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THE EFFECT OF EGGSHELL MEMBRANE REMOVAL ON THE POLYLACTIC ACID/EGGSHELL COMPOSITE CHARACTERISTICS

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ABSTRACT

Mineral calcium carbonate is a common, cheap, and readily available filler material which is applied in polymer composites. Recently, eggshell particulates which contain a high amount of calcium carbonate have been added to polylactic acid (PLA) as an alternative filler which represents an innovative solution to add value to this bio-based eggshell material. The eggshell contains an organic membrane that is well adhered to the calcium carbonate which may present an obstacle to the properties of a PLA polymer composite material. In this study, a low concentration of a chemical treatment (25% bleaching agent for a soaking time of 10 minutes) was applied for complete removal of the eggshell membrane. The aim is to determine if eggshell particles with and without membrane have an effect on the characteristics of the PLA composite. PLA containing 0, 1, and 6 wt. % eggshell loadings (with and without membrane) were manufactured using a twin screw extruder followed by injection molding. Tensile, bending, and water absorption tests were carried out to investigate the effect of eggshell fillers on the PLA composite properties. The results showed that by raising the eggshell (with and without membrane) content, the tensile and flexural strengths of the PLA composites were reduced, although the elastic modulus and flexural modulus increased. Furthermore, the results showed that the presence of membrane on the eggshell particles produced better mechanical properties which suggests eggshell membrane removal may not be required. The water absorption tests showed that PLA composites with a higher content of eggshell fillers as well as eggshell fillers with membrane had higher water absorption characteristics compared to the pure PLA (control). Overall, this study showed that eggshells are promising bio-filler in PLA composites.

1 INTRODUCTION

Mineral calcium carbonate is a common and cheap filler used as a filler in polymer materials, such as polylactic acid (PLA). Adding a filler to PLA has some advantages, such as reduction of the fabrication cost and enhancement of thermal and mechanical properties compared to pure PLA [1,2]. On the other hand, eggshells consist of 96-97 % calcium carbonate and the remaining substance is organic matter referred to as eggshell membrane. It has been hypothesized that since both are calcium carbonate based, eggshells can be an appropriate replacement for commercial mineral calcium carbonate [3]. There are several studies which showed the addition of eggshell fillers to polymer composites was possible. For example, Cree et al. [4] investigated the effect of adding 5, 10 and 20 wt.% of brown eggshell fillers to PLA on the mechanical properties. The results showed an increase in filler content resulted in an improvement of flexural and elastic modulus, but a decrease in tensile and flexural strength [4]. In a related study, Owuamanam et al. investigated the fabrication and characterization of bio-epoxy containing 5, 10 and 20 wt.% eggshell fillers. This study showed similar results observed for PLA/eggshell composites such that the elastic and flexural modulus increased up to the maximum eggshell content of 20 wt.% [5].

Several methods have been reported to remove eggshell membranes from the shells. For example, MacNeil et al. investigated a mechanical method where the eggshells were initially placed in a tank filled with water, and subjected to a turbulent force of a stirrer for membrane removal [6]. In another research, Cusack et al. studied different methods, such as plasma etching, sodium hypochlorite (bleach agent), and hydrochloric acid (HCl). The results showed that plasma etching, and sodium hypochlorite treatments were effective methods for removing the eggshell membrane [7]. In another research, Cree et al. investigated the effect of different bleaching agent concentrations and holding times on eggshell membrane removal and determined 10% bleach for soaked for 48 h or 50% bleach soaked for 10 min was appropriate [3].

This study evaluates the effect of eggshells fillers added to PLA (with and without membrane) at different weight percentages on the mechanical properties and water absorption characteristics. Different bleach agent concentrations and soak times were assessed to determine the lowest bleach concentration and time required for removal of membrane.

2 Materials and methods

2.1 Materials

White chicken eggshells were obtained from a local producer in Saskatchewan, Harman Eggs (a Star Egg Company Limited product). IngeoTM biopolymer 2003D was purchased from NatureWorks LLC, Minnetonka, MN, USA, and used as the matrix for the polymer composites. Furthermore, the term "pure PLA" was used for the 2003D PLA grade.

2.2 Eggshell preparation

The as-received eggshells were washed to remove any residue followed by drying at 105 °C for 24 hours. After an initial drying, eggshells containing membranes were firstly manually crushed in a mortar and pestle. Then eggshells were grounded by a high-speed multifunction grinder (HC-300). To investigate the effect of eggshell without membrane, a chemical treatment method using a household chlorinated Clorox bleaching agent (sodium hypochlorite) was used. For the chemical treatment procedure, 5 gr of ground eggshell powder was added to 25 % bleach solution for a holding time of 10 minutes in the solution. A stirrer was used to maintain solution homogeneity. The samples were rinsed with de water five times to ensure removal of bleach residue. Finally, eggshells were dried at 105 °C for 24 hours before adding to the PLA.

2.3 Preparation of composites

For PLA composite preparation, PLA was blended with eggshell fillers (0, 1 and 6 wt.%) using a twin-screw co-rotating extruder at a temperature of 195 °C. After cooling, the extrudates were pelletized. Prior to the injection molding procedure, all ingredients were dried at 60 °C for 12 hours in a Conair dryer. Then, pellets were used in an injection molding machine (BOY 30A, BOY Machines, Inc., Exton PA, Northwest of Philadelphia, USA) using a temperature profile of 165, 185, 195, and 195 °C from feed to die zone.

2.4 Mechanical tests

2.4.1 Tensile test

The Mark-10 Force Test Stand, Model ESM 1500LC machine with a load cell of 3.75 kN in the Department of Mechanical Engineering, University of Saskatchewan was used to conduct the tensile tests following the guidance of ASTM D638-14. Dog-bone specimens had dimensions of 200 mm × 12.7 mm × 3.2 mm (length × width × thickness). The specimens had 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.

2.4.2 Flexural test

Three-point bending method was considered to determine bending properties. The Mark-10 Force Test Stand, Model ESM 1500LC equipment with a load cell of 3.75 kN was used. The flexural tests were done following the guidance of ASTM D790-17. The sample dimensions were 127 mm × 12.7 mm × 3.2 mm (length × width × thickness) with a span-to-depth ratio of 16:1 as recommended by the ASTM standard. For each composite, five samples were tested and averaged.

2.5 Water absorption test

Samples were cut using a band saw to dimensions of 57.4 mm × 12.7 mm × 3.2 mm (length × width × thickness). The cut edges were then made smooth using a 120-grit silicon carbide paper. Prior to testing, the specimens were dried at 50 °C for 24 in an oven. A water absorption test was performed following ASTM D570–18 where three samples were totally submerged in distilled water at room temperature for 35 days. At 35 days, there was no significant change in weight which suggested the samples were at equilibrium. Before weighing the samples, they were blotted gently with a paper towel to remove surface water [8]. The percent water absorption for different samples was calculated using Equation (1), where W_w and W_d are the wet weight after exposure to water, and the initial dry weight before exposure to water, respectively.

$$Water\ absorption\ (\%) = \left(\frac{Ww - Wd}{Wd}\right) \times 100 \tag{1}$$

3 Results and discussion

3.1 Mechanical properties

3.1.1 Tensile characteristics

Figure 1 shows the tensile strength of the samples investigated in this study. According to Figure 1, by increasing the concentration of eggshell fillers with and without membrane, the tensile strengths decreased. As the filler loadings increased, the possibility of making some aggregation/ agglomeration also increased [3,4]. However, the tensile strength reductions were greater for PLA composites reinforced with eggshells without membrane. Furthermore, PLA composites filled with eggshell containing membrane had higher tensile strengths than PLA composites filled with treated eggshells (without membrane). For example, PLA composites filled with 1 wt.% and 6wt.% eggshell (with membrane) had a higher tensile strengths of 3.24% and 4.85%, respectively compared to composites filled with eggshell without membrane. As shown in Figure 2, by increasing the filler content for both types of eggshell fillers (with and without membrane), the elastic modulus increased, although a considerable difference was observed when 6wt.% eggshell was added to the PLA formulation. The results showed that PLA composites filled with eggshell (with membrane) had a higher elastic modulus compared to similar samples filled with treated eggshell (without membrane). At this loading level, the elastic modulus of PLA composites reinforced with eggshell (with membrane) was 5.72% higher than the samples reinforced with eggshell (without membrane). It appears the eggshell membrane has a positive effect on the tensile characteristics [3,4].

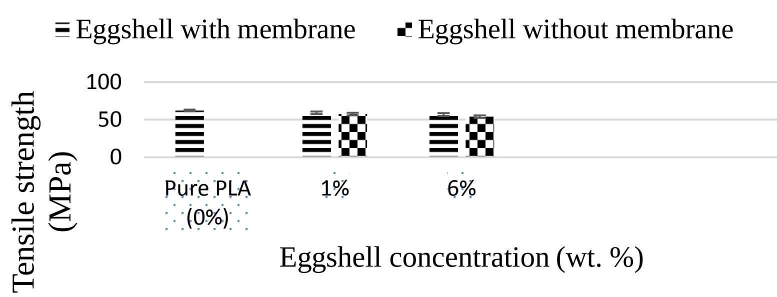

Figure 1. The effect of eggshell filler loading (with and without membrane) on the tensile strength of PLA composites.

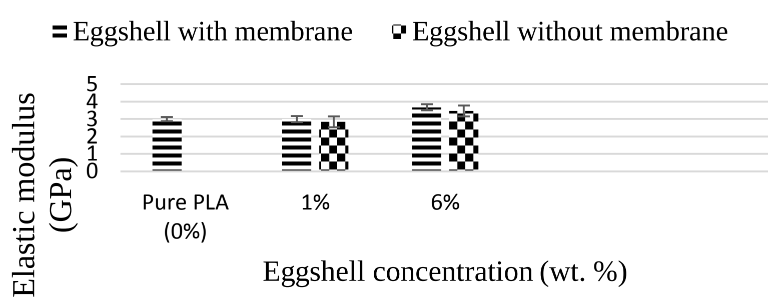

Figure 2. The effect of eggshell filler loading (with and without membrane) on the elastic modulus of PLA composites.

3.1.2 Flexural characteristics

Figure 3 and Figure 4 show the flexural strength and flexural modulus results, respectively. Similar to the tensile property results, by increasing the eggshell filler loading contents, the flexural strengths reduced due to the agglomeration phenomenon, and flexural modulus increased compared to pure PLA. Furthermore, PLA composites reinforced with eggshell filler (with membrane) had higher flexural strengths and modulus compared to the samples reinforced with treated eggshells (without membrane).

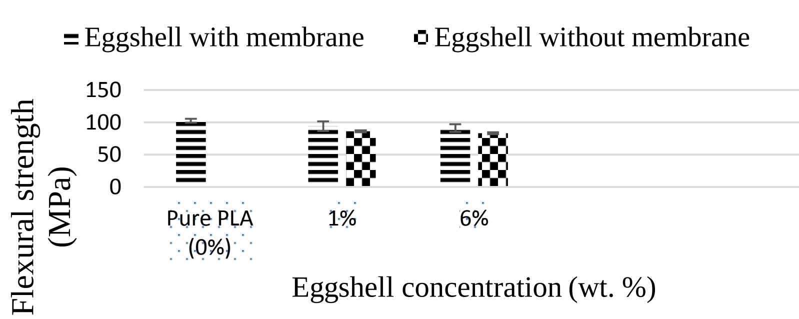

Figure 3. The effect of eggshell filler (with and without membrane) on the flexural strength of PLA composites.

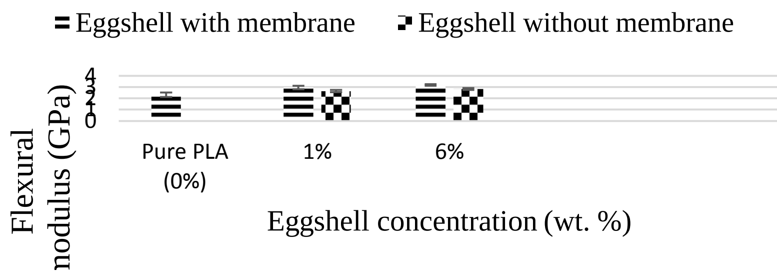

Figure 4. The effect of eggshell filler (with and without membrane) on the flexural modulus of PLA composites.

3.2 Water absorption

Figure 5 and Figure 6 show the water absorption for pure PLA and PLA reinforced with eggshells (with and without membrane). In general, composites reinforced with eggshells (with and without membrane) had a higher % water absorption compared to pure PLA. This can be justified from the hydrophobic characteristic of pure PLA polymer [8,9]. Furthermore, PLA composites reinforced with eggshell fillers (with membrane) had a slightly higher % water absorption compared to eggshell fillers (without membrane) due to the hydrophilic characteristics of the organic membrane, although by increasing the eggshell loading for both types of composites (reinforced with eggshell with and without membrane), increasing % water absorption is observed [8]. This phenomenon is justified by decreasing the amount of pure PLA as a hydrophobic material in different formulations.

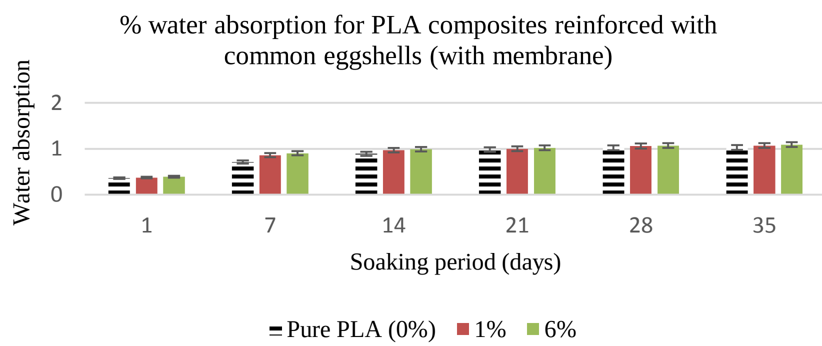

Figure 5. % water absorption of pure PLA and PLA composites reinforced with common eggshell (with membrane).

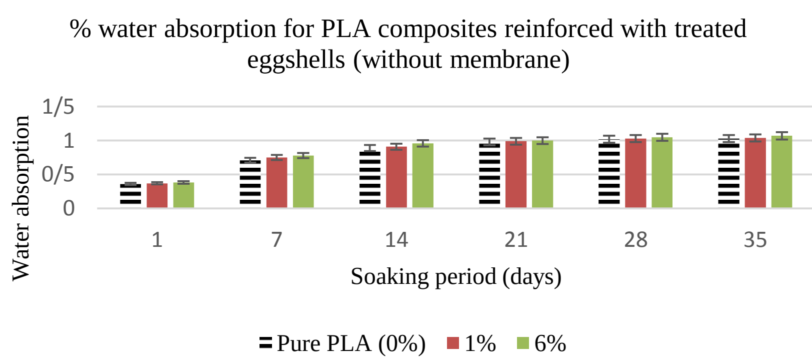

Figure 6. % water absorption of pure PLA and PLA composites reinforced with treated eggshell (without membrane).

4 Conclusion

The results showed that by increasing the eggshell filler loadings, (with and without membrane) the tensile and flexural strengths of PLA composites were reduced due to the filler agglomeration phenomenon. However, the tensile and flexural strengths of PLA composites reinforced with eggshell filler (with membrane) were higher than samples reinforced with treated eggshell fillers (without membrane). On the other hand, by increasing the filler concentration, elastic and flexural modulus increased, although the increment was higher for PLA composites reinforced with eggshells containing membrane. Results showed keeping the organic membrane may be beneficial when added to polymers and a removal process may not be necessary. The water absorption results showed that PLA composites with a higher concentration of eggshell loadings had a higher % water absorption justified by the hydrophilicity characteristic of the organic membrane compared to pure PLA. One of the applications of PLA composites reinforced with $CaCO_3$/eggshell filler is in the biomedical application for the production of tissue scaffolds. Another application is in the construction industry for the production of building materials.

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