaks between 2θ ranges 10 to 30 could explain the brittle nature of the resin. The sharp narrow diffraction peaks corresponds to the crystalline regions while broad peaks corresponds to the amorphous regions of the resin. The presence of crystalline regions resulted in the brittleness of the resin [36]. XRD pattern of BMI Epoxy composite [Fig. 6 (B)] confirms that addition of epoxy resin decreases the brittle nature of the resin.

3.4. FTIR analysis

FTIR spectra of BaTiO₃ exhibited peaks at 630 and 868 cm⁻¹ corresponding to the metal-oxygen (Ti-O) stretching vibrations. Peaks at 1641 and 3412 cm⁻¹ corresponded to the –OH deformation and stretching vibrations due to the presence of adsorbed –OH group. A weak absorption peak at 1641 cm⁻¹ attributed to the bending vibration of H-O-H arose from adsorbed water molecules. A strong peak at 1436 cm⁻¹ is related to C-O stretching vibration arose from the trace of BaCO₃ present in BaTiO₃ (Fig. 10)[37].

From the ATR FT-IR spectra of the uncured BMI resin (Fig. 11) and the cured BMI/Epoxy nanocomposites, it can be seen that the strong absorption band at 1147 cm⁻¹ attributes to the maleimide C-N-C stretching vibration disappeared during curing, indicating the conversion of maleimide functionality. The characteristic absorption peak of the imides are at $1705 \text{ cm}^{-1}(+\text{or}-10 \text{ cm}^{-1})$, in all the cured BMI/Epoxy composites and the uncured BMI resin there exists a strong absorption peak at 1705 cm^{-1} indicating the presence of strong C=O asymmetric stretching. At 2341 cm⁻¹ and 2320 cm⁻¹ peak of atmospheric CO₂ due to asymmetric stretching mode of gas phase CO₂ was found.

The strong absorption bands due C-N-C and C-N stretching were observed at 1512 cm^{-1} and 1386 cm^{-1} . Characteristic absorptions due to the maleimide ring observed at 686 cm^{-1} , 823 cm^{-1} , 1147 cm^{-1} , 1386 cm^{-1} and C=C stretch was observed at 1510 cm^{-1} . Analysis and comparison of the FT-IR absorption spectrum of the cured composites and the uncured BMI resin showed reduced number of peaks in the range of $600-1600 \text{ cm}^{-1}$ indicating the completion of curing of BMI resin [36,

Table 4

The tentative assignment of the main absorption bands of FT-IR.

BMI Epoxy nano composites					Tendative assignment
1%	2%	3%	4%	5%	
3495	3396	3533	3475	3496	Presence
3392 medium	Very weak		3518 Very weak	3518	Of –OH group
680	680	680	682	682	Presence of Maleimide benzene
1382	1382	1384	1384	1384	Ring and imide group
1705 strong	1705 strong	1705 strong	1705 strong	1705 Strong	Presence of C=O group
1510 (strong)	1512	1512	1512 (strong)	1512 (strong)	C=C Benzene ring
1149 weak	1143 Very weak	Very Weak Hard to find	Very Weak Hard to find	1095	-C-N-C Maleimide group
806 strong	808 medium	800 medium	800 strong	798 strong	Benzene ring
946 Very weak	941 weak	Very Weak Hard to find	Very Weak Hard to find	Very Weak Hard to find	Benzene ring
3101 Very weak	Very Weak Hard to find	Very Weak Hard to find	3109 weak	2956 weak	-CH-Maleimide
157Very weak	1610 Weak	1623 Weak	1521medium	1595 weak 1510medium	Ероху
1020 Weak	1025 weak	Very Weak Hard to find	Very Weak Hard to find	1110 weak	Weak C-N-Stretch
	BMI Epoxy nano cor 1% 3495 3392 medium 680 1382 1705 strong 1510 (strong) 1149 weak 806 strong 946 Very weak 3101 Very weak 157Very weak 157Very weak 1020 Weak	BMI Epoxy nano composites 1% 2% 3495 3396 3392 medium Very weak 680 680 1382 1382 1705 strong 1705 strong 1510 (strong) 1512 1149 weak 1143 Very weak 806 strong 808 medium 946 941 weak Very weak 3101 Very Weak Very weak Hard to find 157Very weak 1610 Weak 1020 1020 1025 weak	BMI Epoxy nano composites 1% 2% 3% 3495 3396 3533 3392 medium Very weak 360 680 680 680 1382 1382 1384 1705 strong 1705 strong 1705 strong 1510 (strong) 1512 1512 1149 weak 1143 Very Weak 806 strong 808 medium 800 medium 946 941 weak Very Weak Very weak Hard to find 3101 Very Weak Very Weak Very weak Hard to find 157Very weak Hard to find 1500 1623 Weak Weak 1020 1025 weak Very Weak	BMI Epoxy nano composites 1% 2% 3% 4% 3495 3396 3533 3475 3392 medium Very weak 3518 Very weak 680 680 682 1382 1382 1384 1384 1384 1705 strong 1705 strong 1705 strong 1705 strong 1510 (strong) 1512 1512 1512 (strong) 1149 weak 1143 Very Weak Very Weak Very weak Hard to find Hard to find 806 strong 808 medium 800 medium 800 strong 946 941 weak Very Weak Very Weak Very weak Hard to find Hard to find 3101 Very Weak Very Weak 3109 weak Very weak Hard to find Hard to find 157Very weak 1610 1623 1521medium Weak Weak Weak Weak Very Weak 1020 1025 weak Very Weak Very Weak	BMI Epoxy nano composites 1% 2% 3% 4% 5% 3495 3396 3533 3475 3496 3392 medium Very weak 3518 3518 680 680 682 682 1382 1384 1384 1384 1705 strong 1705 strong 1705 strong 1705 1705 strong 1705 strong 1705 strong 1705 strong 1510 (strong) 1512 1512 1512 (strong) 1512 (strong) 1149 weak 1143 Very Weak Very Weak 1095 Very weak Hard to find Hard to find Hard to find 806 strong 808 medium 800 medium 800 strong 798 strong 946 941 weak Very Weak Very Weak Very Weak 2956 weak Very weak Hard to find Hard to find Hard to find 1521medium 1595 weak 1501 Very Weak Very Weak 100 1623 1521medium 1500medium



Fig. 12. FTIR Analysis of (a)BMI Epoxy composite(b)unmodified uncured BMI Resin.

38] (see Table 4).

FTIR spectra of E-GF and SC-EGF reinforced BMI-Epoxy composites with varying weight percentages (1–5%) are shown in Fig. 13. Comparative studies reveal that the characteristics peaks are not that much altered in differently reinforced BMI-Epoxy BT nanocomposites. The characteristic absorption peak of the imides at 1705 cm⁻¹, the C=C stretching of aromatic rings 1603-1613 cm⁻¹ in epoxy, C-C stretching of aromatic ring at 1509 cm⁻¹ are retained in both FTIR spectra. In the FTIR spectra of E-GF reinforced BMI-Epoxy nanocomposites, small peak between 2873 and 2965 cm⁻¹ has been observed which is due to the



Fig. 14. Intercrosslinking between BMI and epoxy resin.



Fig. 13. FTIR Analysis of the BMI Epoxy nanocomposites reinforced with (A) E -GF (B) SC - EGF.



Fig. 15. (A) and (B)-comparitive study of effect of weight % of BaTiO₃ nanoparticles on tensile strength and flexural strength of the composites reinforced with Eglass fiber (EGF) and Silane coated E-glass fiber(SC- EGF).



Fig. 16. Frequency -dielectric permittivity graph of BMI epoxy nanocomposites reinforced with (A) E-GF (B)SC-EGF.



Fig. 17. Frequency -tan δ graph of BMI epoxy composites reinforced with (A) E-GF (B) SC-EGF.

stretching of C-H of CH_2 and C-H aromatic and aliphatic. More intense peaks are observed in FTIR spectra of SC-EGF reinforced BMI-epoxy nanocomposites.

The IR peak for the oxirane ring of the epoxy resin is absent at 915 cm^{-1} in both BMI-Epoxy composites with and without nanofiller(Fig. 12 and 13). This suggests the possibility of ring opening and consequent

crosslinking between epoxy and BMI. The appearance of OH peak beyond 3500 cm⁻¹due to the opening of the oxirane ring of the epoxy is found in all the BMI-Epoxy nanocomposites (Fig. 13) that indicates intercross linking between BMI and epoxy resin which proceeds through the ring opening of epoxy (oxirane ring) and formation of -N-CH(OH) CH₂- bonds between N of maleimide ring and –CH of epoxy resin



Fig. 18. Weight percentage-dielectric permittivity graph (A & B) and weight percentage-tan delta graph (C & D)of BMI epoxy nanocomposites with EGF and with SC-EGF at frequencies.



Fig. 19. Effect of weight percentage of $BaTiO_3$ nanoparticles of BMI epoxy composites on break down voltage.

(Fig. 14).

3.5. Mechanical properties of BMI epoxy nanocomposite

The flexural and tensile strength measurements were studied as per ASTM standards. The flexural and tensile strength of BMI epoxy nanocomposites (Fig. 15) are higher than that of BMI epoxy composite whose flexural strength and tensile strength are 224 Mpa and 110 Mpa respectively. For samples of BMI/BT-1 to BMI/Epoxy-BT-5 the flexural strength and tensile strength change when the ratio of BaTiO₃ nanoparticles are different and maximum value obtained when the percentage of BaTiO₃ nanoparticle is 2%.

The comparative analysis of the above test results showed that there is remarkable increase in the tensile strength and flexural strength of Silane coated E-glass fiber reinforced nanocomposite, establishing the fact that there exists greater interaction between Silane coated E-glass fiber and the matrix [39]. The tensile and flexural strength increases first and the decreases with the increase in weight % of the nanofiller. The increased rigidity contributed by the loaded nanofiller owing to the increased matrix to filler interaction is responsible for the enhanced tensile and flexural strength. When the weight % of the nanofiller is above a certain value, there is chance for filler agglomeration that may hinder the interchain interactions during the curing process and this result in decreased tensile and flexural strength.

3.6. Dielectric properties of the nanocomposites

3.6.1. Dielectric permittivity

Fig. 16 depicts the dependence of dielectric permittivity of BMI epoxy nanocomposite on the weight percentage of $BaTiO_3$ nanoparticles measured at room temperature at frequency range 10^1 – 10^7 Hz. Also with gradual increase in the ratio of $BaTiO_3$ nanoparticles, dielectric permittivity also increases gradually. The dielectric permittivity reached to maximum value when the weight percentage of $BaTiO_3$ nanoparticles was 2% in the case of BMI epoxy nanocomposites reinforced with E-GF and 2% in the case of BMI epoxy nanocomposites reinforced with SC-EGF

Dielectric permittivity usually decreases with increase in the frequency which is ascribed to an interfacial relaxation. Here the increased permittivity with increase in frequency may be attributed to either interfacial polarization or because of breakage of certain bonds at higher frequency or because of both effects.

(1) Interfacial polarization - Nanofiller content is responsible for the heterogeneity of the systems and the extended interface. Space charges migrate under the influence of the field and accumulated at the interfaces where they form dipoles with enhanced inertia. This charge trapping procedure at the interface contributes to the dielectric response and permittivity [40].

Interfacial polarization had no time enough to orient themselves in the direction of the alternating field [41].

(2) Bond Breakage – With increase in frequency, there is possibility for the breakage of bonds under severe oscillation resulting in the formation of charge centres in the matrix. So with increase in frequency, the extent of bond breakage also increases leading to increased permittivity.

3.6.2. Dielectric loss

Electrical conductivity, dielectric polarization etc. mainly depends on loss tangent or tan $\delta.$

Due to high polarization of $BaTiO_3$ nanoparticles compared to that of BMI/Epoxy matrix, increase of dielectric permittivity was observed. By increasing the ratio of the $BaTiO_3$ nanoparticles, no trends can be seen in the values of the dielectric loss of the composites (Fig. 17). At very small ratio of $BaTiO_3$ (2%) the dielectric loss of the composite remained very low. The BMI epoxy nanocomposites have attracted much attention in practical applications due to its high dielectric permittivity and low dielectric loss.

3.6.3. Dielectric properties of the nanocomposites at high frequencies

Dielectric constants and dielectric loss of the fabricated nanocomposites have been obtained at higher frequencies (in GHz) by using Vector Network Analyser at room temperature and was found to be highest for the BMI-Epoxy nanocomposite with 1% weight nanofiller [42]. Dielectric permittivity depends on thickness of the sample, uniformity of the surface of the sample, presence of air occupied voids etc. So the measured values can change according to the variation in the above factors. We are getting negative delta values in some samples that may due to the above factors.(see Fig. 18)

3.6.4. Break down voltage and dielectric strength

The energy storage capacity and energy density of polymer nanocomposites depend upon the value of break down field strength. The AC Break down studies are performed on BMI/Epoxynanocomposites as per ASTM D149. Break down voltage varies with the material composition, shape of the material and the length of the material between the electrical contacts..(see Fig. 19)

4. Conclusions

Glass fiber reinforced Bismaleimide/Epoxy composite and Bismaleimide/Epoxy nanocomposite with BaTiO₃ nanoparticles at different filler loadings have been prepared. The effect of BaTiO₃ nanoparticles on the mechanical, thermal and dielectric properties of Bismaleimide/ Epoxy composites was studied. Both Glass fiber reinforced (E-GF & SC-EGF)BMI/Epoxy/BaTiO₃ nanoparticles with 3% of BaTiO₃ have better insulating properties and with 2% exhibits better mechanical properties. Dielectric constants and dielectric loss of the fabricated nanocomposites have been obtained at higher frequencies (in GHz) by using Vector Network Analyser at room temperature and was found to be highest for the BMI-Epoxy nanocomposite with 1% weight nanofiller.

Declaration of competing of interest

Authors have no conflict of interest.

CRediT authorship contribution statement

K. Savitha Unnikrishnan: Conceptualization, Methodology, Data curation, Writing - original draft, Software, Visualization, Investigation, Project administration, Resources. T. Sunil Jose: Supervision, Writing - review & editing, Validation, Project administration, Resources. S. Dinoop lal: Writing - review & editing, Software. K.J Arun: Formal analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2020.106505.

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