The Effect of Treated Filler and Plasticizer on Polylactic Acid Composite Properties Containing Eggshell Particles

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1. Abstract

The circular economy concept and environmental concerns highlight the importance of sustainable materials development in the context of biocomposite materials. Polylactic acid (PLA) is a well-utilized biopolymer, but it requires improvements in its mechanical properties. Herein, mineral calcium carbonate was replaced by avian eggshells as an alternative filler. In this study, the effect of increasing eggshell loading, addition of stearic acid-treated eggshell particles and the use of a plasticizer on the properties of injection molded PLA composites were investigated. PLA composites containing 0, 6, and 12 wt. % eggshell loadings (untreated, stearic acid-treated and stearic acid-treated with a plasticizer (thermoplastic polyurethane elastomer)) were studied. Mechanical tensile, flexure and impact properties and physical water absorption were evaluated. Scanning electron microscopy (SEM) was used to view the fractured surfaces. The results showed that incremental eggshell (untreated and stearic acid-treated) loading in the absence and presence of a plasticizer led to reduction of the tensile, flexural, and impact strengths, due to the formation of aggregation/agglomeration at higher filler loadings. By comparison, the tensile/flexural modulus properties underwent an increase. PLA composites filled with stearic acid-treated eggshell particles have enhanced mechanical properties, as compared to composites containing untreated eggshells due to the positive effect of stearic acid. Furthermore, the addition of stearic acid-treated eggshells in the presence of a plasticizer had reduced tensile/flexure strengths and modulus due to the lubricant role of the plasticizer in the mixture, although the impact strengths increased. On the other hand, PLA composites filled with stearic acid-treated eggshells had lower water absorption (%) due to the hydrophobic nature of stearic acid, whereas the presence of a plasticizer resulted in a higher water absorption (%). According to the SEM results, greater filler loadings (both untreated and treated with stearic acid) indicate the formation of aggregation, which is consistent with the reduction in tensile/flexural strengths. Injection molding of PLA composites were successfully manufactured and findings confirmed the surface treatment of fillers exerted a positive effect on their mechanical properties which serve to support sustainable applications of such composites.

2. Introduction

Mineral calcium carbonate is a common low-cost filler used in polymer materials, such as polylactic acid (PLA). Adding a filler to PLA causes reduction of the fabrication cost and in some cases, enhancement of thermal and/or mechanical properties [1, 2]. Eggshells consist of 96-97 % calcium carbonate and the remaining substance is organic matter in the form of a membrane. Since an eggshell is a calcium carbonate-based substance, it can be an appropriate replacement for calcium carbonate derived from conventional mineral resource extraction [3]. There have been several studies highlighting the effect eggshell fillers to polymer composites. For example, Cree et al. [4] investigated the addition of 5, 10 and 20 wt. % eggshell fillers (without any modifications) to a PLA matrix. The results showed an increase in filler content led to an improvement of tensile and flexural modulus, along with a decrease in tensile and flexural strengths. In a related study, Owuamanam et al. [5] investigated the fabrication of bio-epoxy composites containing 5, 10 and 20 wt. % eggshell fillers. The results showed similar trends where the tensile and flexural modulus increased up to the maximum eggshell content whereas the tensile and flexural strengths reached their highest values at 5 wt. %.

In composite manufacturing, it is well known that particulate fillers pose a challenge by aggregation and agglomeration, attributed to the formation of electrostatic and van der Waals bonding forces between the micron-sized particles [5]. This undesirable phenomenon was reported to reduce mechanical properties such as tensile and flexural strengths [6]. A strategy to reduce aggregation/agglomeration is to provide a surface chemical treatment/coating of the filler material. For instance, Li et al. [7] studied the mechanical properties of PLA composites filled with eggshell particles treated with calcium phenylphosphonic acid. In their study, 5, 10, 15, and 20 wt. % of untreated and chemically treated eggshell powders were added to PLA. The results revealed a maximum in the tensile strength and tensile modulus when 5 wt. % and 20 wt.% of chemically treated eggshell were added to PLA, respectively.

One of the most important drawbacks of PLA is its brittle characteristic where the addition of a plasticizer can improve its ductile behavior [1]. In a related work, Kong et al. [8] studied the properties of PLA composites filled with functionalized calcium phenylphosphonate eggshell particles in the presence of a polyester poly(diethylene glycol succinate) (PDEGS) plasticizer. The composites contained 10, 20, and 30 wt. % of the chemically treated eggshells and 15 wt. % plasticizer. The tensile strength and tensile modulus observed reductions in the presence of a plasticizer due to its higher content (15 wt.%) and plasticizer lubricant effect. In a similar study, Petchwattana et al. [9] investigated the effect of different loadings of a glycerol plasticizer on PLA mechanical properties. The results emphasized an optimized range of plasticizer for maximum tensile and impact properties should be between 10-15 wt. %. Overall, the addition of plasticizer reduced the rigidity and increased the ductility of PLA.

The goal of this research study was to determine the effect of incremental loading of untreated and chemically treated eggshells, in the absence and presence of a plasticizer. Mechanical properties and % water absorption of PLA composites were evaluated. The preliminary results provide insight into the manufacturing and characterization of this PLA/eggshell composite material.

3. Preparation and submission

3.1. Materials

White chicken eggshells were obtained from a local producer in Saskatoon, Saskatchewan, Canada (a Star Egg Company Limited product). Ingeo™ biopolymer 2003D was procured from NatureWorks LLC, Minnetonka, MN, USA. The term "pure PLA" was used for the 2003D PLA grade, which was applied as the matrix for the polymer composites.

3.2. *Eggshell and composite preparation*

The eggshells were thoroughly washed to remove residue and dried at 105 °C for 24 h to remove moisture. After drying, the eggshells were powdered with a high-speed multifunction grinder. The powder was sieved to 25 µm. The ground eggshells were chemically treated with a 2 wt. % stearic acid solution of ethanol and distilled water at a fixed volume ratio (1:1:3). The solution was stirred for 2 h at 80 °C to homogenize. Finally, stearic acid-treated eggshell particles were dried at 105°C for 24 h.

To prepare the composites, pure PLA pellets were blended with untreated and stearic acid-treated eggshells at different loadings with some formulations containing 12 wt. % thermoplastic polyurethane (TPU) as the plasticizer as given in Table 1. A twin-screw co-rotating extruder was used to combine the materials. The extruded filaments were passed through a water bath and pelletized. The injection molding process was used to manufacture the test specimens.

Table 1. *PLA formulations in this study.*

No.	PLA (wt.%)	Untreated eggshell (wt.%)	Stearic acid-treated eggshell (wt.%)	Plasticizer (wt.%)
1	100	0	0	0
2	94	6	0	0
3	88	12	0	0
4	94	0	6	0
5	88	0	12	0
6	94	0	6	12
7	88	0	12	12

3.3. Mechanical tests

3.3.1. Tensile test

The Mark-10 Force Test Stand, Model ESM 1500LC with a load cell of 3.75 kN was used to conduct the tensile tests following the guidance of ASTM D638-14. Dog-bone shaped 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.

3.3.2.Flexural test

Three-point bending method was applied to determine bending characteristics. 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.

3.3.3. Impact test

The Instron model 450 MPX (Instron, Norwood, MA, USA) was used for measuring Charpy impact strength (un-notched) at room temperature, according to the guidance of ASTM D6110-18. Un-notched Charpy specimens were cut using a band saw from untested flexural samples with dimensions 55.0-56.0 mm × 12.7 mm × 3.20 mm (l × w × t).

For all mechanical tests and each formulation, five samples were tested and averaged. Before conducting the mechanical tests, the samples were dried at 50 °C for 24 h in an oven to remove any absorbed moisture. All mechanical tests were applied at room temperature (23°C).

3.4. Scanning electron microscopy (SEM)

Tensile fractured surface morphologies were observed by scanning electron microscopy (SEM) using a JEOL JSM-6010 LV (Tokyo, Japan). All samples were placed on metal stubs and covered with a thin gold coating. The operating voltage was 10 kV.

3.5. Water absorption test

For measuring the water absorption values, a band saw used to cut the samples in dimensions of 57.4 mm × 12.7 mm × 3.2 mm (length × width × thickness). The edges were made flat by applying a silicon carbide paper. First, the specimens were dried at 50 °C for 24 h in an oven to remove the initial moisture. The water absorption test was performed following ASTM D570–22. The samples were totally submerged in distilled water at room temperature for 35 days and covered with parafilm to minimize evaporation. At 35 days, the samples reached equilibrium status. Before weighing the samples, they were blotted gently with a paper towel to remove surface water [5]. 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.

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

4. Results and discussion

4.1. Mechanical properties

Figures 1 and 2 show the tensile strength and tensile modulus results of pure PLA and PLA composites filled with untreated eggshells and stearic acid treated eggshells at different loadings. According to Figure 1, for both filler types, increasing the eggshell loadings led to decreased tensile strengths. When the 6 and 12 wt. % stearic acid treated fillers were added, the composite tensile strengths were reduced by 13% and 17%, respectively compared to pure PLA. As the filler loadings increased, the possibility of aggregation or agglomeration also increased [5]. However, the tensile strength of PLA composites filled with 6 and 12 wt. % stearic acid-treated eggshells was higher than the same samples filled with untreated eggshell particles by about 2% and 3%, respectively. According to Figure 2, the tensile modulus improved by increasing the filler loadings for both types of eggshell fillers (untreated and stearic acid-treated) due to the addition of a filler with a higher tensile modulus (eggshell particles or mineral calcium carbonate) compared to PLA. The results showed that PLA composites filled 6 and 12 wt. % stearic acid-treated eggshells had a higher tensile modulus of 35% and 53%, respectively, as compared with samples filled with untreated eggshells. These observations showed a positive effect of the filler chemical treatment on the improvement of mechanical properties of PLA composites. Stearic acid has been reported to improve filler dispersion and reduce the formation of filler aggregation/agglomeration when added to polymers [10].

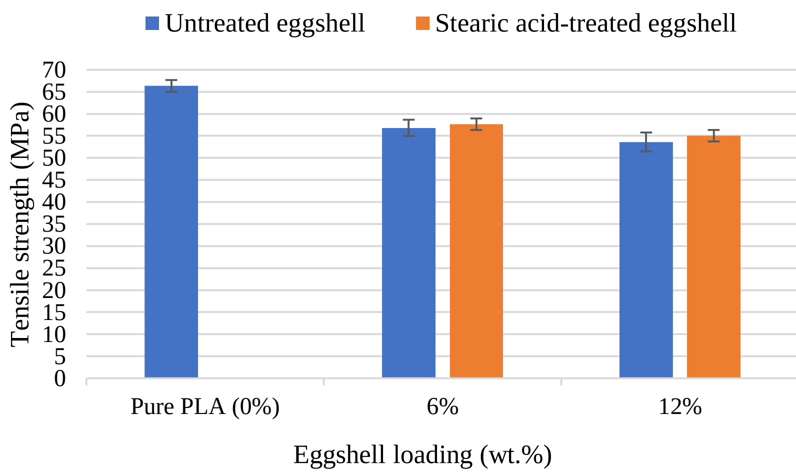

Figure 1. *The effect of filler loading of untreated/stearic acid treated eggshells on the tensile strength of PLA composites.*

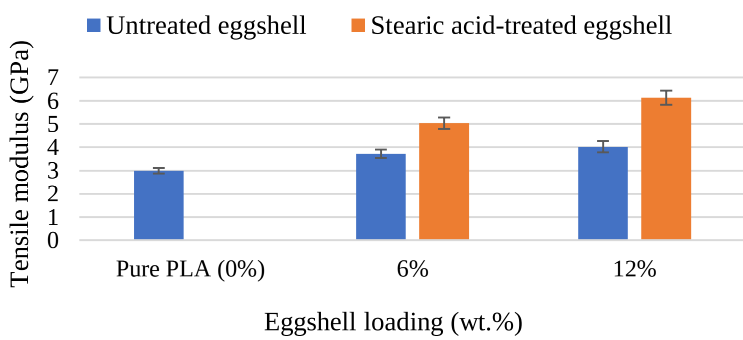

Figure 2. *The effect of filler loading of untreated/stearic acid treated eggshells on the tensile modulus of PLA composites.*

Figures 3 and 4 show the flexural strength and modulus values of pure PLA and PLA composites filled with untreated eggshells and stearic acid treated eggshells at different loadings, respectively. By increasing the loadings to 6 and 12 wt. %, the composites with untreated fillers decreased by 16% and 20%, respectively, while composites containing stearic acid-treated fillers were reduced by 13% and 18%, respectively. The lower flexural strengths of the composites may be due to the process of aggregation or agglomeration. Similar to the tensile modulus results, the flexural modulus increased for all composites due to the presence of filler particles and the prevention of polymer chain mobilities [8]. The composites incorporating 6 and 12 wt. % stearic acid treated fillers showed better flexural modulus of 74% and 97%, respectively, as compared to pure PLA. For both flexural strength and modulus, PLA composites filled with stearic acid-treated eggshell particles were greater than the same samples filled with untreated eggshell particles.

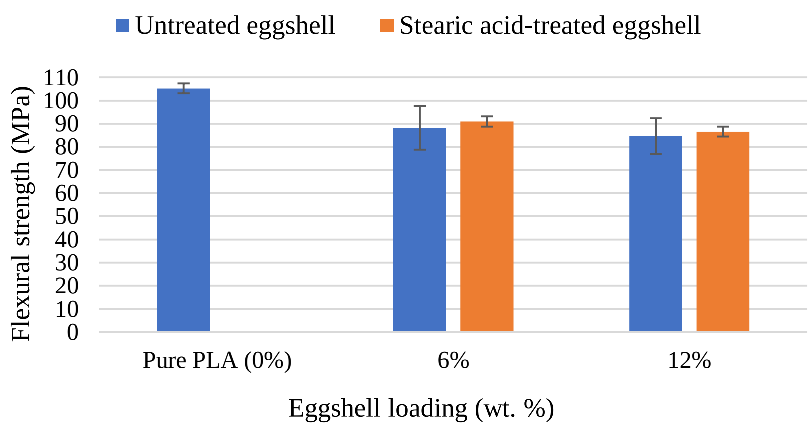

Figure 3. The effect of filler loading of untreated/stearic acid treated eggshells on the flexural strength of PLA composites.

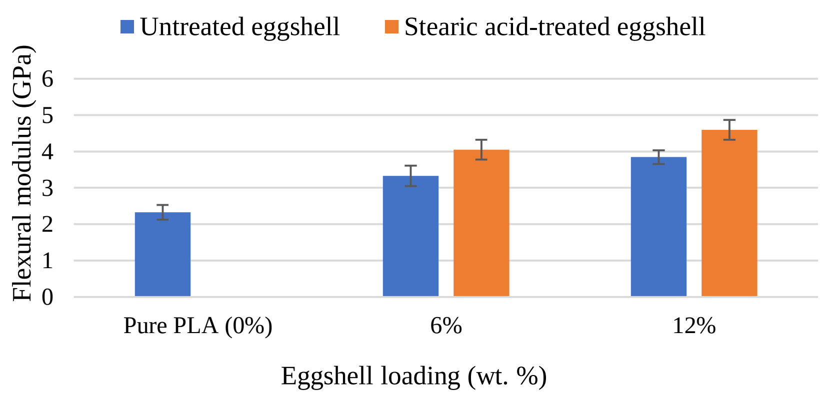

Figure 4. The effect of filler loading of untreated/stearic acid treated eggshells on the flexural modulus of PLA composites.

Figures 5 shows the impact strength of pure PLA and PLA composites filled with untreated eggshells and stearic acid treated eggshells at different loadings.

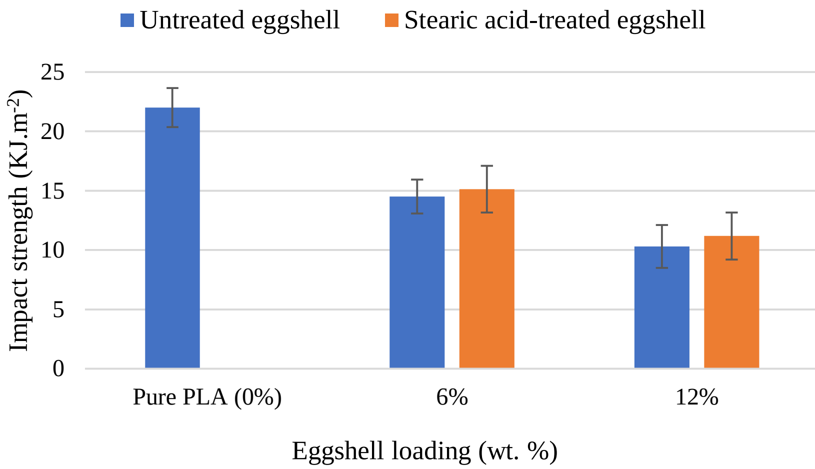

Figure 5. *The effect of filler loading of untreated/stearic acid treated eggshells on the impact strength of PLA composites.*

According to Figure 5, the same decreasing trend was observed for the impact strengths. By increasing both types of filler loadings, the impact strengths decreased due to the reduction of elasticity behavior of polymer chains [8]. However, the impact strength of PLA composites filled with stearic acid-treated eggshells are higher than untreated samples. For example, the impact strengths for the composites filled with 6 and 12 wt.% treated eggshells compared to untreated improved by 4% and 8%, respectively. The higher impact strength values for composites containing stearic acid treated fillers presents a positive effect of stearic acid.

The composites containing stearic acid-treated eggshell fillers had better mechanical properties than composites with untreated eggshell fillers. Thus, a TPU plasticizer was added to PLA composites filled with stearic acid-treated eggshells. According to Table 2, after addition of the plasticizer to PLA (Formulations No. 6 and 7), the values of tensile strength, tensile modulus, flexural strength, and flexural modulus were reduced, as compared to the PLA composites in the absence of a plasticizer (Formulations No. 4 and 5). The presence of the plasticizer increased the polymer chain mobilities which increased the flexibility and reduced the possibility of eggshell aggregation or agglomeration [10]. Since the plasticizer acted as a lubricating agent between the polymer chains, the elastic behavior of the overall composite improved due to the role of polymer chains that absorb additional energy to yield higher impact strengths [8].

Table 2. *The effect of a plasticizer on the mechanical properties of PLA composites filled with stearic acid-treated eggshells.*

No.	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ.m-2)
4	57.6±0.5	5.03±0.5	90.9±2.1	4.05±1.4	15.1±0.8
5	55.0±1.0	6.13±0.6	86.5±3.8	4.59±1.0	11.1±0.4
6	44.8±0.7	4.03±0.9	75.4±0.2	1.34±0.1	16.3±0.7
7	36.7±1.0	5.23±1.0	67.3±1.1	1.48±0.1	13.7±1.0

4.2. SEM results

Figure 6 shows the SEM images of the tensile fractured surfaces of pure PLA (a), PLA composites filled with 12 wt. % untreated eggshells (b), PLA composites filled with 12 wt. % stearic acid-treated eggshells (c), and PLA composites filled with 12 wt. % stearic acid-treated eggshells in the presence of 12 wt. % plasticizer (d). According to Figure 6, pure PLA (Fig. 6a) has a smooth and flat surface morphology due to its brittle characteristic [8]. However, by adding the untreated eggshells (Fig. 6b), stearic acid-treated eggshells without plasticizer (Fig. 6c) and with plasticizer (Fig. 6d) revealed a rougher surface morphology due to the rigid filler [9]. When untreated eggshells (Fig. 6b) are included, aggregation and/or agglomeration was observed, as shown by black circles, due to the electrostatic and van der Waals bonding forces between the micron sized filler particles. Additionally, treatment of eggshells with stearic acid is a way to reduce the possibility of aggregation/agglomeration and provide a better dispersion and adhesion between the filler particles and the PLA matrix [8], which is noted in Figure 6c (see black circles). This phenomenon is justified by the improvement of mechanical properties for PLA composites filled with stearic acid-treated eggshells, as compared to untreated samples. The PLA composites containing 12 wt. % stearic acid-treated eggshells in the presence of a plasticizer (Fig. 6d), had many voids compared to the samples in absence of a plasticizer (Fig. 6c). The role of the plasticizer is to allow polymer chains to slide against each other more readily, which may also serve to increase the free volume of the composite, and provides an account for the reduction in the mechanical properties of the presence of a plasticizer [10].

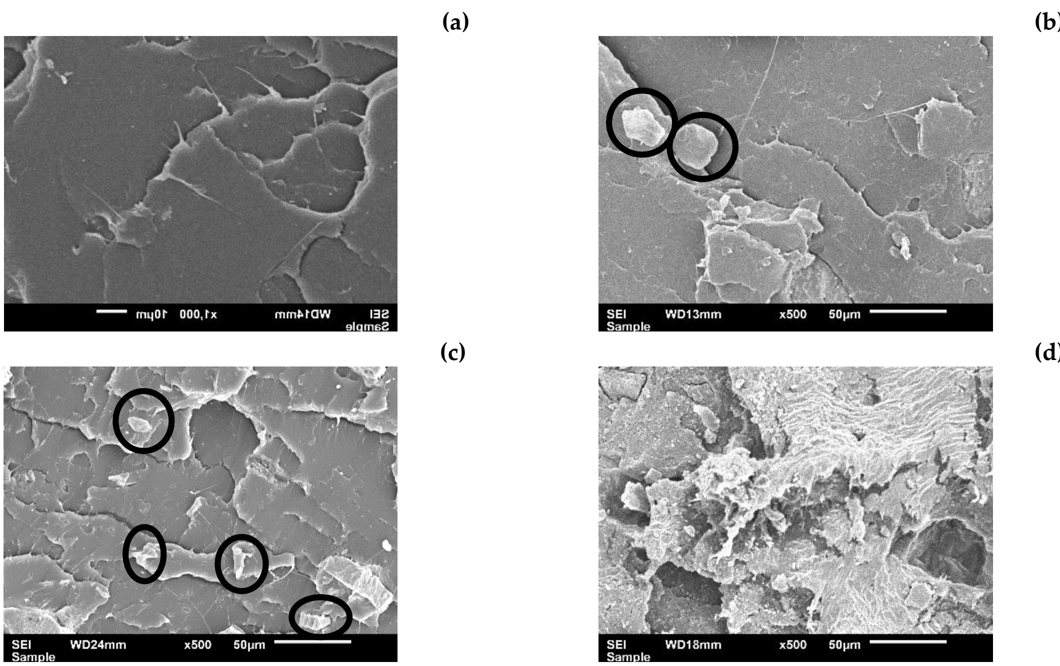

Figure 6. *SEM images of the tensile fractured surface of (a) pure PLA, (b) PLA/12 wt.% untreated eggshells, (c) PLA/12 wt.% stearic acid-treated eggshells, and (d) PLA/12 wt.% stearic acid-treated eggshells in the presence of 12 wt.% plasticizer (TPU). The magnification was ×500.*

4.3. Water absorption values

Table 3 shows the water absorption results of pure PLA, and PLA composites containing 12 wt. % eggshell filler with and without stearic acid treatment, along with composites containing stearic acid treated eggshells incorporating a plasticizer. During the soaking periods, PLA always had a lower absorption than composites filled with 12 wt. % untreated eggshells. However, the level of water absorption increased more for composites with untreated eggshell loadings. This concurs with the hydrophobic nature of the stearic acid coating [9], and the hydrophilic nature and porous structure of the eggshell filler [10]. After 35 days of soaking, PLA composites filled with 12 wt. % untreated eggshell had a water absorption of 1.19% which compare favorably to the results of a previous study where a 1.15% water absorption was reported for PLA composites that contain 10 wt. % eggshells [5]. The PLA composites filled with stearic acid-treated eggshell particles had lower water absorption compared to composites with untreated eggshell particles. This can be justified by the hydrophobic nature of the long hydrocarbon chain of stearic acid [10]. Additionally, PLA composites filled with stearic acid-treated eggshells in the presence of a plasticizer had higher water absorption, as compared to samples without plasticizer. The plasticizer, TPU contains polar functional groups such as carbonyl which are highly polar, which increases the water absorption for such PLA composites [8].

Table 3. *Water absorption (%) results for pure PLA and PLA composites.*

Soaking days	Pure PLA	PLA + 12 wt.% untreated eggshell	PLA + 12 wt.% stearic acid-treated eggshell	PLA + 12 wt.% stearic acid-treated eggshell + 12% plasticizer
1	0.364±0.5	0.503±1.1	0.342±0.4	0.512±1.7
7	0.712±0.8	0.981±1.3	0.706±0.5	0.960±2.6
14	0.893±1.2	1.03±2.4	0.781±1.8	0.986±1.9
21	0.981±0.3	1.06±1.7	0.904±1.1	1.14±0.8
28	1.02±2.0	1.14±1.2	0.930±0.9	1.16±1.4
35	1.03±1.4	1.19±1.9	0.940±0.7	1.16±0.3

5. Conclusion

In this research study, the effect of eggshell loadings, stearic acid filler treatment and addition of a plasticizer to a PLA matrix were evaluated for their mechanical properties (tensile/flexural strength, tensile/flexural modulus, and impact strength) and water absorption. The results showed by increasing the loadings of untreated and stearic acid treated eggshells, the tensile, flexural, and impact strengths were reduced, attributed to the formation of aggregation or agglomeration, whereas the tensile and flexural modulus increased. Additionally, PLA composites filled with stearic acid-treated eggshells had greater mechanical properties compared to the samples without treatment. The stearic acid coating had a positive effect for reducing agglomeration and providing a better adhesion between the filler particles and the PLA matrix. Composites filled with stearic acid-treated eggshells in the presence of a plasticizer had lower mechanical properties (tensile and flexural characteristics) due to the lubricant behavior of the plasticizer among the polymer chains. However, the impact strengths increased due to higher energy absorption from improved flexibility. PLA composites filled with stearic acid-treated filler particles had lower water absorption than composites filled with untreated eggshells due to the hydrophobic characteristic of stearic acid. In contrast, greater water absorption was observed when the plasticizer was added since TPU is hygroscopic in nature. Although the mechanical properties were lower than pure PLA, the final application will dictate the strength requirements. The composites developed in this study could find various applications, such as in automotive, construction and building industries due to their environmental benefits.

6. References

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