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Mechanical Properties of Poly (lactic acid) Composites Reinforced with $CaCO_3$ Eggshell Based Fillers

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ABSTRACT

Poly (lactic acid) (PLA) bioplastics are recyclable and biodegradable thermoplastics. They are derived from environmentally friendly sources such as potatoes, cornstarch and sugarcane. However, PLA is inherently brittle with low impact strength. The goal of this study is to improve mechanical properties of PLA by the addition of calcium carbonate ($CaCO_3$) fillers. PLA composites were prepared by injection molding conventional limestone (LS) and white chicken eggshell (WES) powders with particle sizes of 63 μm and 32 μm in amounts of 5 wt. %, 10 wt. % and 20 wt. %. Mechanical properties such as, tensile strength, tensile modulus, and Charpy impact strengths were investigated. These three properties were evaluated and the results statistically analyzed using ANOVA F-test. For both particle sizes, the tensile strength decreased as the filler content increased, but was highest for a filler loading of 5 wt. %. In general, the 32 μm powder fillers had better tensile strengths than 63 μm sized fillers. The tensile modulus increased with filler content and was highest at 20 wt. % for both particle sizes. The LS/PLA composites had better toughness than the WES/PLA composites. The particle filler morphology and fractured surfaces were observed by scanning electron microscopy (SEM) and determined to have well dispersed particles with smooth fractured surfaces. Water absorption behavior of PLA/$CaCO_3$ composites were studied by immersion in distilled water at room temperature for 56 days. Virgin PLA absorbed the least amount of water while the water absorption of $CaCO_3$ composites were a function of powder type and content.

INTRODUCTION

For the past two decades, the area of sustainable, green polymers has been growing quickly [1]. A common bio-polymer that has gained interest in the research community for the past 25 years is polylactic acid (PLA) [2]. PLA is a biopolymer that can be recycled or provided with the right environmental conditions can safely degrade back into the environment. Adding conventional calcium carbonate ($CaCO_3$) fillers to polymers is known to have a reinforcing effect [3]. Industrial limestone could potentially be replaced fully or partially with a renewable source such as white chicken eggshells (WES). Eggshells are a source of calcium carbonate as they contain 96-97 % $CaCO_3$ with the remaining 3-4 % consisting of membrane [4]. The majority of investigations on polymer composites containing eggshell fillers were conducted on polypropylene matrices [5]. One study examined the mechanical and thermal properties of thin (50 μm thick) PLA/eggshell films [6] but research using PLA/eggshell composites with sheet thicknesses (> 500 μm) are lacking. This work examines the production of PLA/eggshell polymer composites (sheet thicknesses) using an injection molding process. The filler materials are eggshell and conventional limestone with 63 µm and 32 µm sized powders added in 5 wt. %, 10 wt. % and 20 wt. % loadings. The aim of this work was to investigate the mechanical (tensile and Charpy impact) and physical (morphology and water absorption) properties of PLA with and without the effect of LS and WES fillers.

EXPERIMENT

Polylactide in pellet form was purchased from NatureWork® LLC, Minnetonka, MN USA. It was a mixture of two types of PLA: 4032D and 4043D, both with densities of 1.24 g/cm^3 and melting temperatures of 160 °C and 145-160 °C, respectively. The filler materials were $CaCO_3$ obtained from Imasco Minerals Inc. and white waste eggshells obtained from Burnbrae farms, a local breaking plant located in Ontario, Canada.

The eggshell fillers were prepared by coarse crushing and rinsing with water to remove the eggshell membranes as outlined in our previous study [7]. The particles were then further ball milled to reduce particle size, rinsed and dried. Both conventional and eggshell based $CaCO_3$ were sifted to pass through a 63 µm and 32 µm sieve.

Composites were made with LS and WES in loadings of 5, 10 and 20 wt. % for both particle sizes. The PLA/filler composites were processed by melt-blending in a twin-screw extruder (SHJ-35, Nanjing Yougteng Chemical Equipment Co. Ltd., Jiangsu, China) at a temperature of 175 °C. The injection molding machine, (Shen Zhou 2000) used a temperature profile of 175, 180, 185 and 190 °C from feed zone to die.

The $CaCO_3$ filler morphology and fractured surfaces were observed by scanning electron microscopy (SEM) using a JEOL JSM-6010 LV (Tokyo, Japan) with an operating voltage of 10-15 kV. Prior to analysis, the samples were coated with a thin layer of gold.

Water absorption tests were conducted according to ASTM D570-2010. The sample sizes measured 57.4 mm x 36.4 mm x 2.7 mm (l x w x t) and initially dried at 50 °C for 24 hours. For each batch, three samples were immersed in distilled water at room temperature for a period of 8 weeks (or 56 days). The weight gain (%) was calculated using the dry and wet weights.

An Instron 1137 universal testing machine with a load cell of 10 kN was used to conduct the tensile tests following the guidance of ASTM D638-14. Dog-bone specimens had dimensions of 200 mm x 12.74 mm x 3.25 mm (l x w x t). The specimens used a 50 mm gauge length and were tested at a strain rate of 5 mm/min. For each composite, five samples were tested and averaged. ASTM D6110-10 was used as a guideline for Charpy impact strength (un-notched) measurements using an Instron model 450 MPX. Un-notched Charpy specimens were cut from each center of a tensile dog-bone samples and measured 55-56 mm x 12.74 mm x 3.25 mm (l x w x t). The tests were based on an average of 10 samples.

Statistical analysis was performed using one-way analysis of variance (ANOVA) (F-test) by means of Microsoft Excel 2013. The F-test determined if differences in the mean values were statistically significant.

DISCUSSION

SEM micrographs

SEM images of the LS and WES filler particulates are shown in Figure 1. The morphology of the LS had jagged, cubical edges and was irregular in shape similar to the WES particles. The WES particles displayed a more porous structure as observed by the pin holes in Figure 1 (b). In an eggshell, this porosity allows the entrance of oxygen and removal of carbon dioxide produced by the chicken embryo [8].

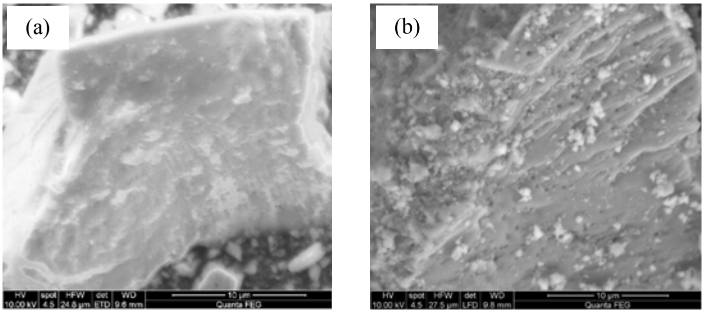

Figure 1. SEM image showing $CaCO_3$ particle surface morphology for (a) LS and (b) WES.

Tensile fractured surfaces are given in Figure 2. Figure 2 (a) shows the smooth brittle fracture of virgin PLA, while the composite surfaces appeared to have smaller, non-uniform fractures exhibiting a more ductile fracture. Figure 2 (b), shows a good dispersion of particles within the PLA matrix. When a 20 wt. % filler was added, the particles were dispersed but some had an affinity to agglomerate as observed in Figure 2 (c). The matrix had large holes indicating particle agglomeration and pullout of matrix.

Fractured Charpy surfaces are shown in Figure 3. Figure 3 (a) shows the fractured surface of virgin PLA, which is analogous to the tensile behavior. Figure 3 (b) and (c) show fractured surfaces for PLA containing LS and WES with 20 wt. % fillers. With the addition of fillers, there is an increased amount of white ridges indicating matrix plastic deformation and improvement in ductility. Both composites show good dispersion, well embedded particles with some particle splitting indicating good bonding between the filler and matrix.

Water absorption

The water weight gain as a function of immersion time for virgin PLA, PLA/LS and PLA/WES composites for different $CaCO_3$ loadings are shown in Figure 4. PLA polymers absorbed the least amount of water due to their hydrophobic nature, while $CaCO_3$ fillers tended to absorb more water due to their hydrophilic nature. The initial curves increased linearly for the first twenty days, then followed a constant plateau which indicated saturation. Water absorption was higher for smaller particles as compared to larger particles for all filler loadings which can be due to the higher surface area of the smaller sized powders. PLA/WES composites absorbed more water than PLA/LS composites for both particle sizes and filler contents. The increased water absorption by the PLA/WES may be due to the more porous surface of WES as shown in Figure 1 (b).

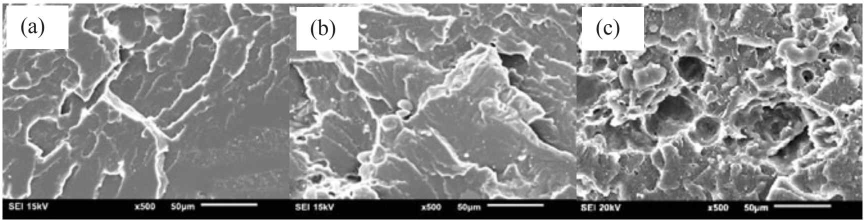

Figure 2. SEM micrographs of tensile fractured surfaces (a) PLA, (b) PLA filled 5 wt. % LS-32 µm and (c) PLA filled 20 wt. % WES-32 µm.

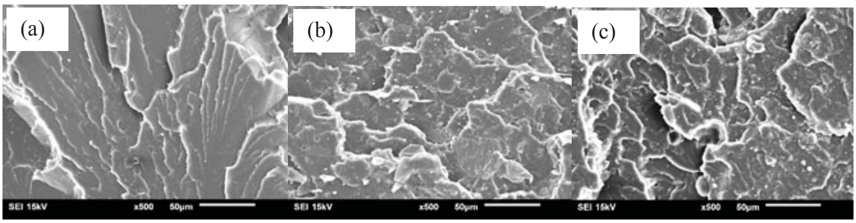

Figure 3. SEM micrographs of Charpy fractured surfaces (a) PLA (b) PLA filled 20 wt.% LS-32 µm and (c) PLA filled 20 wt. % WES-32 µm.

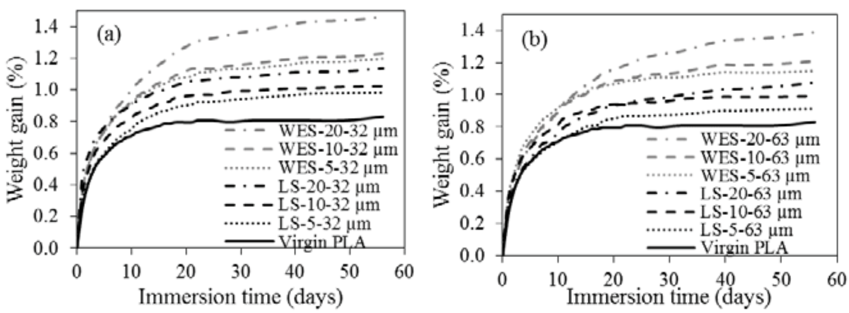

Figure 4. Water absorption of LS and WES filled PLA composites for different filler types and loadings. (a) 32 µm particles and (b) 63 µm particles).

Tensile strength

The tensile strength of the virgin PLA decreased with an increase in filler loading as shown in Figure 5 (a). The 32 µm sized fillers had slightly better strengths than the 63 µm particulate fillers. Bigger particles form larger agglomerates than smaller particles and the size of the agglomerates tends to influence the mechanical properties. Agglomerates result from the tendency of micro-particles to be attracted to one another by electrostatic forces and van der

Waals forces [9]. When a tensile load is applied to low filler composites there is an efficient stress transfer between single particles and the matrix. However, the stress transfer becomes less efficient when particles are agglomerated.

The tensile modulus was increased with the addition of fillers from 10 wt. % to 20 wt. %. as shown in Figure 5 (b). With 5 wt. % of either particle size or particle type, the modulus remained identical to the virgin PLA. At higher loadings of 20 wt. %, the composite stiffness was the highest for both particle sizes, but slightly better for the 32 μm fillers. The composites containing LS performed slightly better than those containing WES. The improved stiffnesses are due to the addition of a filler material with a higher modulus than the virgin PLA.

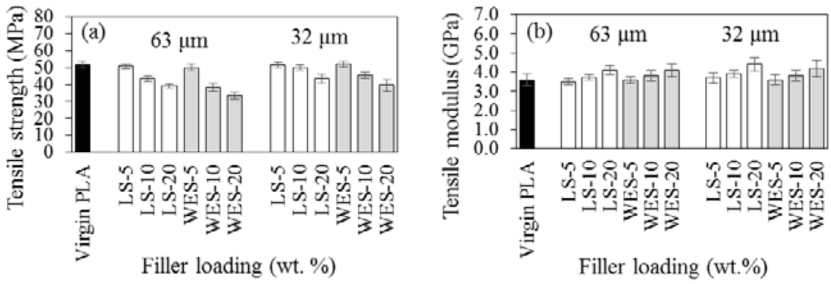

Figure 5. Effect of filler type and loading on the (a) tensile strength and (b) tensile modulus of LS and WES filled PLA composites.

Charpy impact toughness

Figure 6 shows the Charpy impact strength results of PLA composites with various amounts of fillers. The results showed adding 32 μm fillers of LS in any amounts did not significantly increase the impacts strengths, while 63 μm fillers decreased the impact toughness for all composites. In general, the LS/PLA had better toughness than the WES/PLA composites possibly due to a better interfacial bonding between the LS particles and the PLA matrix. During the high impact loading, the poor bonding between particle and matrix, may produce sites where

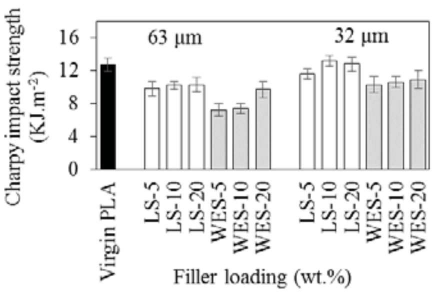

Figure 6. Effect of filler type and loading on Charpy impact of LS and WES filled PLA.

micro-cracks can initiate. Similar to the tensile strength results, the greater reduction of impact strengths may be due to agglomeration of particles in the PLA matrix. Agglomeration leads to reduced bond strength between particles and an overall poorer dispersion of $CaCO_3$ particulates in the PLA matrix.

CONCLUSIONS

The effects of adding conventional and chicken eggshell derived $CaCO_3$ to PLA on the water absorption and mechanical properties were studied. Both filler materials tended to increase the water absorption of the composites due to their hydrophilic nature and water intake was higher for smaller particle size due to their larger surface areas. The tensile and Charpy strengths were better for smaller particle sizes. The tensile strengths decreased when the addition of filler materials were greater than 5 wt. % possibly due to particle agglomeration at higher loadings, but the tensile modulus increased with filler loading. The LS composites had better toughness than the WES composites. Statistical analysis using ANOVA suggested the addition of particles with different sizes and filler loading into the PLA matrix had significant statistical differences in tensile strength, tensile modulus and Charpy toughness. Therefore, the addition of particles and filler loading had an effect on the mechanical properties of the PLA composites. However, the Charpy toughness for the 32 µm particle sizes did not have significantly different mean values. This suggests impact strengths for this particle size did not affect the impact strengths over the virgin PLA. Depending on the application, white chicken eggshells could be used as a prospective filler for PLA composites.

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