70(8A): 1-479; 2022. DOI: 10.18311/jmmf/2022/31987

Print ISSN : 0022-2755

Journal of Mines, Metals and Fuels

Contents available at: www.informaticsjournals.com/index.php/jmmf

Effect of Hybrid Fillers on Electrical, Thermal and Mechanical Properties of Glass Epoxy Composites

Bommegowda K. B.

Department of ECE, N.M.A.M. Institute of Technology (Affiliated to Visvesvaraya Technological University, Belagavi) Nitte-574110, Udupi, Karnataka, India. Email: bgowda_kbl@nitte.edu.in.

Abstract

Failure of composites in various industrial applications has directed the requirement for further improvement in the electrical, mechanical, and thermal characteristics of polymers to meet the challenging requirements of the industry. In this study, different fillers namely SiO_2, Al_2O_3, SiC, MoS_2, graphite and cenosphere have been incorporated into the ECR glass fabric reinforced epoxy matrix. To exploit the application of these composites for electrical applications, the V-I characteristics is determined with a voltage range of 1V to 20V and impedance of the composites were determined in the range of 20 Hz to 10 MHz, at 25, 50 and 75±2°C. Also, an attempt is made to investigate the mechanical and thermal properties of composites. Composite with 5 wt.% of graphite filler has a maximum surface and volume current of 1.4nA and 0.05nA with a DC voltage that varies from 1V to 20V. Thermal stability improves in 10 wt.% of silicon carbide and 5wt.% of silica (nano and micro filler) at 70 and 80% weight loss, respectively. The glass epoxy with alumina has the highest density of 2.12 g/cm^3. The highest value of hardness is achieved in 10 wt.% of cenosphere composite over the base material.

Keywords: *Epoxy resin, micro and nano fillers, electrical properties, thermal properties, mechanical properties.*

1.0 Introduction

Polymer nanocomposites were used as potential substitutions for conventional polymers for insulation applications (Liang and Wong, 2017, Glushkov, 2014). Innovations and advancement achieved in the fabrication of fiber reinforced have been a major driving force behind the increased use of polymer composites in recent years. The current developments in the high-performance polymer resins with fabric reinforcements have facilitated further advancements in the new generation polymers with micro and nano fillers. The reinforcements report unique physical and mechanical properties to improve the overall characteristics of the polymers (Mahmood et al., 2017).

The electrical and thermal properties of an epoxy matrix can be improved further by using nano meter-sized fillers, micron-sized fillers, or a combination of nano and micron-sized fillers. Fillers including silicon carbide, alumina, and silica are utilised to make electrically insulating and thermally conducting polymer matrix composites.

Investigations by Sathish Kumar et al., (2014) has reported that to increase the tribological and mechanical characteristics of polymer composites, with different glass fiber reinforcements namely a chopped, woven fabric mat and longitudinal fiber can be used. The authors have reported that impact strength decreases with an increase in the volume fraction to 25%. Gupta (2018) has revealed that the properties of the composites would be subject to on the fiber reinforcement and its alignment in the polymer matrix becomes extremely critical during the fabrication of the composites. Electrical and electronics

applications are said to benefit greatly from such composites. Because of its low cost, low susceptibility to moisture absorption and greatly enhanced insulating properties. E-glass fibers are considered as major reinforcement in polymer composites (Eesarapu et al., 2016). The use of hybrid polymer composites consisting of two fillers is warranted by the fact that one filler can enhance the characteristic properties that are found lacking in another filler (Nassar and Nassar, 2020). The modified polymeric matrix with a hybrid filler combination has become a pioneering research method for accomplishing a good thermal, mechanical, and viscoelastic properties for a wide range of industrial applications (Jesuarockiam et al., 2019). Plesa et al., have carried out extensive investigations to attain a good balance of thermal, electrical and mechanical properties by combining an inorganic filler combination of nano-silica, nano-alumina, and silicon carbide for electrical insulation applications (2016).

2.0 Experimental Method

2.1. Materials

The specifics of the resin, reinforcement, fillers and hardener are depicted in Table 1. The nanofillers were locally sourced in the case of MoS_2, graphite and SiC.

2.2. Method of Fabrication

In this investigation, the wet hand layup method was employed for fabrication. The flow diagram for the processing of glass epoxy hybrid composites is depicted in Fig.1 (Bommegowda et al., 2021). The particulars of fabricated composites and their identification for the purpose of discussions of results are shown in Table 2.

2.3. Method of Measurement

2.3.1. Electrical Properties

Impedance of the glass epoxy hybrid composites was determined using a high-frequency LCR meter (model 6500P) as per specifications of ASTM D 150-11. A circular specimen of 50 mm diameter and a thickness of 3mm is placed between a pair of solid electrodes to measure impedance (Z) with an applied voltage 1Vrms over a frequency range of 20 Hz to 10 MHz. Measurements were carried out at 25, 50 and 75±2°C, respectively. Five measurements were carried out at each frequency and the average of five measurements is reported.

The V-I characteristics of glass epoxy hybrid composites were measured using 2636B - Source Measure Unit, Source Meter, ± 200mV to ± 200V, ± 1nA to ± 10A, 60W. The dual channel system was used for its unique features like true current source, precision power supply, 6½ digits readout, pulse generator, waveform generator and electronic load. The instrument has a voltage range of 100mV to 40V and a current measurement range of 1nA to 10A.

2.3.2. Thermal Properties

To determine the glass transition temperature according to ASTM E1582, the Differential Scanning Calorimeter (DSC) model Q2000 of a TA instrument was used and worked in a nitrogen atmosphere. The DSC instrument was first calibrated using pure indium metal. As a reference material, an empty aluminium pan was used. The DSC runs were recorded in the temperature range of 25°C-270°C at a heating rate of 10°C/minute in nitrogen in accordance with ASTM E1582. The method entails heating 4 to 5 mg of sample powder, then measuring the heat absorbed or released as a function of temperature in relation to a reference material.

Table 1: Resin, Reinforcement, Fillers and Hardener used in the Composite

Sl. No.	Materials	Source	Density (g/cm3)
1	Epoxy MY740	Huntsman, USA	1.16
2	ECR glass fabric	Owens Corning, India	2.66
3	Alumina		2.62
4	Silica		4.0
5	Graphite	Sigma Aldrich, USA	2.6
6	Silicon Carbide		3.1
7	Molybdenum disulfide		5.06
8	Cenosphere	Thermal Power Station	2.23

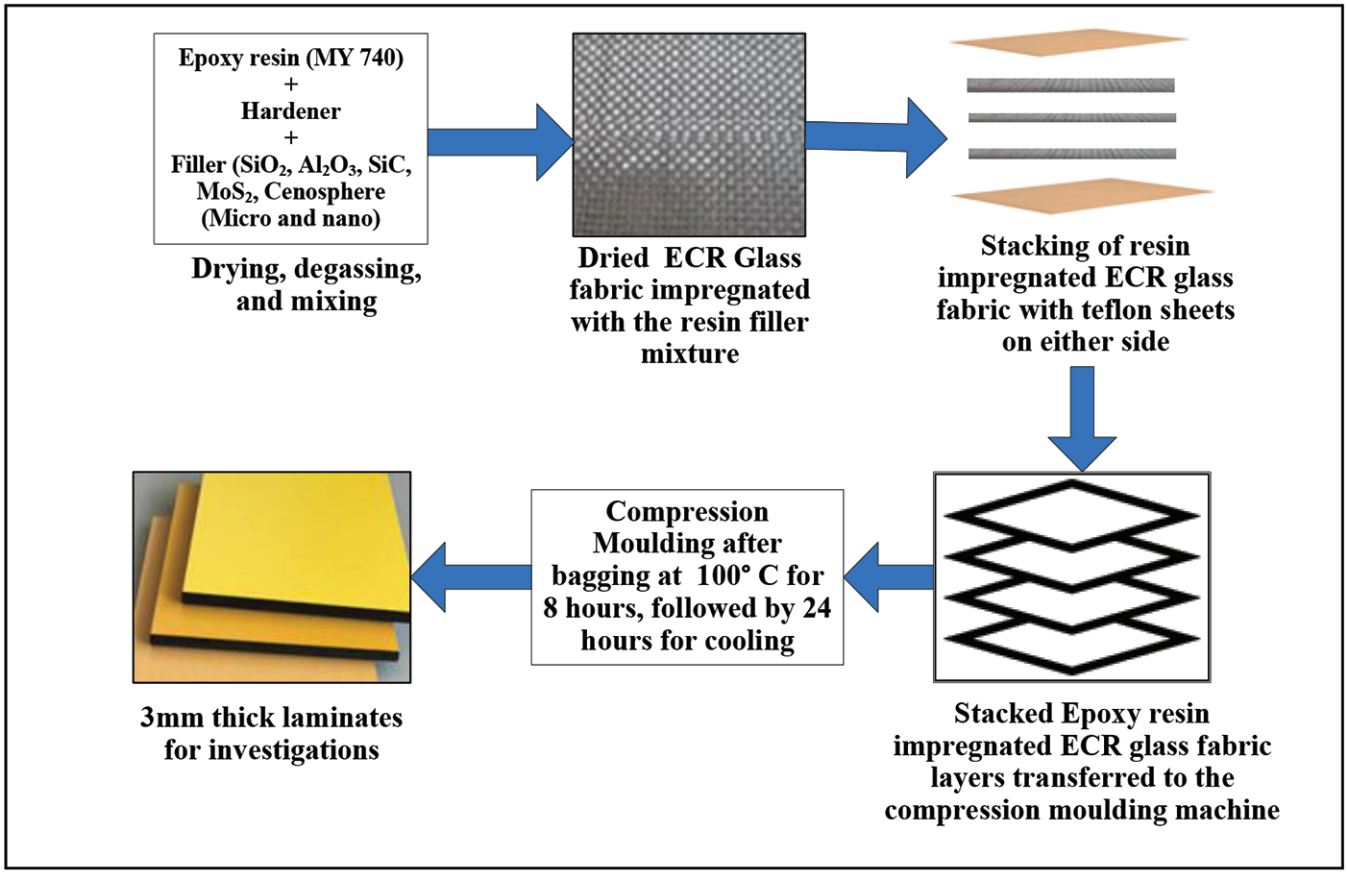

Figure 1: Flow diagram for processing of glass epoxy hybrid composites

Table 2: Nomenclature of Fabricated Composites

Nomenclature	Description
GE	ECR glass fabric (60) + epoxy (40)
GEA	ECR glass fabric (60) + epoxy (35) + nano alumina (1) +micro alumina (4)
GES	ECR glass fabric (60) + epoxy (35) + nano silica (1) +micro silica (4)
GESiC	ECR glass fabric (60) + epoxy (30) + micron siliconcarbide (8) + nano silicon carbide (2)
GEC5	ECR glass fabric (60) + epoxy (35) + cenosphere (5)
GEC10	ECR glass fabric (60) + epoxy (30) + cenosphere (10)
GEG	ECR glass fabric (60) + epoxy (35) + micron graphite (4)+ nano graphite (1)
GECM	ECR glass fabric (60) + epoxy (30) + cenosphere (5) +micron molybdenum disulfide (4) + nano molybdenum disulfide (1)

2.3.3. Physico Mechanical Properties

The density of the epoxy composites was determined by using METTLER AE 200 densitometer by adopting the procedure outlined in ASTM D 792 00. The displacement method was used for this purpose and the instrument was calibrated before use.

The hardness is a material property that measures the resistance to the surface indentation. Shore hardness of the central core rods was measured using HT-6510D instrument in accordance with ASTM D2240-00 at a load of 45 N.

3.0 Results and Discussion

3.1. V-I Characteristics

The variations in DC surface and volume current of glass epoxy hybrid composites over a range of potential from 1V to 20V at 25°C is depicted in Figs.2 and 3 respectively.

From Figs.2 and 3, it is observed that composite with 5 wt.% of graphite has a maximum surface and volume current of 1.4nA and 0.05nA respectively when the DC voltage is varied from 1V to 20V in the step of 2V. From Figs.2 and 3, a non-linear V-I relationship of the composites with hybrid fillers is evident. The non-ohmic behaviour of the composites is attributed to the tunnelling mechanism.

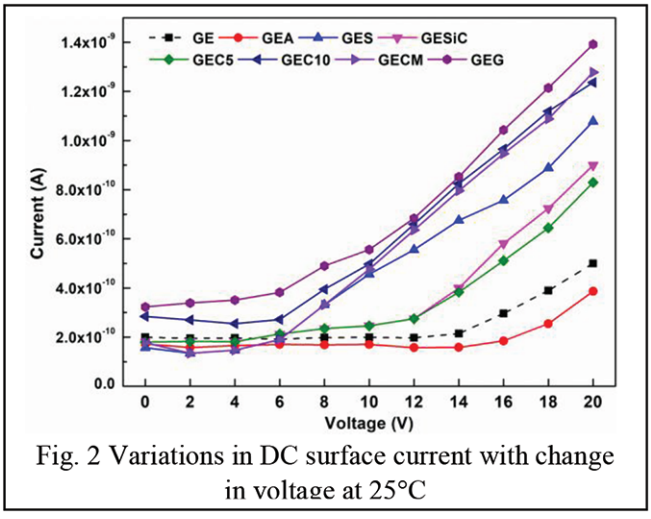

Fig. 2 Variations in DC surface current with change in voltage at 25°C

Figure 2: Variations in DC surface current with change in voltage at 25°C

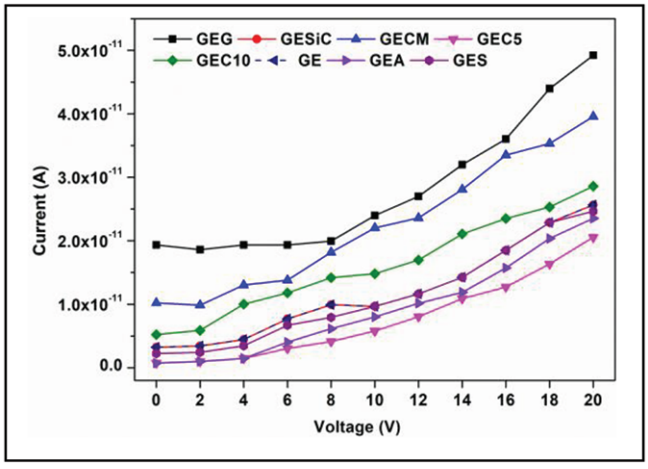

Figure 3: Variations in DC volume current with change in voltage at 25°C

Aseel A. Kareem (2017) has reported that conduction can happen by electron hopping from one micro or nanoparticle to an adjacent particle when they are in proximity. The nonlinear voltage-current behaviour is a typical characteristic for most of the polymer composite materials. The amount of conducting filler in the composite is found to affect the non-linear behaviour. To explain this non-linear electrical behaviour, various mechanisms have been proposed. The most popular mechanism relies on electron tunnelling and hopping to transport electrons between conductive filler particles. In the case of DC conduction, the V-I characteristics of most micro and nanofiller polymer composites satisfy the following equation:

$$I = C V^m \quad \text{... (1)}$$

Where V is the applied voltage, I is the corresponding current, C is the reciprocal of resistance and m is the slope of the plot of log V- log I. When m=1, then the composite has ohmic behaviour. Equation 1 becomes

$$\log I = m \log V + \log C \quad \text{... (2)}$$

From the plot of log V vs log I plots, the values of exponent 'm' has been determined for the composites and are tabulated in Table 3. It is evident from Table 3 that all the composites with 5 wt.% of nano or micro filler exhibit a value of m less than 1, indicating that the conducting fillers used in this work do not reach the percolation levels.

A strident rise in the value of m is expected near the percolation threshold. Since such sharp increase is not seen in the composites, it can be concluded that higher wt.% of conducting fillers are required. As a result, it is fair to infer that the percolation threshold can also be termed as the volume fraction at which the current nature changes from ohmic to non-ohmic. It is also

Table 3: Value of Exponent M for Hybrid Composite

Composite	Value of exponent 'm'
GE	1 õ 10-11
GEA	7 õ 10-12
GES	5 õ 10-11
GESiC	3 õ 10-11
GEC5	3 õ 10-11
GEC10	5 õ 10-11
GECM	6 õ 10-11
GEG	5 õ 10-11

important to note that SiC, MoS_2 and graphite, though electrically more conductive, are not in the percolation threshold regions for the wt.% used.

3.2. Variations in Impedance

The variation in the impedance as a function of frequency at 25, 50 and 75±2p C of the composites with different fillers are shown in Figs.4, 5 and 6, respectively. Due to the enhancement in interfacial polarization with the increase in frequency, there is a significant reduction in impedance of the epoxy composites (Elimat, 2015).

The frequency response of the composite's impedance can be divided into two distinct provinces. At low frequencies, the impedance is frequency dependent, implying that the ohmic resistance is important, whereas capacitive effects are minimal. As the frequency increases, the magnitude of the impedance decreases, implying that the impedance follows the typical characteristics of a capacitor.

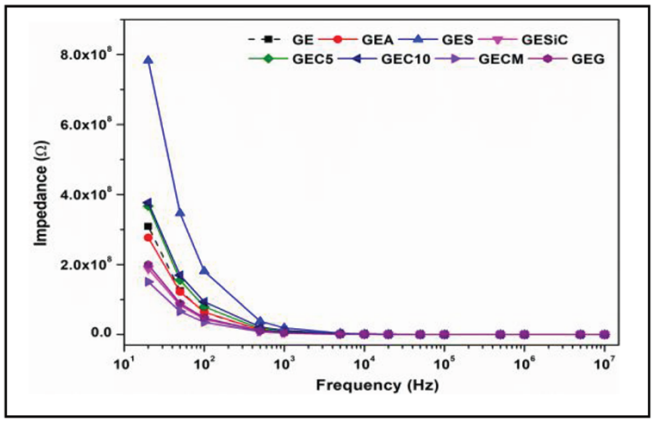

Figure 4: Variation of impedance of the composites at 25°C

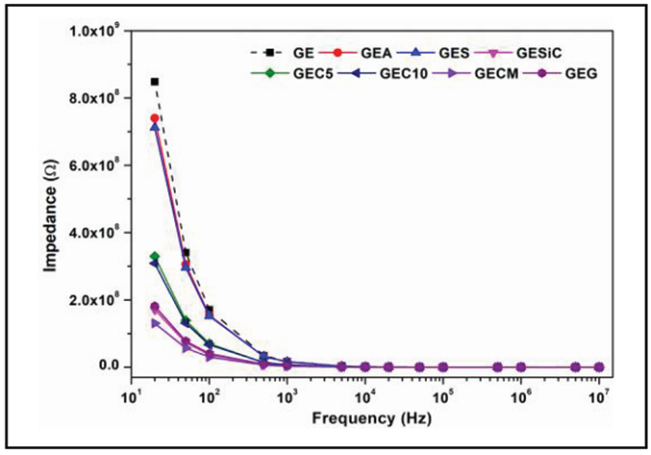

Figure 5: Variation of impedance of the composites at 50°C

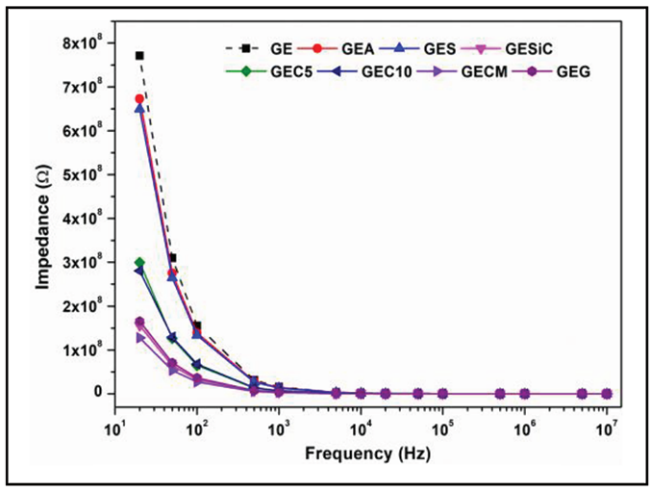

Figure 6: Variation of impedance of the composites at 75°C

When the frequency in the low-frequency region increases, there's a chance that the composite's impedance will decrease due to an increase in conductivity. In the higher frequency range (10 kHz to 10 MHz), the impedance values of the composites overlap, indicating that (a) impedance at high-frequency is independent of the fillers (b) space charge effects and (c) the lowering of the barrier properties of the composites. The variations of epoxy composites electrical properties due to the polarization of space charges (Lau et al., 2014). At 25°C, the impedance of GES is the highest in the low-frequency region. At 50 and 75°C, the impedance of GE, GEA and GES are nearly the same in the low-frequency range.

3.3. Differential Scanning Calorimetry Analysis

The variations in T_g of pure glass epoxy and glass epoxy composites with different fillers are depicted in

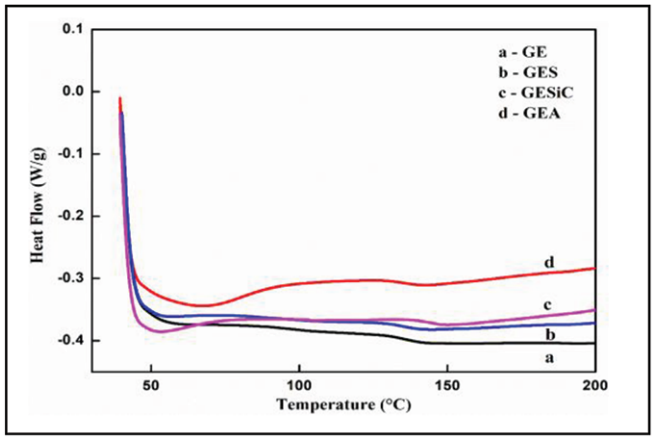

Figure 7: DSC thermograms of GE, GES, GESiC and GEA

Figs.7 and 8. The variations in the glass transition temperature of pure glass epoxy and glass epoxy with different fillers is also shown in Table 4. The T_g of the base resin is observed to be 137°C, which is marginally above the nominal range of T_g of 120 to 135°C, as per the manufacturer's datasheet. Except for GEA, GES and GEC10, all the composites have shown an increase in the T_g value. T_g values of the GEA and GES nanocomposites is in the range of 115-120°C as discussed in the literature for the same resin-hardener systems (Porras et al., 2019), but the use of hybrid filler combination, helps to increases the T_g values.

3.4 Thermogravimetric Analysis

Thermograms of the composites GE, GEA, GES and GESiC depicting the weight loss are shown in Fig.9(a) and the corresponding derivatives of the weight loss are shown in Fig. 9 (b). For composites GEC5, GEC10, GECM and GEG the corresponding results are shown in Fig.10(a) and (b). The corresponding data of the weight loss at different temperature is shown in Table 5. The TGA data shows the changes in weight loss at different stages of the thermal transition, right from the temperature of onset of decomposition T_0, to the temperature at 70% of weight loss: T_{70}, followed by the temperature at 80% of weight loss: T_{80}, and the temperature at 90% of weight loss: T_{90}. The Tmax is the maximum temperature which is considered for assessing the thermal stability of the composites with different fillers. From Table 5, it is observed that thermal stability improves relatively better with 5 wt.% of silicon carbide, silica, and graphite. It shows that silica and silicon carbide in the matrix provides better resistance to thermal oxidation to the composites. Further, the composites show better performance in thermal stability when a combination

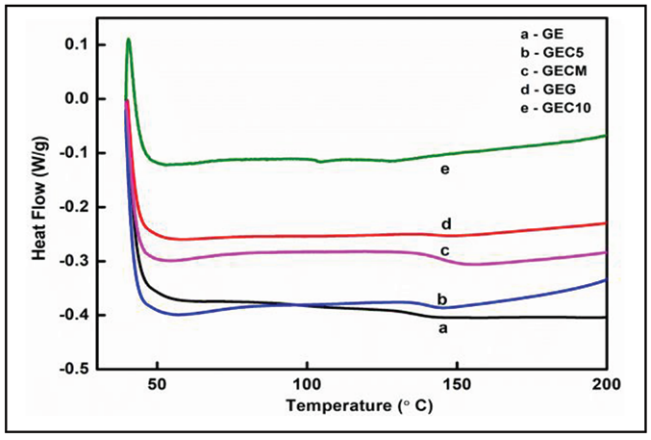

Figure 8: DSC thermograms of GE, GEC5, GECM, GEG and GEC10

Table 4: Glass Transition Temperature of Composites

Composite	Glass transition temperature (°C)
GE	137.06
GEA	135.44
GES	135.27
GESiC	146.16
GEC5	140.25
GEC10	126.46
GECM	144.85
GEG	142.90

of micron and nanofillers are used, initially up to a temperature of 300°C, when minimum weight loss is observed. However, the peak of derivative of the weight loss is observed to be reduced to 325°C in comparison with the 400°C observed with nanocomposites, which is reported in literature (Suchitra and Renukappa, 2016). Further, the second peak is observed to occur at the same temperature of 580-600°C, regardless of the type of the filler used

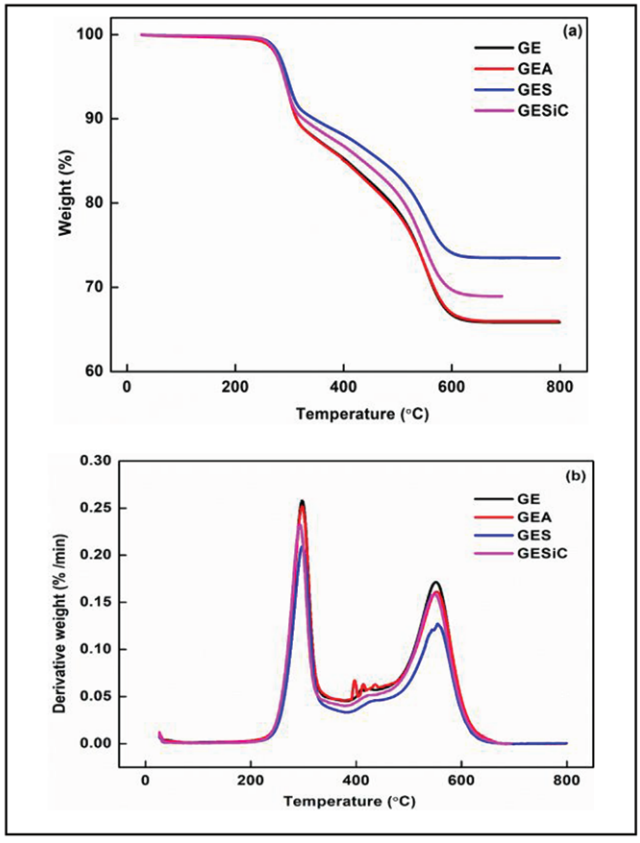

Figure 9: TGA thermograms showing the (a) weight loss and (b) derivative of the weight loss of the composites

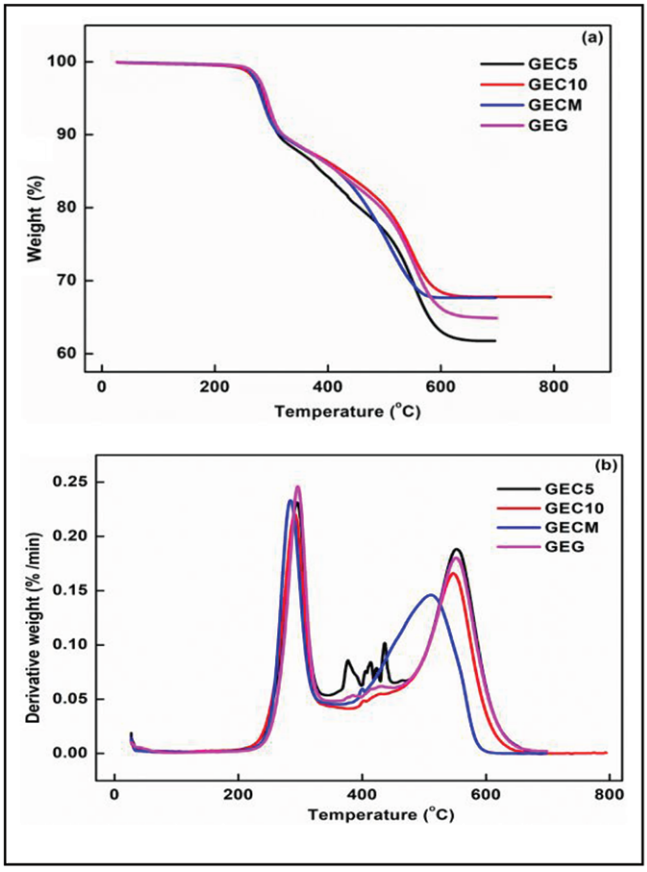

Figure 10: TGA thermograms: (a) weight loss (b) derivative weight of GEC5, GEC10, GECM and GEG composites

Table 5: Weight Loss at Different Temperatures based on TGA

Composite	Temperature at different weight loss %				
	T0	T10	T20	T30	Tmax
GE	225	305	487	566	799
GEA	216	340	537	***	799
GES	220	305	480	566	798
GESiC	237	325	510	590	698
GEC5	220	313	455	549	699
GEC10	213	317	503	576	799
GECM	227	317	470	545	698
GEG	230	321	493	565	680

*** Maximum weight loss < 25%

(Suchitra and Renukappa, 2016). But the derivative weight loss in % per °C, is relatively lower in nanocomposites in comparison the hybrid composites. The composites are observed to be stable in the temperature range of 125 to 135°C and are thus suitable for use in applications in which the continuous operating temperatures are around 100°C is required and the material can easily absorb occasional spikes in temperature. This ability would help in the short-term thermal re-rating of the composite, which is very much required for many industrial applications.

3.5. Physico-Mechanical Properties

3.5.1. Density

Density is an important property of the polymer which is critical for many weight-sensitive applications. It is common to notice the differences in the measured and the theoretical and the expected density values due to the existence of voids.

From the experimental density of GE and epoxy composites with fillers, it is apparent that the density improves with the addition of fillers. The glass epoxy with alumina has the highest density of 2.12 g/cm^3. The void fraction is observed to reduce with the addition of fillers indicating complete filling of voids. It also reveals lesser agglomeration of filler particles. This may be attributed to a better processing method consisting of high shear mixing and ultra-sonication of resin and mixing of fillers during fabrication. The lowest void fraction is observed in GES and GEA. hence in general, the properties of these GES and GEA are expected to be better than the other composites. The use of cenosphere leads to higher void content and it does not reduce even with the inclusion of MoS_2 filler.

The Archimedes displacement method was used to determine the density of the composites. The theoretical density, measured density and void contents of glass epoxy hybrid composites are shown in Table 6. From the experimental density of base

Table 6: Density and Void Fraction of Composites

Composite	Density (g/cm^3)		Void fraction (%)
	Theoretical	Experimental	
GE	1.98	1.92	3.03
GEA	2.12	2.10	0.94
GES	2.06	2.05	0.48
GESiC	2.08	2.02	2.88
GEC5	2.05	1.96	4.39
GEC10	2.09	1.99	4.78
GECM	1.71	1.65	4.81
GEG	2.07	2.03	1.93

material (GE) and its hybrid glass- epoxy composites, it is apparent that the density of hybrid composites improves with the addition of fillers. The glass epoxy with alumina has the highest density of 2.12 g/cm^3.

The least void fraction is observed in GES and GEA as compared to the base material and other composites and hence the density dependent properties of these composites are expected to be better than other composites.

3.5.2. Hardness

The influence of fillers on hardness (Shore-D) of glass epoxy composites are shown in Fig. 11.

The highest value of hardness is achieved in the GEC10 composite with 6% improvement over the base epoxy. It is due to uniform filler distribution and increased filler-filler interactions. This is also since the hybrid composites have reduced void content. These factors contribute to the transfer load from the matrix to the filler. Additionally, hardness relies on the intrinsic properties of the constituents of the polymer composites. Therefore, there is an increase in hardness as compared to the base epoxy in the GEC10 composite which consists of fillers with higher hardness values. It is important to note that glass fibers are mainly responsible for hardness and that the combination of fillers result in an improvement of the hardness by 6%.

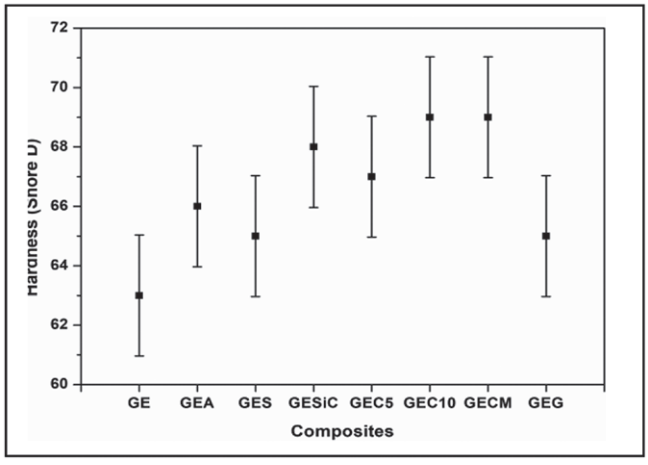

Figure 11: Hardness of hybrid composites

Table 7: Tensile Strength and Modulus of Hybrid Composites

Composite	Tensile strength (MPa) ±5	Tensile modulus (GPa) ±1.3	Elongation at break (mm) ± 0.31
GE	305.4	12.62	6.67
GEA	324	10.6	6.41
GES	300	9.43	6.7
GESiC	402.2	13.05	6.01
GEC5	320.5	12.91	6.41
GEC10	305.8	13.87	7.17
GEG	342.1	12.78	7.37

3.5.3. Tensile Strength and Modulus

Tensile tests were carried out on glass epoxy composites to understand the influence of hybrid filler incorporation on the tensile strength of the glass epoxy matrix. The tensile strength and modulus of the composites are depicted in Table 7.

From the results, it is observed that glass epoxy with silicon carbide filler results in the highest tensile strength and lower values of elongation at break as compared to the base epoxy (GE). There is a minimal change in the tensile strength of other composites. The maximum tensile modulus of 13.87GPa is observed in case of GEC10, due to the presence of 10 wt.% of cenosphere. The increase in tensile strength of the composites primarily attributed to the transfer of the applied tensile load to uniformly distributed and well bonded cenosphere, an increase in grain boundary area due to grain refinement, and multidirectional thermal stress at the interface between the cenosphere particles.

Conclusions

In this study, the dielectric properties of glass fabric reinforced epoxy with different hybrid fillers composites have been investigated. Based on the experimental results, the following conclusions are drawn:

(a) The 5 wt.% of graphite filled glass fabric composite permits the flow of maximum surface and volume current of 1.4nA and 0.05nA at DC potential of 1V to 20V. Thus, the composite GEG is relatively more electrically conducting than the other composites.

(b) The impedance of the composites decreases gradually at lower frequencies and from 10 kHz to 10 MHz, the impedance is frequency invariant. This trend exists regardless of the fillers employed.

(c) The good enhancement of the T_g is observed by using hybrid fillers., and it is confirmed that the filler combination contributes towards thermal stability.

(d) Composites investigated have shown that thermal stability with 10 wt.% of silicon carbide

and 5 wt.% of silica is relatively better as compared to other composites. Though composites with cenosphere filler have the maximum T_g and tensile strength as compared to the hybrid fillers, it is evident that the hybrid filler combinations also perform satisfactorily.

References

1. D. A. Glushkov (2014): Polymeric insulation: advantages and disadvantages. Advanced Materials Research 1008, 615- 619.10.4028/www.scientific.net/AMR.100 8-1009.615
2. Eesarapu Vijaya Kumar, Saidulu Pagidipalli, V Suresh and G V Ramesh Kumar (2016): Study and testing of glass fibre reinforced plastics. International Conf. Recent Trends in Engineering and Research 2, 115-123.
3. Hussain Waleed A., Abdullah A. Hussein, Jabar M. Khalaf, Ali H. Al-Mowali and Abdullwahab A. Sultan (2015): Dielectric properties and a.c. conductivity of epoxy/alumina silicate NGK composites. *Advances in Chemical Engineering and Science* 5, 282-289.
4. Jesuarockiam Naveen, Mohammad Jawaid, Edi Syams Zainudin, Mohamed Thariq Hameed Sultan and Ridwan Yahay (2019): Enhanced thermal and dynamic mechanical properties of synthetic/natural hybrid composites with graphene nanoplatelets. *Journal of Polymers* 11(7), 1-18. 10.3390/polym11071085
5. K B Bommegowda, N. M. Renukappa and J. S. Rajan (2021): Effect of hybrid fillers on the bandgap energy of glass epoxy composites. *IEEE Transactions on Dielectrics and Electrical Insulation* 28(6), 1875-1882. 10.1109/TDEI.2021.009598
6. Kareem Aseel A. (2017): Preparation and electrical properties of polyimide/carbon nanotubes composites. *Material Science* - Poland 35(4), 755-759. 10.1515/msp-2017-0096
7. K. Y. Lau, A. S. Vaughan, G. Chen, I. L. Hosier, A. F. Holt and K. Y. Ching (2014): On the space charge and dc breakdown behaviour of polyethylene/silica nanocomposites. *IEEE Transactions on Dielectrics and Electrical Insulation* 21(1), 340-341. 10.1109/TDEI.2013.004043
8. Liang Mu and K L Wong (2017): Improving the long-term performance of composite insulators use nanocomposite: Review. Energy Procedia 110,168-173. https://doi.org/10.1016/j.egypro.2017.03.12
9. Mahmood Abdullah Al, Abdul Mobin, Rezwon Morshed and Tasmia Zaman (2017): Characterization of glass fibre reinforced polymer composite prepared by hand layup method. *American Journal of Bioscience and Bioengineering* 5(1), 8-11.10.11648/j.bio.20170501.12
10. M. K. Gupta (2018): Investigations on properties of glass fibre reinforced polymer composite. *American Journal of Polymer Science and Engineering* 6(1), 31- 44.
11. M Suchitra and N M Renukappa (2016): The thermal properties of glass fiber reinforced epoxy composites with and without fillers. Macromolecular. Symposia 361(1),117-122.https://doi.org/10.1002/masy.20140022
12. Nassar Amal and Eman Nassar (2020): Effect of fiber orientation on the mechanical properties of multilayers laminate nanocomposites. *Journal of Heliyon Material Science* 6(1), 1-9. https://doi.org/10.1016/j.heliyon.2020.e031 67
13. Plesa Ilona, Petru V. Notingher, Sandra Schlogl, Christof Sumereder and Michael Muhr (2016): Properties of polymer composites used in high voltage applications. *Journal of Polymers* 8(5), 1-63. https://doi.org/10.3390/polym8050173
14. Porras Cesar Leyva, Pedro Cruz Alcantar and Maria Z. Saavedra Leos (2019): Application of differential scanning calorimetry and modulated differential scanning calorimetry in food and drug industries. *Polymers* 12(1), 1-21. 10.3390/polym12010005
15. T P Sathish Kumar, S Satheesh Kumar and J Naveen (2014): Glass fiber-reinforced polymer composites - a review. *Journal of Reinforced Plastics and Composites* 33(13),1258–1275. 10.1177/0731684414530790
16. Z M Elimat (2015): AC impedance and dielectric properties of hybrid polymer composites. *Journal of Composite Materials* 49(1), 1-13. 10.1177/0021998313514256