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EFFECTS OF CHITIN NANOWHISKERS ON THE THERMAL AND MECHANICAL PROPERTIES OF THERMOSET EPOXY NANOCOMPOSITES

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ABSTRACT

Nanocomposites have emerged as a sought-after class of materials due to their enhanced mechanical, electrical, and optical properties. Organic and inorganic nanofillers have been incorporated into both organic and inorganic matrices to form nanocomposites. Chitin, a naturally abundant polymer, distinguishes itself among these fillers because of its biodegradability, lack of toxicity, and favorable mechanical properties in comparison to other synthetic nanofillers. Chitin nanowhiskers (CNWs), derived from chitin, exhibit significant potential as substitutes for conventional nanofillers. This study delves into the examination of CNWs' impact on the mechanical, and thermal properties of a thermosetting polymer i.e. epoxy resin. Bulk epoxy nanocomposites containing 0-1.5 wt% CNWs were systematically evaluated. Employing a modified slurry compounding method, the composites demonstrated well-dispersed CNWs within the epoxy matrix. However, an increase in CNW content resulted in clustering, diminishing overall properties. The addition of 0.25 wt% CNWs to neat epoxy notably improved tensile strength, impact strength, and flexure modulus. Importantly, all CNW-containing composites exhibited impressive impact strength, especially the 0.75 wt% CNWs-epoxy composites, showcasing enhanced crack propagation resistance and increased chain support attributable to CNWs in the nanocomposites. This research underscores the promising role of chitin nano-whiskers in enhancing the performance of epoxy nanocomposites across various mechanical and thermal parameters.

1 INTRODUCTION

Epoxy resin is a thermosetting polymer and is widely used in adhesives, encapsulations, and coatings [1]. It is inexpensive and very robust in harsh environmental conditions. Its excellent electrical and thermal stability, along with good mechanical performance, make it especially valuable in aerospace applications and advanced composites [1,2]. However, epoxy resin can become brittle and less resistant to bending after extended use [3]. To address this limitation, excessive research has been done incorporating various inorganic nanomaterials like TiO2 and SiO2 into the resin formulation [4]. Various organic fillers are also being used such as carbon nanotubes and graphene [5]. Many bio-based fillers such as nanocellulose crystals and chitin nanowhiskers, lignin nanoparticles have also been employed to increase the overall physical properties of the polymer matrix. Biobased nanomaterials combine the power of nanotechnology with the inherent benefits of renewable resources and low production costs.

While bio-based nanofillers are attracting increasing interest from the scientific community, the potential of nano chitins remains largely unexplored. Chitin, a polysaccharide found in fungi, shrimp shells, and crab exoskeletons [6], can be processed into nano-sized materials with a high modulus (150 GPa) [6]. This makes them promising candidates as nanofillers for polymer matrices, potentially enhancing the overall mechanical properties of composites.

This study explores the utilization of chitin nanowhiskers (CNWs) to mitigate the inherent brittleness of epoxy resins and enhance their mechanical properties. The varied amount of CNWs will be introduced into the epoxy matrix to fabricate nanocomposites devoid of agglomeration. The chemical, thermal, and mechanical properties of resulting nanocomposites are studied and compared with pristine epoxy resins. The research aims to elucidate the potential of CNWs as a sustainable and efficient reinforcement strategy for augmenting the performance characteristics of epoxy resins.

2 MATERIALS AND SAMPLE PREPARATION

Epoxy resin EPON 826 distributed by Miller-Stephenson Chemicals (USA) was used as a polymer matrix. Epikure 3140 (Miller-Stephenson Chemicals, USA) was used as a hardener of epoxy compositions. Chitin nanowhiskers dispersed in ethanol were obtained by Neptune Nanotechnologies Inc. To measure the concentration of CNWs in the ethanol solution, thermogravimetric analysis (TGA) was utilized. The concentration was found to be approximately 8 wt%. All chemicals were employed as received without any further purification steps.

For better dispersion of CNW in nanocomposites, we ultrasonicated the chitin in ethanol. Ultrasonication for 30 minutes, is likely to break up and disperse the material. This was followed by centrifugation for 20 minutes, to separate the chitin nano whiskers from the ethanol. This step increases the homogeneous dispersion of CNW in nanocomposites.

Next, epoxy resin was heated to 50°C to improve its flow properties. Measured amounts (0 to 1.5%) of the centrifuged chitin were then mixed with the warm epoxy using a low-speed stirrer to minimize air bubbles. Hardener was mixed in epoxy with continued stirring. The ratio of epoxy and hardener was taken as (100:13). The mixture was degassed for at least 45 minutes to ensure complete removal of air bubbles.

Bubble-free epoxy mixture was poured into the silicone mold and left overnight at room temperature. This was followed by a final curing step in an oven at 100°C for 24 hours. After cooling to room temperature, the composite was cut into different specimens to do mechanical testing on them.

3 CHARACTERIZATION

3.1 ***Chemical properties*****:** A Thermo Fisher Fourier-Transform Infrared Spectroscopy (FTIR) spectrometer was employed for chemical analysis of the nanocomposites in the range of 400-4000 cm^{-1}.

3.2 ***Thermal properties*****:** TGA was done by a TA Q500 instrument (New Castle, DE) under N_2 flow to analyze the thermal stability of the nanocomposites. The heating rate was set at 10 °C/min from 25 °C to 600 °C.

3.3 ***Mechanical Properties*****:** After preparing the samples using the compound slurry method, mechanical testing specimens were cut from the laser-processed material in the desired form. A universal testing machine (Tinius Olsen H25KS) was used for tensile and flexural testing. Tensile testing was performed on type 4 dog-bone shaped specimens according to ASTM D638 standards with a grip speed of 2 inch/ min. Flexural strength was determined following ASTM D790. IZOD impact strength was measured using an impact tester (Qualitest) following ASTM D256 with the Impact energy of pendulum is 5.5J.

4 RESULTS AND DISCUSSION

4.1: Chemical and thermal analysis of epoxy CNWs nanocomposites:

FTIR was employed for the initial chemical analysis of CNW (Figure 1). Prior to the FTIR measurement, CNW underwent heating at 105°C to remove any residual ethanol. The spectrum reveals several key features associated with chitin's structure. The various bands present from 1027 to 1163 cm^{-1} confirm the presence of the C-O stretching vibrations [7]. Two characteristic absorption peaks are observed at 1660 cm^{-1} and 1627 cm^{-1}. These correspond to the amide I vibrations. Additional bands are present at 1558 cm^{-1} and 1312 cm^{-1}, assigned to the amide II and amide III vibrations, respectively [7]. The bands at 3248 and 3427 cm^{-1} region represent the stretching vibrations of OH and NH groups within the chitin structure.

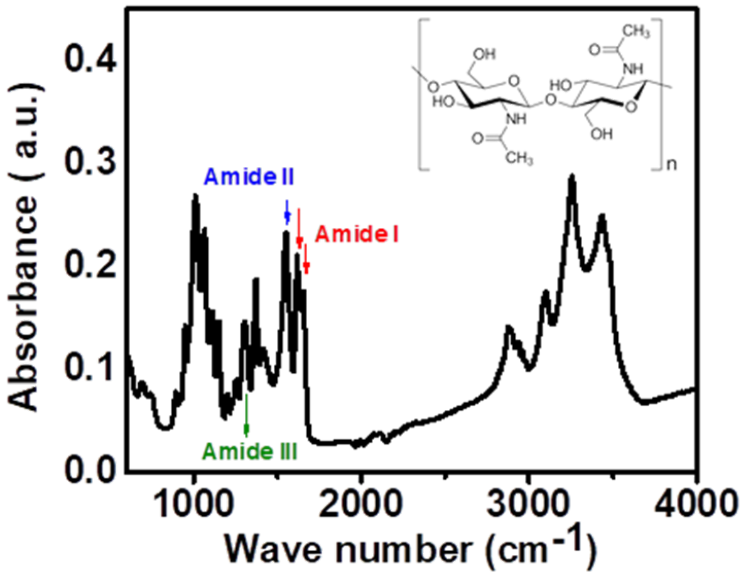

Figure 1. FTIR spectra of chitin nano whiskers. Inset depicts molecular structure of chitin.

Figure 2 illustrates the TGA of epoxy-CNW nanocomposites. The reference epoxy specimen exhibits a multi-step degradation process. The initial weight loss corresponds to moisture evaporation. The second step involves the decomposition of uncured epoxy and hardener residue. The main, rapid mass loss signifies the degradation of cured epoxy around 435 °C [8]. Beyond 500°C, there might be additional degradation due to remaining char oxidation [8]. Interestingly, nanocomposites with lower CNW content (0.1-0.25 wt%) display similar degradation characteristics to the reference epoxy. This is likely due to the low concentration of CNW within the epoxy matrix.

However, when the CNW content surpasses 0.5 wt%, a slight decrease in decomposition temperature is observed. The lowering in degradation temperature becomes more pronounced with further increases in CNW content. The observed reduction in thermal stability at higher CNW loadings could be attributed to nanoparticle agglomeration.

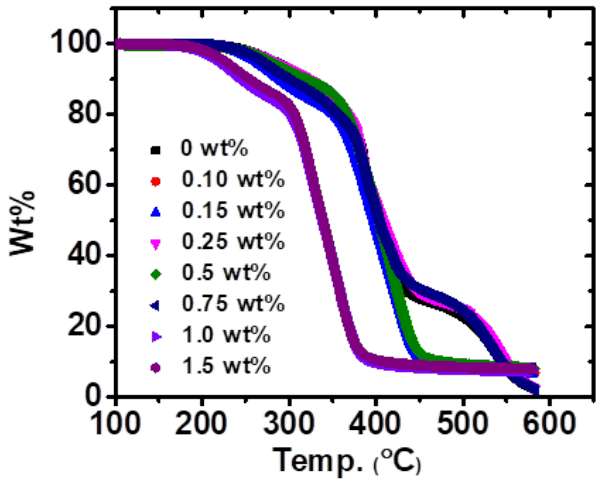

Figure 2. Thermal degradation behavior of epoxy CNWs nanocomposites observed from TGA analysis.

4.2 Mechanical properties of epoxy CNWs nanocomposites

Figure 3 explores the intriguing effect of CNWs on the flexural properties of the epoxy nanocomposites. Flexure modulus is a material's resistance to bending under an applied load. Pure epoxy samples exhibited flexure stress and modulus around 40 and 1250 Mparespectively. It was observed that the initial addition of CNWs leads to a decrease in flexural properties. However, this trend reverses at a critical loading of 0.25 wt% CNW. At this point, both flexure modulus and ultimate tensile stress experience significant improvement, exceeding those of the reference epoxy (without CNWs) by up to 2.5 times.

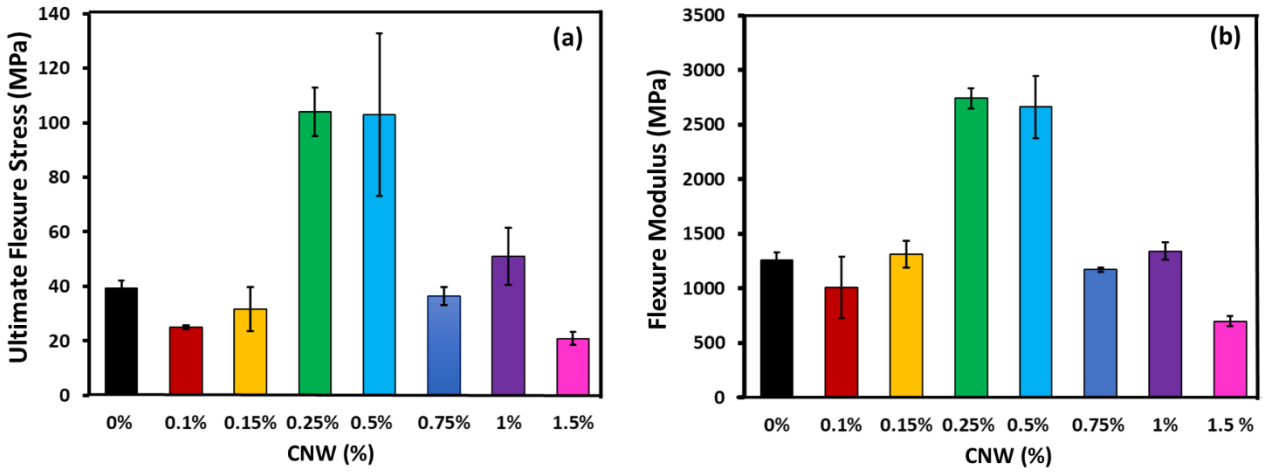

Figure 3. Flexure load behavior of epoxy CNWs nanocomposites: (a) Ultimate flexure stress and (b) Flexure modulus.

The significant improvement in flexural properties observed at CNW content (0.25-0.5 wt%) can be attributed to the inherently high modulus and mechanical strength of the CNWs [5]. When incorporated into the epoxy matrix, CNWs effectively reinforce the composite, leading to enhanced overall mechanical performance. However, exceeding the optimal loading threshold of 0.5 wt% CNW content has the opposite effect, causing a decline in flexural strength. This detrimental effect is primarily attributed to a phenomenon known as agglomeration. At higher concentrations, CNWs tend to clump together, which increases the size of nano whiskers reducing the available surface area for interaction with the epoxy matrix. This limited interaction weakens the composite structure, ultimately leading to a decrease in flexural strength after the optimal loading. This aligns perfectly with the observed trend in the thermal degradation behavior of the nanocomposites (Figure 2). As seen in the figure 2, exceeding a CNW loading of 0.5 wt% leads to a decrease in the overall thermal stability of the material.

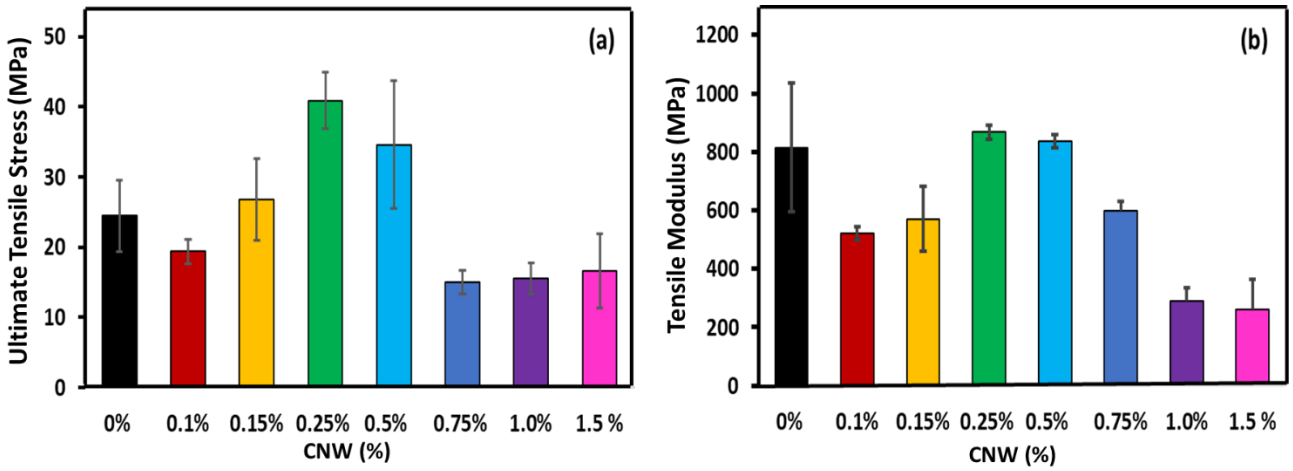

Figure 4. Tensile characteristics of epoxy CNWs nanocomposites: (a) Ultimate tensile stress and (b) Tensile modulus.

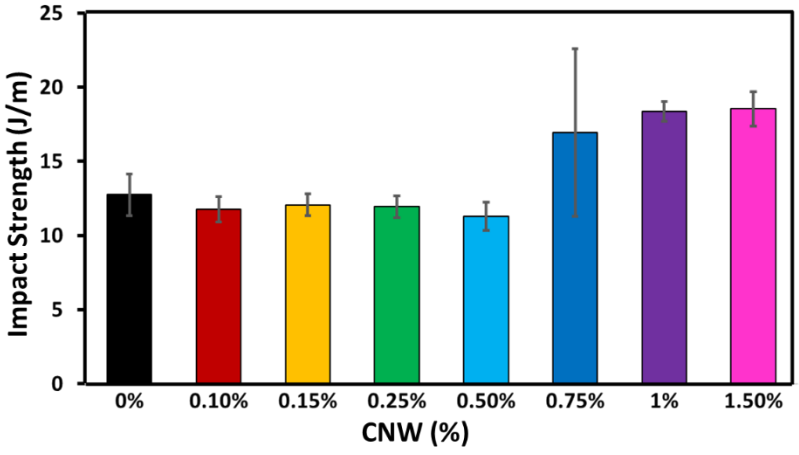

Figure 5. IZOD Impact strength of the epoxy CNWs nanocomposites.

The influence of CNW incorporation on tensile properties (Figure 4) mirrored the observations for flexural properties. Initially, both tensile strength and modulus decreased. However, a significant improvement was observed at the 0.25 wt% CNW loading, with average tensile stress increasing by an impressive 66% and modulus showing a slight increase as compared to the reference sample with 0% CNW. Similar to flexure properties, further increases in CNW content beyond 0.25 wt% resulted in a decline in tensile properties. The decline of tensile results at higher loading can be again correlated with the agglomeration of nanowhiskers.

Figure 5 shows the results of IZOD impact testing on the nanocomposites. We observed that there is not much difference in the impact strength at lower weight percentages of CNW. However, there is a trend of increasing impact strength beyond 0.75 wt% CNW. This enhancement can be attributed to the fact that the introduction of nanowhiskers leads to a higher crack propagation resistance and supports the material under impact.

5 CONCLUSION

This study convincingly highlights the significant reinforcing potential of bio-based chitin nanowhiskers. While thermosetting polymers like epoxy offer excellent thermal stability, their mechanical strength can be limited. Our research demonstrates that incorporating a minimal amount of CNWs (just 0.25 wt%) into the epoxy matrix significantly enhances its mechanical performance, particularly flexural strength without sacrificing the material's thermal stability. These findings position bio-based nanoparticles as strong contenders for polymer reinforcement, paving the way for the development of sustainable, high-performance composite materials with minimal environmental impact.

6 REFERENCES

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