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SYNTHESIS AND CHARACTERIZATION OF BIO-BASED CaCO$_3$/POLYLITE POLYMER NANOCOMPOSITES

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ABSTRACT

Bio-based calcium carbonate nanoparticles were synthesized via size reduction of waste eggshells. Mechanical attrition followed ultrasonic irradiation technique was used for synthesis of these bio-based CaCO$_3$ nanoparticles. The high resolution transmission electron microscopy (HR-TEM) and X-ray diffraction studies indicated that the CaCO$_3$ particles have reduced their sizes and increased porosity by the effect of high power ultrasonic irradiation. Polymer nanocomposites of these Bio-based CaCO$_3$/polylite nanocomposites were fabricated by infusion of different weight fractions of as-prepared CaCO$_3$ nanoparticles into Polylite® 31325-00 resin system using non-contact Thinky® mixing method. As-prepared nanocomposites were characterized for their thermal and mechanical properties. The TEM studies showed that the particles were well dispersed over the entire volume of the matrix. Thermal analyses indicated that these polymer nanocomposites are thermally more stable than the corresponding neat systems. Mechanical tests have been carried out for both polymer nanocomposites and neat resin systems. The tests results showed significant enhancement in the mechanical properties due to the incorporation of the bio-based CaCO$_3$ nanofillers. As-prepared polymer nanocomposite with 2% bio-CaCO$_3$ nanoparticles by weight, exhibited a substantial increase in the compressive strength (14.3%) and modulus (27%) compared to the neat system. These improvements in compressive properties have been observed repeatedly for multiple batches and with a minimum of five specimens tested from each batch.

Keywords: Bio-Based Nanoparticles, Noncontact Mixing, Polymer Nanocomposites.

1. INTRODUCTION

Nanostructured materials have been utilized in the manufacturing of composite materials that are extensively used in many engineering applications due to their remarkable properties. They have a significant role in improving the properties of thermoset and thermoplastic polymers by adding small amounts of nanofillers. These nanofiller-infused polymer systems exhibit enhanced mechanical and thermal properties as compared with neat polymer systems[1, 2]. Recently, growing efforts have emerged to develop new classes of bio-inspired composite materials. The main advantage of these types of materials is that they are environmentally friendly and does not contribute to the depletion of energy resources because they are derived from renewable resources. Reasons for this development also include the continuous increase in the prices of oil derived products along with their destructive effects on the environment [3]. Researchers from the University of Delaware have developed a broad range of chemical routes to use natural soy oils to make polymers and composite materials [4-7]. These materials have economic and environmental advantages that make them attractive alternatives to petroleum-based materials.

Eggshell is a natural bio-ceramic composite with a unique chemical composition consist of high inorganic content (~ 95% of calcium carbonate) and ~4% of organic components [8-10]. The mechanical properties of the eggshells are influenced by the interaction between these organic and inorganic constituents [11]. The distinctive structure of eggshell combined with the substantial availability makes eggshells a potential source of bio-fillers that can be efficiently used for polymer nanocomposites. Researchers have reported the use of eggshells as a reinforcement material in polymer matrices. Toro et al. used different weight fractions of chicken eggshell as bio-filler to improve the properties of polypropylene. The average size of the eggshell particles was ~ 8.4 μm and the surface area was ~ 18 m^2/g. The mechanical properties of eggshell/polypropylene composite showed significant improvements compared to other polypropylene composites reinforced with commercial talc and calcium carbonate fillers. Moreover, eggshell/polypropylene composites demonstrated better eggshell/matrix interface. The formed polypropylene composite contained eggshell reinforcements with weight fractions varied from 20 to 60% [12]. Bautista et al. developed eggshell/polypropylene composites with

improved mechanical and thermal properties compared to polypropylene composite reinforced by traditional mineral particles [13]. Ji and coworkers also reported substantial improvements in the mechanical performance of diglycidylether bisphenol A epoxy resin infused with 5 wt% of chicken eggshell microparticles (average particles size 9.36 μm and 17.4 m^2/g surface area) [14]. Xu and Hanna studied the infusion of 2%, 6% and 10% by weight of eggshell particles in a composite foam material derived from corn starch for food packaging application. The as-prepared composites exhibited enhanced thermal and mechanical properties due to the infusion of micron size eggshell particles [15].

The dispersion of additives and fillers in the polymer matrix is one of the important aspects of polymer processing. The degree with which the nanoparticles can be homogeneously dispersed in the polymer matrix would significantly influence the thermal and mechanical properties of the material. Poor dispersion can lead to diminution of the properties in the resulting material. Researchers have reported a number of nanoparticles dispersion methods include (1) mechanical agitation, such as ball milling or magnetic stirring, (2) ultrasonic vibration, (3) shear mixing, (4) non-contact mixing, and (5) using the dispersing agent. In this investigation we have used the non-contact mixing method. Non-contact mixing is one of the proven techniques for mixing of polymers, powders and fillers.

In the present investigation, we used a non-contact mixing technique for mixing of bio-calcium carbonate nanoparticles synthesized from eggshells with Polylite 31325 bio-based resin polymer. In parallel, a control panel was also fabricated from the neat resin to compare the enhancement or degradation of the thermal and mechanical properties due to bio-calcium carbonate nanoparticles reinforcement.

2. EXPERIMENTAL SECTION

The materials used in this study are bio inspired materials that are obtained from renewable resources. Eggshells were used as raw material for the synthesis of bio-$CaCO_3$ nanoparticles that was used as reinforcement nanofillers. Commercially available Polylite® 31325-00 thermoset resin was used as polymeric matrix. This polymer is a non-promoted, medium reactive, low viscosity unsaturated polyester molding resin that is based on soy bean oil resin and has a green content of ~25%. Polylite® 31325-00 resin was provided by Reichhold, USA, Research Triangle Park, NC. Methyl ethyle ketone peroxide (MEKP) and cobalt naphthanate with 6% metal content (CoNap) were used as the initiator and accelerator respectively in the fabrication of neat Polylite and the bio-nanocomposite systems. Chemicals used in this study were purchased from Sigma-Aldrich, St. Louis, MO. Fabrication of Bio-$CaCO_3$/Polylite 31325 Bio-Nanocomposites. Bio-$CaCO_3$ nanoparticles were synthesized using mechanochemical and sonochemical methods.

In order to investigate the quasi-static compression response of neat Polylite 31325 and bio-$CaCO_3$/Polylite 31325 nanocomposite systems, quasi-static compression tests were performed. Specimens were tested in the thickness direction using servo-hydraulically controlled material testing system (MTS-810) with 100 KN capacity. ASTM C365–57 standard was followed for the quasi-static compression test. The size of test specimens was 12.7 mm in diameter and 25.4 mm in thickness. The test was carried out at room temperature in displacement control mode and the crosshead speed was 1.27 mm/s. In order to maintain evenly distributed compressive loading, each test specimen was sanded and polished with high accuracy to ensure that the opposite faces were parallel to one another. A total of five specimens of each type of material were tested. A software Test Ware-SX was used to develop a program which controlled the test conditions and recorded both the load and crosshead displacement data. The load-deflection data recorded by the data acquisition system was converted to stress-strain curves and used in the calculations of the compressive strength and modulus.

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Scanning electron microscopy (SEM) analysis was carried out using a JEOL JSM 5800 scanning electron microscope to study the fracture surface of samples in response to flexural load at microscopic level. The failed samples of neat Polylite 31325 resin and bio-$CaCO_3$/Polylite nanocomposites were cut into small pieces and placed on a double-sided adhesive conductive carbon tape and coated with a thin layer of gold/palladium mixture (Au/Pd) using a sputter coater Hummer 6.2 to prevent charge buildup by the electron absorption by the specimen.

3. RESULTS AND DISCUSSION

To investigate the crystal structure and impurities presented in the bio-$CaCO_3$ nanoparticles derived from eggshells, XRD analysis was conducted. The XRD pattern of bio-$CaCO_3$ nanoparticles is presented in figure 1a and all the peaks matched very well that of calcium carbonate $CaCO_3$ in the form of calcite (JCPDS card No. 47-1743). These results clearly indicate the high purity of inorganic calcium carbonate in the bio-inspired nanoparticles and no impurities were observed. The

XRD patterns of neat Polylite 31325 resin and bio-CaCO₃/Polylite 31325 nanocomposites are also presented in figure 1. The characteristic peaks in XRD patterns of figure 1(a, c, d and e) match with the $CaCO_3$ JCPDS card No. 47-1743. The XRD curve for neat Polylite resin show a distinctive wide peak at ~ 18° of 2θ as seen in figure 1(b), this peak is assigned to the resin polymer. A comparison of the intensities of the characteristic $CaCO_3$ peaks between the XRD pattern of bio-$CaCO_3$ nanoparticles and the XRD patterns for the as-prepared nanocomposites show remarkable decrease in the peak intensities of all the as-prepared nanocomposites suggesting that the bio-$CaCO_3$ nanoparticles are highly exfoliated in the polymer matrix due to the good dispersion attained by the non-contact mixing technique used in the fabrication process [16].
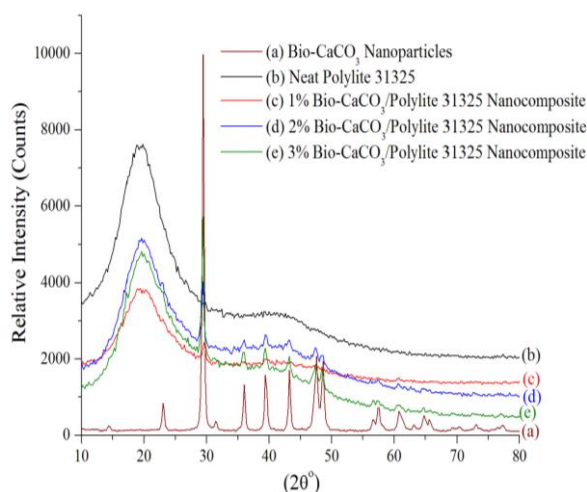

Fig 1. XRD patterns of bio-$CaCO_3$ nanoparticles, as-prepared neat Polylite 31325 and bio- $CaCO_3$/ Polylite 31325 nanocomposites

The mechanical performance of polymeric nanocomposite material depends on the dispersion of nanoparticles and interfacial interaction between nanoparticles and the polymer matrix. To further understand the mechanical behavior of bio-CaCO₃/Polylite 31325 nanocomposites, quasi-static compression tests were carried out for five samples of each neat Polylite 31325 and bio-CaCO₃/Polylite 31325 nanocomposites. Stress–strain curves of 1%, 2% and 3% bio-CaCO₃/Polylite 31325 nanocomposites, along with neat Polylite 31325 resin are shown in figure 10, and the results are summarized in table 4. It is observed from figure 10 that the compressive strength and modulus of 2% bio-CaCO₃/Polylite 31325 nanocomposite are 91.8 MPa and 2618 MPa, respectively. However the neat Polylite 31325 resin compressive strength and modulus are 80.3 MPa and 2061.4 MPa, respectively. These results show 14% increase in strength and 27% increase in modulus as compared to the neat Polylite 31325 resin system. The 2% loading of bio-CaCO₃ nanoparticles shows the highest mechanical properties among the 1% and 3% loading of bio-CaCO₃ nanoparticles. The compressive properties for 1% and 3% loadings of bio-CaCO₃ nanoparticles are lower compared to the 2% loading of bio-CaCO₃ nanoparticles, but they are still

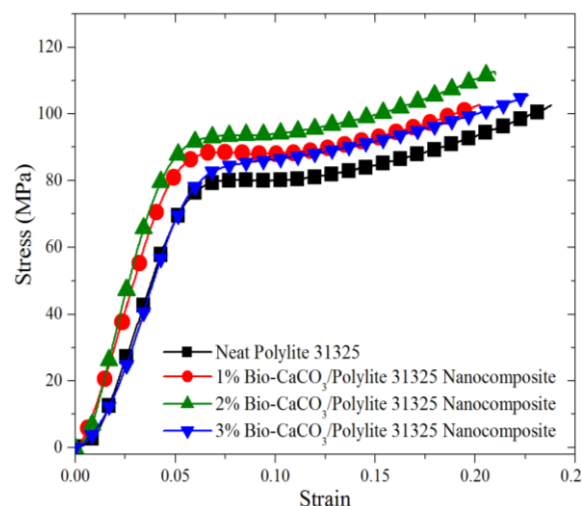higher than the compressive properties for neat Polylite

Fig 2. Quasi-static compression test results for neat Polylite 31325 and bio-CaCO₃/Polylite 31325 nanocomposite

31325 thermosetting polymer. The reason for this can be explained as for the 1% bio-CaCO₃/Polylite 31325 nanocomposite, the amount of bio-nanoparticles is not sufficient to achieve the maximum enhancement of the mechanical properties. For 3% bio-CaCO₃/Polylite 31325 nanocomposite, the increase in the loading of bio-nanoparticle in the resulting bio-nanocomposites will begin to experience more and more particle-to-particle interaction rather than the intended particle-to-polymer interaction. Particle-to-particle interaction will lead to particle agglomerations and poor mechanical properties. These mechanical properties are consistent with the thermal and microscopic properties. Figure 10 also contains a stress plateau region that indicates that these bio-nanocomposites have an ability to absorb compressive damage. These curves are similar to those observed by other researchers [17].

The fracture surfaces of flexure test specimens for the neat Polylite 31325 and bio-CaCO₃ /Polylite 31325 nanocomposites were examined using SEM. During the test, it was observed that an initial crack occurred at the tension edge of all tested specimens. Figure 3 shows SEM micrographs for the fracture surfaces for (a) neat Polylite 31325 resin and (b, c, d) 1%, 2%, 3% bio-CaCO₃/Polylite 31325 nanocomposites, respectively. Neat Polylite 31325 resin exhibits a relatively smooth fracture surface and the SEM micrograph in figure 10(a) indicates a typical fractography feature of brittle fracture behavior, thus, accounting for the low flexure strength of the unreinforced resin. The distance between two cleavage steps is about 10-20 μm, and the cleavage plane between them is flat and featureless. The fracture surfaces of the bio-CaCO₃/Polylite 31325 nanocomposites show considerably different fractographic features. For example, the failure surfaces of all nanocomposite samples are rougher compared to the neat Polylite 31325 samples.
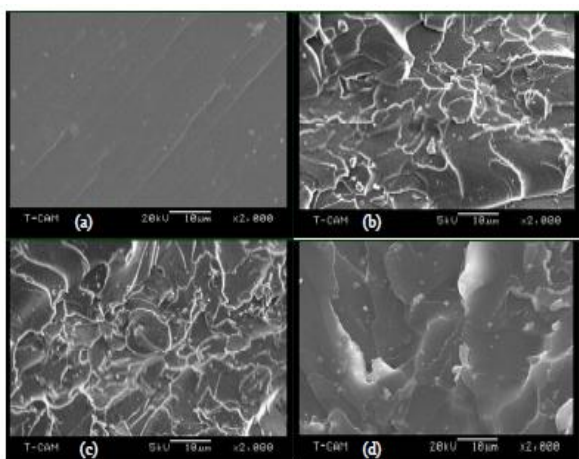
Fig 3. Fracture surfaces for (a) neat Polylite 31325 resin and (b, c, d) 1%,2%,3% bio-CaCO$_3$/Polylite 31325 respectively

Figure 3(b) and 3(c) show the fracture surfaces of 1% bio-CaCO$_3$/Polylite 31325 and 2% bio-CaCO$_3$/Polylite 31325, respectively. The surface roughness increased with higher bio-CaCO$_3$ content. Figures 10(b, c and d) also indicate that the size of the cleavage plane decreased with higher bio-CaCO$_3$ content. The micrographs of the fracture surfaces of the bio-CaCO$_3$/Polylite 31325 nanocomposites show that nanoparticles were uniformly dispersed in the resin. The flat cleavage planes were formed by the network of cleavage steps, and each plane contains an equal amount of the bio-CaCO$_3$ nanoparticles. During the failure process, the crack propagation changed direction as it crossed the bio-CaCO$_3$ nanoparticles. The bridge effect, which prevents crack opening, increased strength in the bio-CaCO$_3$/Polylite 31325 nanocomposites. The SEM micrograph in figure 10(d) shows that the size of the cleavage plane decreased to ~ 5-10 μm after the infusion of the 3% bio-CaCO$_3$ nanoparticles. The decreased cleavage plane and the increased surface roughness imply that the path of the crack tip is distorted because of the bio-CaCO$_3$ nanoparticles, making crack propagation more difficult.

4. CONCLUSIONS

An effective fabrication method have been established to manufacture bio-nanocomposites using bio-inspired CaCO$_3$ nanoparticles derived from eggshells as nanofillers in Polylite 31325 thermoset polymer. XRD studies showed that using the non-contact mixing technique results in a good dispersion of bio-CaCO$_3$ nanoparticles in the polymer matrix and that the bio-nanoparticles were highly exfoliated in the polymer. In addition mechanical tests indicate that there are major improvements in the mechanical properties. The investigation showed that 2% loading of bio-CaCO$_3$ nanoparticles demonstrated superior performance. This significant increase in the materials properties at low loadings of the nanofillers highlights the importance of this new class of bio-based materials to the industry, being particularly beneficial to the automotive sector where the continued need for material weight reduction must always be balanced with consideration of structural requirements.

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