Study on Mechanical Properties of Polymer Composites Filled with Nano Egg-shell Powder

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Authors' contributions

This work was carried out in collaboration among all authors. Author SR conceived and designed the study, author PKB collected the data, author SD contributed data or analysis tools, author SR performed the analysis, authors SR and SA wrote the manuscript. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Polymeric materials, when reinforced with synthetic fibers like glass, carbon, and aramid, offer notable advantages including increased stiffness and strength-to-weight ratio compared to conventional materials such as wood, concrete, and steel. Among these options, glass fiber stands out due to its affordability and widespread availability. Glass fiber reinforced polymer composites exhibit moderate mechanical properties, which can be significantly enhanced by incorporating nano fillers like eggshell powder. This study explores the utilization of nano eggshell powder as well as methods for effectively integrating nano fillers into polymer composites to create value-added products. Four types of composites, varying in weight proportions of nano eggshell powders, were prepared using the hand lay-up technique for mechanical and thermal characterizations. Various mechanical properties including tensile strength, flexural strength, impact behavior, as well as thermal properties via TGA and DMA analysis were investigated. The results indicate that

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incorporating the optimal amount of nano fillers significantly improves the overall strength of glass fiber reinforced composite materials, leading to cost savings of over 30%. This suggests that nano eggshell fillers hold great potential in composite manufacturing, particularly for substituting high-cost glass fibers in low load-bearing applications.

Keywords: Composite; egg shell powder; mechanical properties; TGA; DMA.

1. INTRODUCTION

Recent technological advancements in engineering have propelled material science to the forefront of innovation. Among these materials, composites stand as a significant stride in the perpetual pursuit of material optimization [1]. "Composite materials offer distinct advantages over conventional materials, primarily due to their superior specific properties such as tensile, impact, and flexural strengths, stiffness, and fatigue characteristics. These enhanced properties provide greater versatility in structural design. Consequently, composite materials find widespread use across various industries, including aerospace, mechanical engineering, transportation, sports, leisure, marine, and biomedical applications" [2]. "Composites typically consist of two key components: the matrix and the reinforcement. The matrix material envelops and supports the reinforcement materials, maintaining their relative positions. Meanwhile, the reinforcements contribute their unique mechanical and physical properties, thereby augmenting the overall properties of the matrix. Fiber-reinforced composites (FRCs) represent the predominant class of polymer composites widely employed across diverse sectors such as automotive, marine, and aerospace due to their exceptional specific stiffness and strength" [3]. "Within FRCs, fibers play a pivotal role as they constitute the largest volume fraction within the laminate, thereby bearing a significant portion of the load acting on the composite structure" [4]. Moreover, filled composites emerge through the incorporation of filler materials into plastic matrices, aiming to replace a portion of the matrix and enhance or alter the properties of the composites. These fillers not only contribute to strength enhancement but also facilitate weight reduction. Typically, fillers are inert substances added to diminish resin costs and enhance its physical properties, including hardness, stiffness, and impact strength. Commonly utilized fillers encompass calcium carbonate, hydrated alumina, clay, and others. Eggshells, often regarded as domestic kitchen waste and a byproduct of the poultry industry, present a significant environmental challenge. With global egg production hovering around 65.5 million tonnes annually, it's estimated that eggshells account for approximately 11% of an egg's weight. Consequently, a staggering 7.2 million metric tonnes of eggshell waste are generated each year. This surplus of eggshell waste poses substantial environmental concerns, necessitating effective management strategies. Researchers face the daunting task of finding sustainable solutions to address this challenge and mitigate its impact on society and the environment. Several studies have investigated the influence of nano fillers and different filler sizes and shapes on the properties of polymer composites: Crosby et al. (2007) found that "the nano-effect was influenced by the polymer matrix, nanoscale fillers, and interfacial materials. The combination of particles and polymer chains on similar length scales offered significant advantages in developing optimized material structures" [5]. Marghalan (2010) observed that spherical-shaped small-size fillers resulted in the smoothest surface finish, whereas irregular fillers led to rougher surface parameters [6]. Nayak et al. (2015) explored that the addition of eggshell filler (6% by weight) resulted in a modulus of 6.63 GPa in the composite [7]. Leong et al. (2016) observed increases in tensile strength and modulus in eggshell powder-filled composites [8]. "Epoxy-based composites have been used extensively in aerospace, naval, automobile, civil, wind energy and electronic industries due to their attractive properties" [9]. "In the field of multiscale modelling of heterogeneous materials, there exist several methods for modelling of nano- and conventional composites and analysis of their effective properties"[10]. Afshari et al. used "laser sintering process to fabricate the TiO_2/PA12 nano-composite parts by considering the parameters of laser power, scanning speed, and TiO_2 content". "The response surface methodology was used to improve the mechanical properties of TiO_2/PA12 nano-composite parts".[11] "The epoxide-amine nanocoatings enhanced the both densities of the Oriental beech wood, according to the study's findings" [12]. Despite the availability of some literature on the recycling and utilization of bio fillers like eggshell powder (ESP), there remains a scarcity of reports regarding the preparation of

epoxy/glass/ESP composites for structural applications. Given these gaps in the existing literature, the current study aims to investigate the mechanical properties of epoxy-glass fiber-nano-ESP composites with varying filler content under different test conditions. Perform dynamic mechanical analysis to understand the viscoelastic behavior of the developed composites. Conduct thermo-gravity analysis to evaluate the thermal stability and degradation characteristics of the samples. By fulfilling these objectives, the study seeks to provide insights into the mechanical and thermal performance of the epoxy-glass fiber-nano-ESP composites, thereby contributing to the understanding of their potential suitability for structural applications.

2. MATERIALS AND METHODS

The eggshells were collected from the local sources. Then, the eggshells were dried under solar dryer for 48hours. Required amount of powder was taken and ground into nano powder (approximate size: 200nm) with the help of Anton Paar BM500 ball mill. The epoxy resin and the hardener (HY951) were supplied by M/s Tirupati Sales, India. The E-Glass fiber sheets were cut into dimension of 304.8 x 304.8 mm². The epoxy along with nano eggshell powder was mixed thoroughly by simple mechanical stirring. A mould release spray was applied over the mould and the mixture is poured in the mould. After that a layer of glass fiber was kept over it. The process is repeated for nine layers of the glass fibers keeping in view the requirements of various testing conditions and characterization

standards. The composite samples of four different compositions (S-1 to S-4) were prepared. The composite samples S-1 to S-4 are prepared by taking different percentages of nano eggshell powder and epoxy. This was done while keeping the glass fiber content at a fixed percentage (i.e. 57 wt %). The detailed composition and designation of composites are shown in Table 1. Sample preparation route is shown in Fig. 1.

2.1 Tensile and Flexural Test

The tension test was conducted on a Universal Testing Machine (UTM), Instron 1195 model. The specimens were prepared with dimensions of 100 mm in length, 11.5 mm in width, and 4 mm in thickness, in accordance with ASTM D3039-76 test standards [13]. Mechanical properties such as tensile strength, modulus of elasticity, and elongation at break of the composite materials under tension. In a conventional three-point bend test, the flexural strength of a material is typically expressed in mega Pascal (MPa) and can be calculated using the following equation:

$$Flexural\ Strength = 3PL/2bd^2 \qquad (1)$$

Where;
P= applied central load (N)
L= test span of the sample (m)
b= width of the specimen (m)
d= thickness of specimen under test (m)

In this case, a span length of 30 mm was used and the cross-head speed was maintained at 10 mm/min.

Table 1. Designation of composites

Composites	Composition
S-1	Glass fiber (57 wt%)+ Matrix (43 wt%)+ Nano Egg shell powder (0 %)
S-2	Glass fiber (57 wt%)+ Matrix (42 wt%) +Nano Egg shell powder (1 wt%)
S-3	Glass fiber (57 wt%)+ Matrix (41 wt%) +Nano Egg shell powder (2 wt%)
S-4	Glass fiber (57 wt%)+ Matrix (40 wt%) +Nano Egg shell powder (3 wt%)

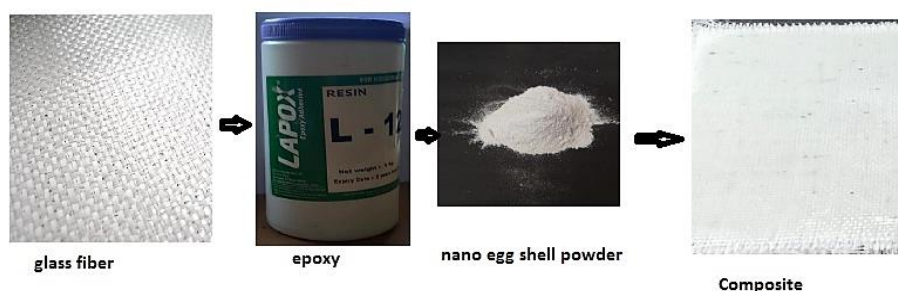glass fiber   epoxy   nano egg shell powder   Composite

Fig. 1. Preparation of composites

2.2 Impact Test

Low velocity impact tests are done as per ASTM D 256 using an impact tester (Presto PSR-292). "The pendulum impact testing machine ascertains the notch impact strength of the material by shattering the V-notched specimen with a pendulum hammer, measuring the spent energy, and relating it to the cross section of the specimen. The standard specimen for ASTM D 256 is 64 × 12.7 × 3.2 mm and the depth under the notch is 10.2 mm" [14].

2.3 Thermogravimetric Analysis Test (TGA)

"Thermogravimetric Analysis (TGA) is a technique used to monitor the mass of a substance as a function of temperature or time, while the sample is subjected to a controlled temperature program in a controlled atmosphere" [15]. During TGA, the weight of a material may either increase or decrease as it is heated or cooled. Overall, TGA provides valuable information about the thermal stability, decomposition kinetics, and composition of materials, making it a versatile tool in various fields including materials science, chemistry, and pharmaceuticals. The average 20mg composite sample is taken for TGA test of composites.

The weight loss of composites was provided by TG analyzer (Perkin Elmer-TGA-8000).

2.4 Dynamic Mechanical Analysis (DMA)

"Dynamic Mechanical Analysis (DMA) is a technique utilized to study and characterize materials, particularly focusing on the viscoelastic behavior of polymers. This method involves applying a sinusoidal stress to the material while measuring the resulting strain, enabling the determination of the complex modulus" [16]. By varying the temperature of the sample or the frequency of the stress, variations in the complex modulus can be observed, aiding in the identification of transitions such as the glass transition temperature and other molecular motions. The composites with dimension 20mm×10mm×4mm were used according to ASTM D5418-15 standard. The dynamic mechanical test of composites was conducted by TA analyzer (Q 800, Thermal analysis instrument, USA).

3. RESULTS AND DISCUSSION

This chapter presents the results of mechanical properties of nano-egg shell powder filled-glass fiber reinforced epoxy-based hybrid composites.

3.1 Mechanical Properties of Glass-epoxy Composites

The mechanical properties of the nano-egg shell powder filled-glass fiber reinforced epoxy based hybrid composites under this investigation are presented in Table 2. It is evident from the Table 2 that at sample 3 (57:37:2 wt%) show better mechanical properties as compared to others.

3.2 Effect of Nano Egg Shell Filler Loading on Tensile Strength and Modulus of Composites

The effect of weight fraction of filler on the tensile strength of the composite is shown in Fig. 2. "As the weight fraction of filler increases in the composites up to S-3, the tensile strength of composite increases up to 137.992 MPa then, shows a decreasing trend. This may be due to improper reinforcement of filler and the fillers are not properly mixed with resin materials" [17]. "A better mixing of nano egg shell powder in epoxy had improved the bonding strength between the fiber and matrix, resulting in improved tensile strength and modulus of the composites. When more nano egg shell powder (3 wt.%) were blended in the epoxy, the tensile strength of the composites decreased due to the agglomeration of nano egg shell powder and the formation of voids in the composites" [18].

Table 2. Mechanical properties of nano-egg shell/glass-epoxy composites

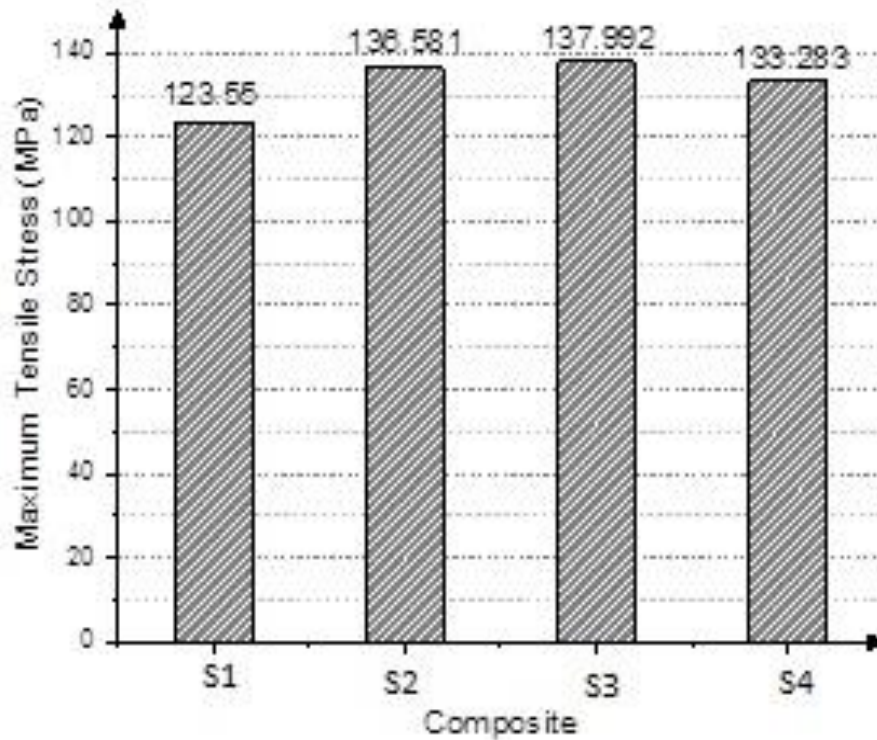| Sample	Tensile Strength (MPa)	Flexural Strength (MPa)	Impact strength (Joule)	Storage Modulus (MPa)	Loss Modulus (MPa)	Tan Delta	TGA (µg)
S-1	123.55	118.174	421.528	7347	1195	0.5076	29956.882
S-2	136.581	145.364	407.513	6490	1210	0.6417	17732.377
S-3	137.992	70.153	494.793	5895	1040	0.7055	30598.322
S-4	133.283	139.989	428.418	6793	1209	0.738	20200.291

Fig. 2. Effect of nano egg shell filler loading on tensile strength of composites

3.3 Effect of Nano Egg Shell Filler Loading on Flexural Strength and Modulus of Composites

Fig. 3 shows the effect of filler loading on flexural strength of hybrid fiber reinforced epoxy composites. The flexural strength of the hybrid composites shows poor strength at of nano egg shell filler loading. However, on increase in nano egg shell filler loading the flexural strength increases from 118.174 MPa to 139.989 MPa respectively. It is also observed from Fig. 3 that a linearly decreasing in trend up to a certain value of filler loading (S-3) and then suddenly increasing (S-4) due to strong interaction between the nano filler and resin material. "This decrease is attributed to the inability of the fiber, irregularly shaped, to support stresses transferred from the polymer matrix and poor interfacial bonding generates partially spaces between fiber and matrix material and as a result generates weak structure. As flexural strength is one of the important mechanical properties of the composites. For a composite to be used as the

structural application it must possess higher flexural strength. However, as far as flexural strength is concerned the hybrid composites show slightly better behaviour then tensile modulus is concerned" [19]. Similarly, the flexural modulus also decreases from 12967 MPa to 9136 MPa (S-1 to S-3) and increases to 16708 MPa for S-4 composite as shown in Fig. 4.

3.4 Effect of Nano Filler Loading on Impact Strength of Composites

In many engineering applications, composite specimens are subjected to impact loads. Hence, it is essential to examine the impact energy absorption of the composites. Fig. 5 shows the impact energy absorption of nano composites. It shows that the impact energy absorption of nano composites increased with increasing filler loading of composites (S-1 to S-3). "This observed behavior was attributed to the presence of glass fiber at the interfacial regions, which reduced the bond strength between the

fiber and matrix. With the weaker fiber-matrix interfaces, the composite broke into many parts when subjected to impact load, which resulted in more energy being absorbed" [20]. Maximum impact strength was observed for S-3 composite and found to be 494.793 Joule [21,22].

3.5 Effect of Nano Filler Loading on Thermogravimetric Analysis Test (TGA) of Composites

TG analysis determined the thermal stability of composites. In this study, the weight loss of composites began at temperatures ranging from 300ºC to 400°C, signified the removal of moisture. Once composites start to disintegrate, the thermal stability, often known as the first stage decomposition temperature, can be determined. The TGA value found to minimum for S-2 composites as 17732.37 µg and maximum for S-3 composites as 30598.32 µg as shown in Fig. 6. The improved nano egg shell

powder blends with epoxy improved the bonding strength between the fiber and matrix, thereby improving the thermal properties of the composites.

3.6 Effect of Fiber Loading on Dynamic Mechanical Analysis (DMA) of Composites

The storage modulus of S-1 composite is found to be maximum as 7347 MPa and the value is found minimum for S-3 composite as 5895 MPa. Loss modulus found to be minimum for S-3 composite as 1040 MPa and maximum for S-4 composite as 1209 MPa as shown in Fig. 7. The solid-like character of the polymer was determined by the storage modulus. It is difficult to break down the polymer when the storage modulus is higher. Nano egg shell powder with epoxy and better bonding between the fiber and matrix. The significant changes in storage modulus values were noted in the temperature range between 300 to 400ºC.
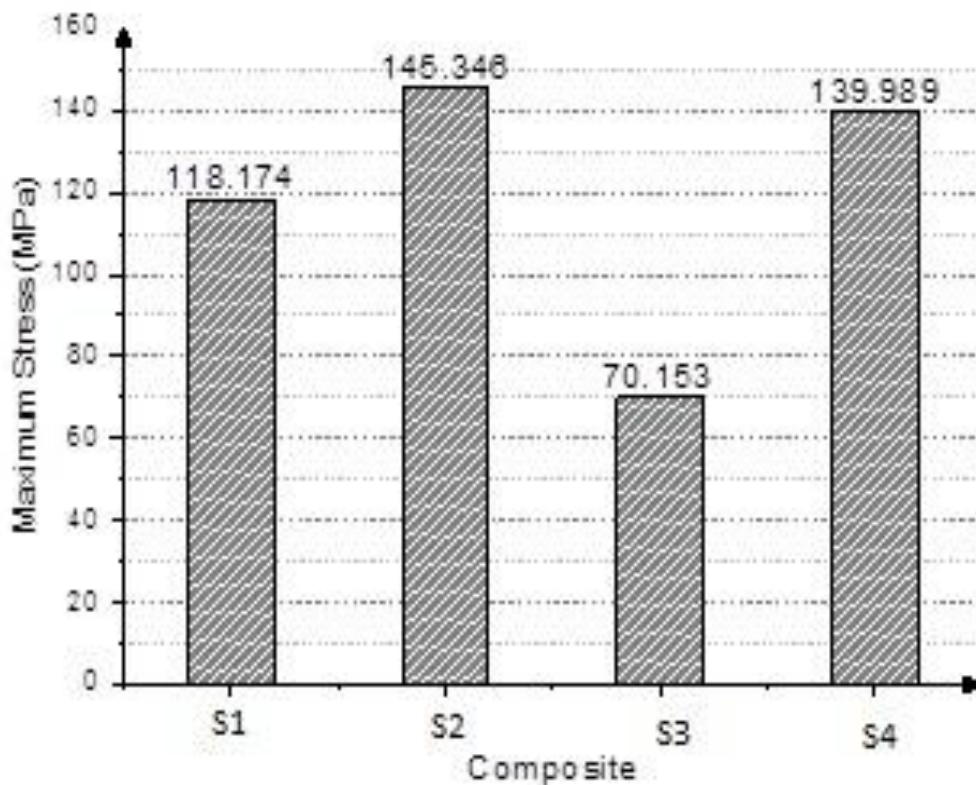

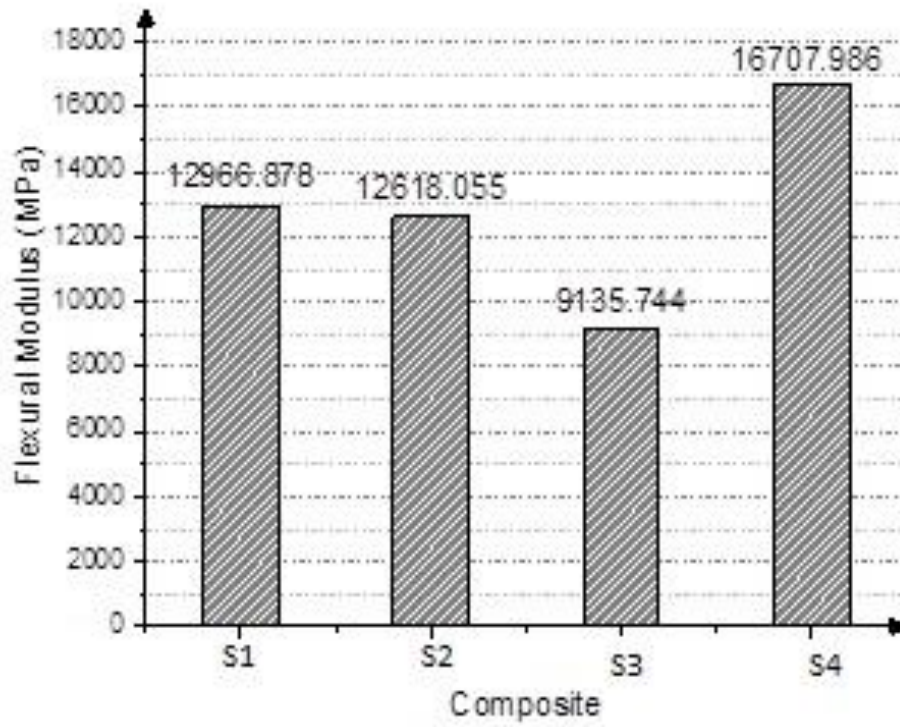**Fig. 3. Effect of fiber loading on flexural strength of composites**

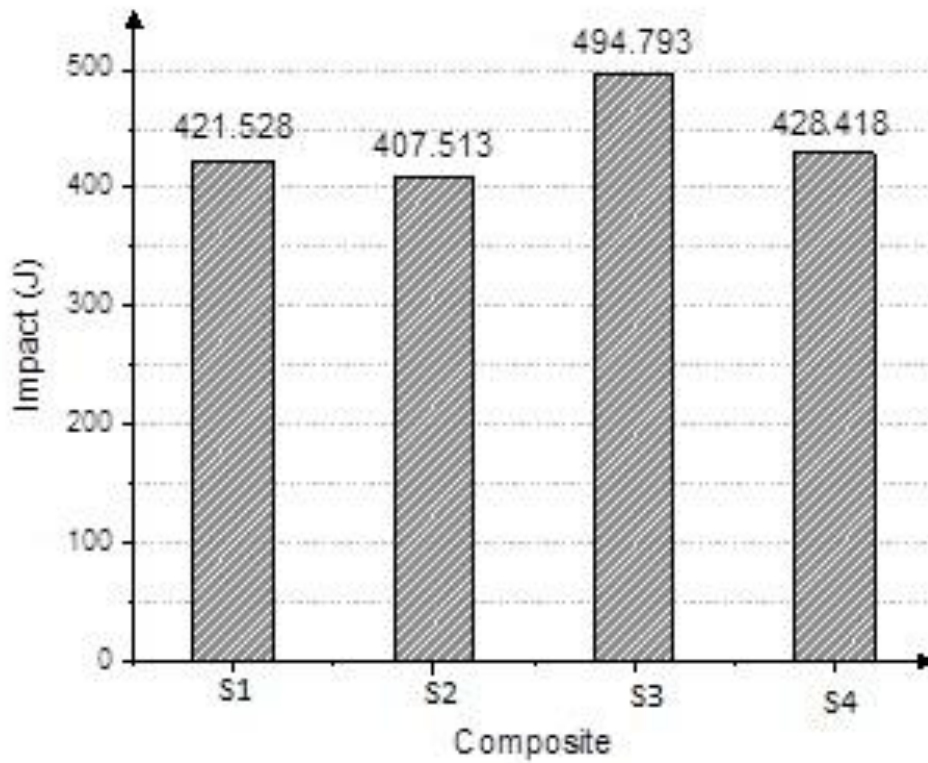**Fig. 4. Effect of fiber loading on flexural modulus of composites**

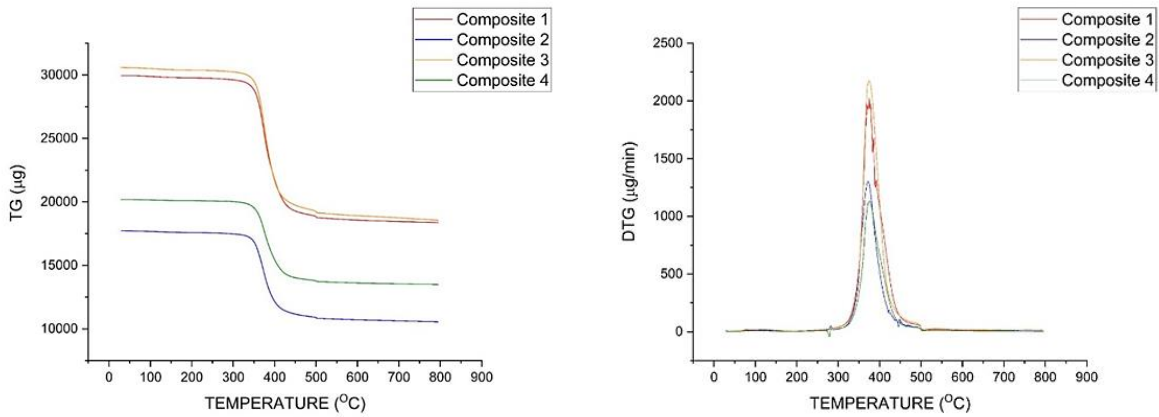**Fig. 5. Effect of nano filler loading on impact strength of composites**

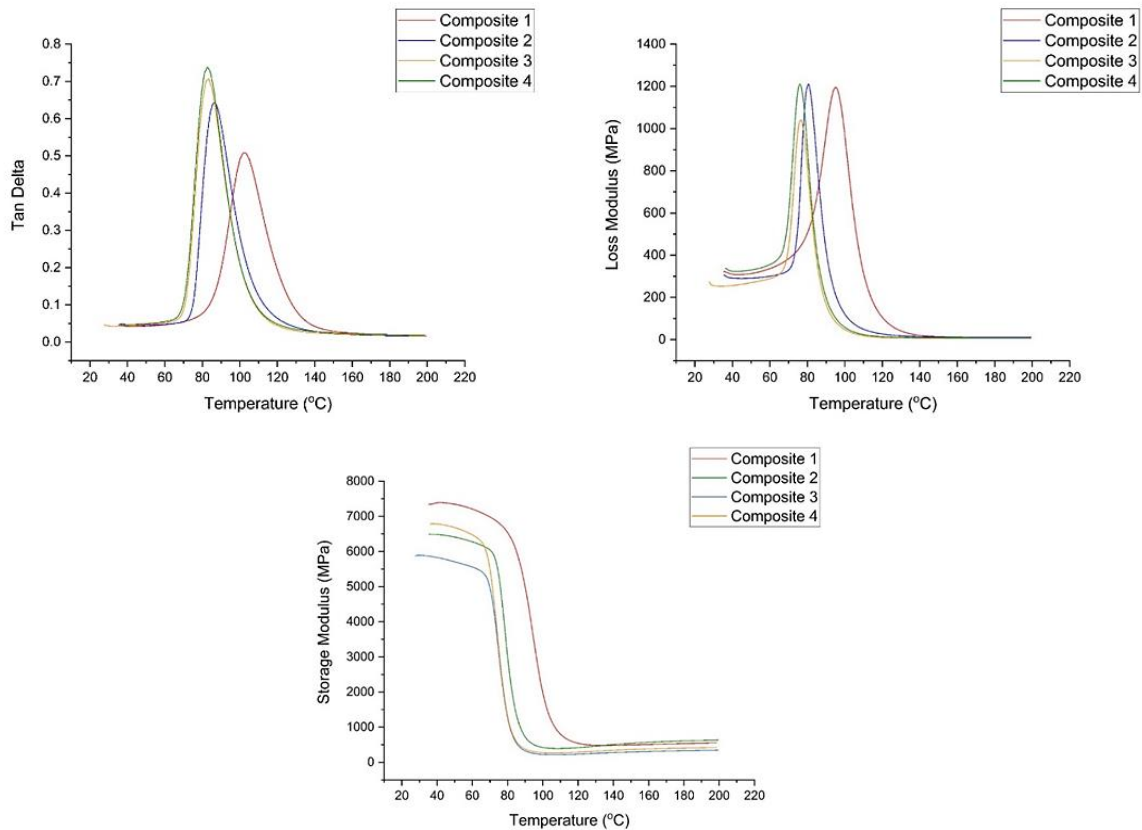**Fig. 6. Effect of nano filler loading on TGA of composites**

Fig. 7. Effect of nano filler loading on DMA of composites

4. CONCLUSION

The experimental investigation on the effect of nano egg shell filler loading on mechanical properties, DMA and TGA of glass-epoxy-nano ESP composites were conducted. Properties such as the tensile strength, tensile Modulus, flexural strength, flexural modulus, impact strength, DMA and TGA were evaluated from various experiments. The experiments lead us to the following conclusions obtained from this study:

1. A new class of epoxy-based composites reinforced with nano egg shell powder (ESP) and glass fibers is developed.

2. As the weight fraction of filler increases in the composites up to S-3, the tensile strength of composite increases up to 138 MPa then, shows a decreasing trend.
3. By increasing the nano egg shell filler loading the flexural strength increases from 118 MPa to 140 MPa respectively.
4. The flexural modulus also decreases from 12967 MPa to 9136 MPa (S-1 to S-3) and increases to 16708 MPa for S-4 composite.
5. The impact energy absorption of nano composites increased with increasing filler loading of composites (S-1 to S-3). Maximum impact strength was observed for S-3 composite and found to be 495 Joule.
6. The TGA value found to minimum for S-2 composites as 17732.37 µg and maximum for S-3 composites as 30598.32 µg.
7. The storage modulus of S-1 composite is found to be maximum as 7347 MPa and the value is found minimum for S-3 composite as 5895 MPa. Loss modulus found to be minimum for S-3 composite as 1040 MPa and maximum for S-4 composite as 1209 MPa.

5. FUTURE SCOPE

The composites developed in this study, incorporating nano eggshell powder as a filler material, exhibit promising mechanical and thermal properties. Considering these favorable characteristics, several potential applications can be recommended: industrial fans, helicopter fan blades, pipes carrying coal dust, desert structures, low cost housing etc. Furthermore, future research can focus on the development of new types of composites using different natural fibers and fillers. By exploring a wider range of materials, researchers can uncover novel combinations that offer unique properties suitable for various applications. The experimental findings from such studies can be analyzed in a similar manner to assess the feasibility and potential of these new composite materials in diverse industries. This continuous exploration and innovation in composite materials hold the key to addressing various engineering challenges and meeting the evolving needs of different sectors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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