INVESTIGATION ON THE PROPERTIES OF BROWN EGGSHELL POWDER FILLED POLY(LACTIC ACID) COMPOSITES

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ABSTRACT

Limestone (LS) or calcium carbonate is used as a low cost filler in polymer materials. Waste eggshells are generated by industrial breaking plants and hatcheries which have the potential to be processed into a sustainable material rather than disposal to landfills as is the current practice. The effect of adding various amounts of LS powder and brown chicken eggshell (BES) powder on the properties of poly(lactic acid) (PLA) was investigated. Composites were prepared by injection molding PLA with 5 wt. %, 10 wt. % and 20 wt. % of LS and BES fillers having particle sizes of 63 µm and 32 µm. Mechanical properties such as tensile and flexural tests were conducted. Typically, the 32 µm powders had better properties than the 63 µm sized fillers. The mechanical properties varied depending on the filler weight ratio. Greater than 5 wt. % LS or BES fillers did not improve the tensile strengths, while the flexural strength increased for LS only. The composite tensile and flexural modulus were superior to pure PLA and LS/PLA when 10-20 wt. % BES were added as fillers. The powder morphology and fractured surfaces were examined by scanning electron microscopy (SEM). Both powder particles were similar in morphology with varied particle size and irregular shapes possibly due to the grinding process. The particle fillers were well dispersed throughout the matrix. Room temperature water absorption behavior of PLA/calcium carbonate composites were studied by immersion in distilled water for fifty six days. The water intake of the unmodified PLA was lower than the calcium carbonate composites and were dependent on the nature of the powder and weight ratios. In general, flexural surfaces showed larger plastic deformation than tensile fractured surfaces.

1 INTRODUCTION

Conventional petroleum based plastics are used in numerous applications. An import use is in packaging products for a one time consumer use such as, thin films for bags, plastic bottles, trays, cups and utensils. In general, most of these items will end up in landfills and take thousands of years to decompose. In the packaging industry there is a trend to use greener packaging made from renewable resources. Interestingly, poly lactic acid (PLA) is a bio-degradable thermoplastic polymer (bio-plastic) considered to be a promising alternative to petroleum based plastics. PLA is produced from bio-mass such as corn, potatoes and sugar cane which are renewable and are sustainable sources [1]. Under normal conditions, PLA is robust and it can be recycled, however when it is exposed to a combination of oxygen, moisture and organisms it will break down into carbon dioxide, water and inorganic compounds and leaves no toxic residue [2]. PLA was invented in 1932 [2], but its use in industrial packaging applications was as early as 2003 [1].

Calcium carbonate ($CaCO_3$), is a common mineral filler obtained from mining. This low cost filler has shown to reduce the overall cost of polymers while maintaining or enhancing its properties [3]. In keeping with sustainable materials, chicken eggshells contain a pure form of $CaCO_3$ (calcite) in the range of 96-97 wt. % with a remaining thin organic membrane [4]. Eggshells are a waste material from homes, restaurants, hatcheries and industrial breaking plants. However, the latter produces thousands of eggshells per week. For example, the egg breaking plant, Egg Processing Innovations Co-operative (EPIC) located in Lethbridge, Alberta, Canada process 180,000 dozen eggs per week. These waste eggshells could be recuperated, ground into powder and used as polymer fillers. Recently, a study examined the use of eggshell powder in a polypropylene matrix and determined the eggshell waste could be used as filler material where it could partially or fully replace convention $CaCO_3$ [5]. Another study added 25 µm eggshell particles to PLA to produce thin films. The tensile strength and modulus of the composite films were found to be higher than those of PLA and increased with eggshell powder content up to 4 wt. % [6].

This study investigates the use of injection molding to produce green PLA/$CaCO_3$ composite materials. The aim of this work was to evaluate the morphology, water absorption, tensile and flexural properties of unmodified and modified PLA containing conventional limestone (LS) and BES fillers.

2 EXPERIMENTAL

2.1 Materials

A proprietary mixture of Polylactide in pellet form was obtained from NatureWork® LLC, Minnetonka, MN USA. Both polymers have a density of 1.24 g/cm^3 and melting temperatures of 160 °C and 145-160 °C, respectively. Filler materials were conventional limestone purchased from Imasco Minerals Inc., while brown eggshells were obtain from a local hatchery, Maple Lodge Farms Hatchery division in Stratford, Ontario, Canada.

2.2 Eggshell Preparation

The eggshell waste was initially coarse crushed and rinsed with water to remove the membrane from the eggshells as was conducted in an earlier study [7]. A ball milling step was added to further reduce the particle sizes, followed by a rinsing and drying step. The as-received and final eggshell powdered sample is shown in Figure 1. Both conventional and eggshell limestone based calcium carbonates were sieved to particle sizes of 63 µm and 32 µm.

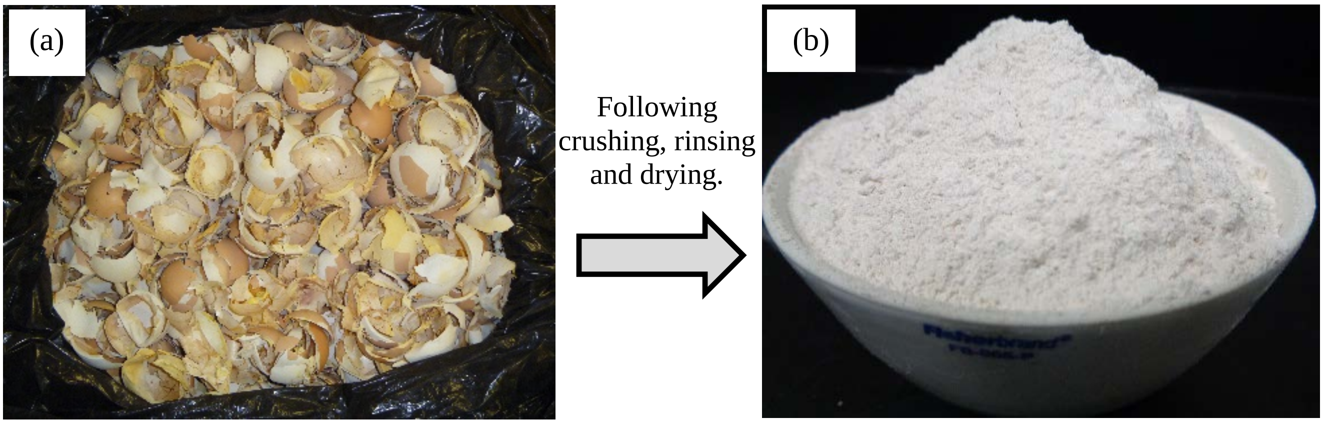

Figure 1. Preparation of $CaCO_3$ filler (a) as-received brown waste eggshells and (b) powdered sample.

2.3 Composite Preparation

Samples for water absorption and mechanical characterization were prepared by a three-step manufacturing process. Initially the ingredients (PLA and fillers) were mixed in a twin-screw extruder (SHJ-35, Nanjing Yougteng Chemical Equipment Co. Ltd., Jiangsu, China). The extruder was operated at a temperature of 175 °C and a screw rotational speed of 16 rpm. Secondly, the plastic strands leaving the extruder were pelletized. The pellets were then dried at 80 °C for 4 hours prior to injection molding. The PLA/filler composites were made using an injection molding machine, (Shen Zhou 2000) with a temperature profile of 175, 180, 185 and 190 °C (feed zone to die zone). The amount of fillers added to each PLA composite is shown in Table 1.

Table 1. Filler loadings in PLA composites

Composite	Calcium carbonate content (wt. %)	PLA (wt. %)
PLA	0	100
LS-5	5	95
LS-10	10	90
LS-20	20	80
BES-5	5	95
BES-10	10	90
BES-20	20	80

2.4 Scanning Electron Microscopy

The scanning electron microscope (SEM), model JEOL JSM-6010 LV (Tokyo, Japan) was used to observe the filler particle morphology and fractured surfaces. Images were taken at an operating voltage of 10-15 kV. To improve the conductivity of the calcium carbonate particles and composites, the specimens were sputter-coated with gold.

2.5 Water Absorption

The water absorption test (ASTM D570-2010) samples measured 57.4 mm x 36.4 mm 2.7 mm (l x w x t). Three samples were immersed in distilled water at room temperature for 56 days. Prior to immersion, the specimens were dried at 50 °C for 24h and stored in a desiccator. The amount of water absorbed was determined by weighing the samples to the nearest 0.001 g at constant intervals. Before taking each measurement the samples were removed from the water and paper towel was used to remove surface water only and not the absorbed water. The percentage of water absorption was determined by equation (1) using the differences in dry and wet weights, where W is the weight gain (%) and W_1 and W_2 are the dry and wet weights, respectively.

$$W\,(\%) = [(W_2-W_1)/W_1] * 100\ \% \tag{1}$$

2.6 Mechanical Characterization

The following tests were carried out to evaluate the properties of the PLA composite materials; tensile strength, tensile modulus, flexural strength and flexural modulus. Before testing, the samples were conditioned at 23 ± 3°C and a relative humidity of 50 ± 4 % for more than 40 hours. Tensile strength was evaluated at room temperature according to ASTM D638-14 using an Instron 1137 universal testing machine with a 10 kN load cell and a strain rate of 5 mm/min. The results are an average of five specimens. Flexural, three-point loading strength tests were performed according to ASTM D790-15 using an Instron 1137 universal testing machine equipped with a 250 N load cell. The support span length was 50 mm in order to maintain a support span-to-depth ratio of not less than 16:1. The specimens were cut from the center of a dog-bone sample and measured 65 mm x 12.74 mm x 3.25 mm (l x w x t). The rate of the crosshead was calculated to be 1.30 mm/min. Five specimens were tested for each composite at room temperature and averaged.

3 RESULTS AND DISCUSION

3.1 Scanning Electron Microscopy Analysis

Figure 2 shows SEM images of LS and BES based powder fillers. Both LS and BES showed similar angular, irregular and elongated shapes with varying particle sizes due to the crushing process. As shown in Figure 2 (b), the BES particles had more holes on its surface than the LS particles, which originates from the structure of the eggshell [8].

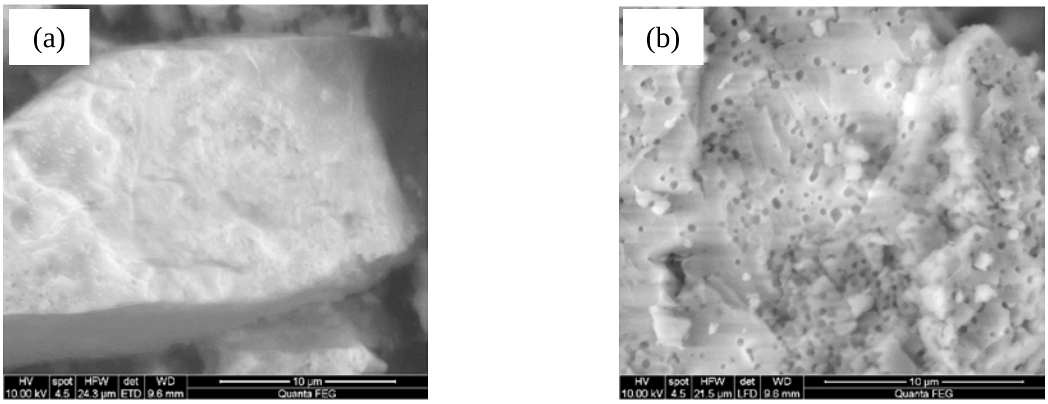

Figure 2. SEM showing particle morphology of (a) LS and (b) BES.

Tensile fractured surfaces are given in Figure 3. The pure PLA polymer has uniform, flat plate-like surfaces indicative of brittle fracture as shown in Figure 3 (a), while the composites have altered fractured surfaces with more, smaller discontinuous plates displaying increased ductile fractures. In both composites, the fillers appear to be well dispersed throughout the matrix, however there is possibility of increased agglomeration in some areas for the higher filler loading. In Figure 3 (b), there are no spaces between the BES fillers and the matrix which implies good bonding. In addition, some particles are fractured which also points towards good adhesion with the matrix. The BES composite in Figure 3 (c), has some empty void spaces where particle were entrenched in the matrix prior to loading, and have been dislodged after application of a tensile load.

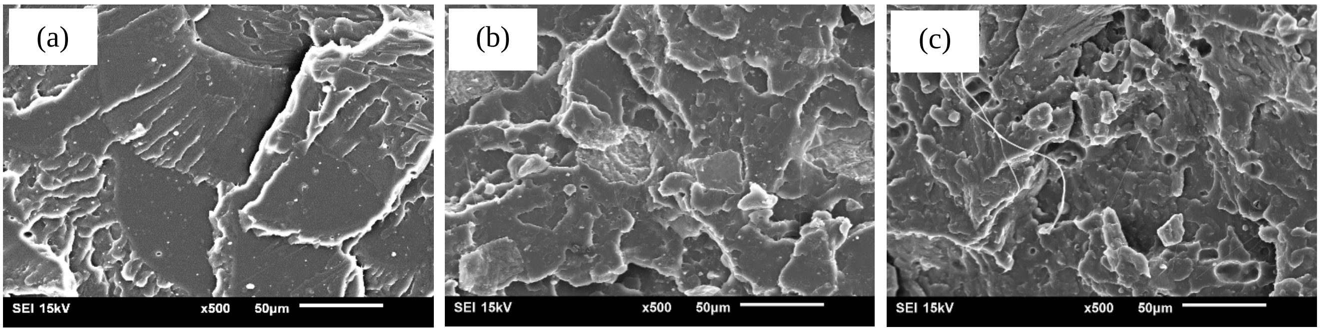

Figure 3. SEM fractured tensile surface of (a) PLA, (b) PLA 5 wt. % BES-32 µm and (c) PLA 20 wt. % BES-32 µm.

The flexural fractured surfaces are shown in Figure 4. Similarly to the behavior in tensile loading, the PLA fractured in a brittle manner as observed by the smooth continuous fractured surfaces in Figure 4 (a), while the composites have a more discontinuous and rougher surface. Both LS-32 µm composites with 5 wt. % and 20 wt. % fillers show particles to have a good dispersion throughout the matrix as observed in Figure 4 (b) and Figure 4 (c), respectively. Interestingly, compared to the tensile fractured surfaces, the flexural surfaces show fillers to have more spaces around the particles indicating yielding of the matrix. These cavities not observed in pure PLA are slightly larger than the particles which implies they were made by the harder filler particles during the testing phase. Although the LS fillers are well embedded in the PLA matrix, it appears the particles have detached, indicating poor bonding between the filler and matrix. The voids surrounding the particles are indicative of matrix plastic deformation.

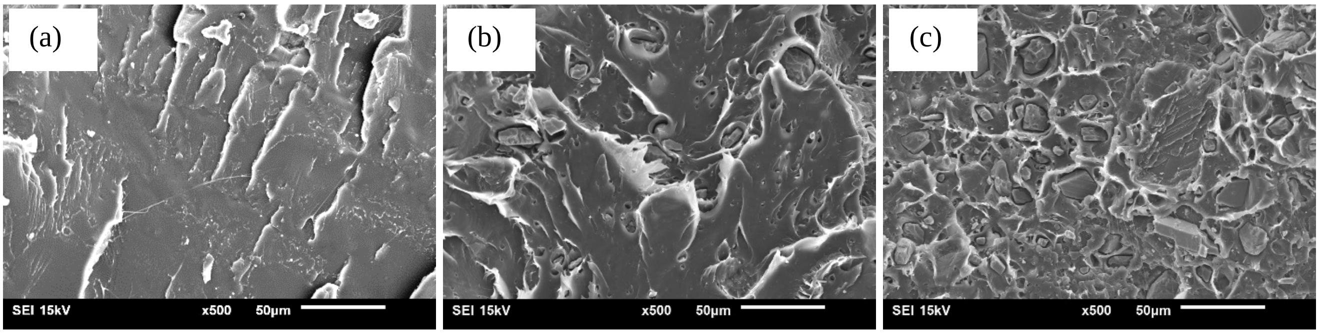

Figure 4. SEM fractured flexural surface of (a) PLA, (b) PLA 5 wt. % LS-32 µm and (c) PLA 10 wt. % LS-32 µm.

3.2 Water Absorption

The moisture uptake was evaluated by monitoring water uptake and absorption quantity over 56 days. The tendency of moisture absorption on pure PLA and PLA containing LS and BES fillers are shown in Figure 5. In general the moisture absorption increased with time for all materials. At the beginning of the test the moisture intake was linear as observed by the positive slopes up to approximately 20 days and gradually decreased until the specimens reached saturation. The amount of water absorbed by each composite varied based on filler type and loading. At the end of 56 days, the total weight gain due to moisture absorption for 32 µm powders with weight percentages of 5 %, 10 % and 20 % of LS fillers was 1.01 %, 1.11 % and 1.13 %, respectively, while for BES the absorption was 1.19 %, 1.22 % and 1.34 %, respectively as given in Figure 5(a). Similarly, for the 63 µm LS powder fillers with weight percentages of 5 %, 10 % and 20 %, the total moisture absorption for LS was 0.98 %, 0.99 % and 1.08 %, respectively, while the BES composites has absorptions of 1.11 %, 1.15 % and 1.17 %, respectively as given in Figure 5 (b). For pure PLA the total weight gain was 0.83 %. Hydrophobic pure PLA absorbed the least amount of water, while hydrophilic calcium carbonates absorbed more as was expected. In addition, moisture absorption was higher for the smaller sized particles due to their larger surface areas. With the addition of conventional limestone or brown eggshell $CaCO_3$ fillers, the results indicated increased water absorption to PLA composites. The LS/PLA based composites absorbed less water than the BES/PLA composites. From SEM observations, the BES particles had a more porous structure as shown in Figure 2 (b), which could explain their increased moisture uptake.

3.3 Mechanical Properties

The tensile strengths as a function of filler loadings are shown in Figure 6, while the modulus as a function of filler loadings are shown in Figure 7. The tensile strength for pure PLA was 51.52 MPa. With the addition of calcium carbonate fillers, the tensile strength for all composite materials was reduced. The highest tensile strengths were for the 5 wt. % loadings. For example, LS-32 µm, LS-63 µm, BES-32 µm and BES-63 µm fillers had tensile strengths of 51.44 MPa, 50.80 MPa, 49.43 MPa and 47.39 MPa, respectively. Overall, the composites with smaller particles had better tensile strengths than those with larger particle sizes. The decrease in tensile strength may be due to greater particle agglomeration as the filler loading content increased and was affected more for the larger sized particles. Micro-sized particles tend to adhere to one another due to electrostatic forces and Van der Waals

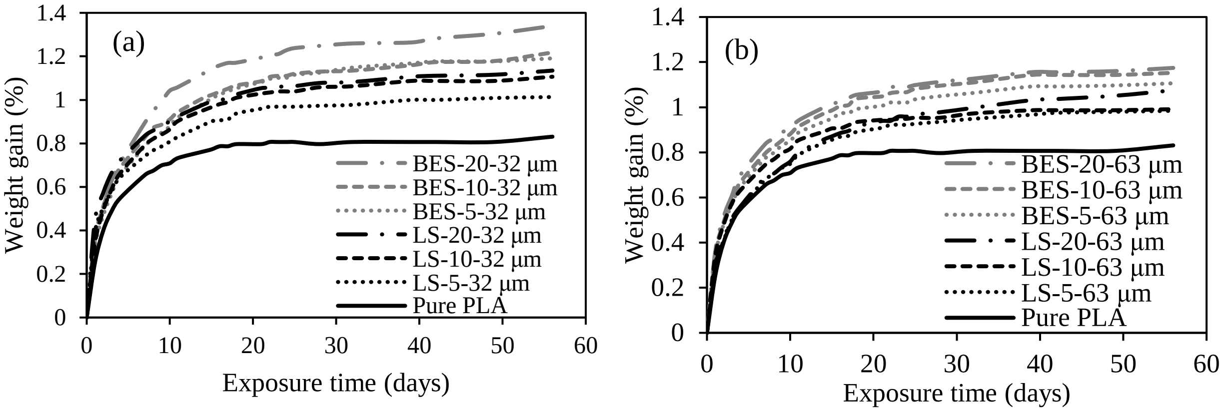

Figure 5. Effect of loading (a) 32 μm and (b) 63 μm and filler type and on moisture absorption of LS and WES filled PLA composites.

bonding forces which results in agglomerates [9]. When the composite is loaded, the stress transfer between touching particles is weak and results in reduced load carrying capability. However, at lower filler loadings, Figure 3 (b), there may be less particulate agglomeration and stronger adhesion between the individual particles and the matrix which improved the stress transfer from particle to particle.

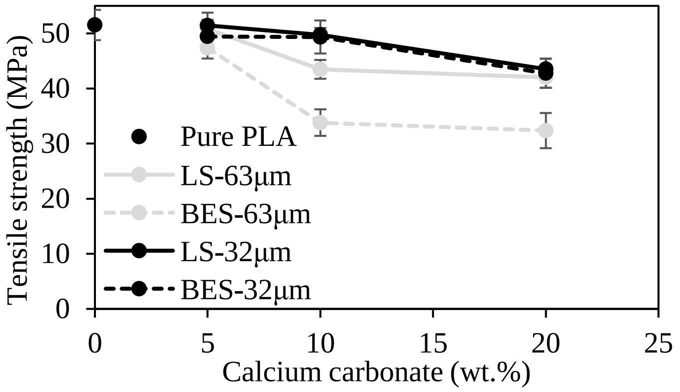

Figure 6. Effect of filler type and loading on the tensile strength of LS and BES filled PLA composites.

The tensile modulus results are shown in Figure 7. In contrast to the tensile strengths, the composites containing calcium carbonate fillers increased simultaneously as the loading content increased. The highest modulus reached 4.4 GPa for composites containing 20 wt. % LS and BES with 32 μm sized fillers as compared to pure PLA (3.6 GPa). The addition of fillers to polymer matrices tended to increase the modulus of the pure polymer due to the more rigid $CaCO_3$ filler materials.

Figure 8 shows the flexural strength of PLA composites with different amounts of calcium carbonate fillers for two particle sizes. The results are compared to pure PLA polymer. The flexural strength was the highest for conventional limestone with 10 wt. % filler and particle size of 32 μm. Incorporating calcium carbonate based fillers enhanced the flexural strength of the individual composites, but adding more than 10 wt. % tended to decrease the flexural strength slightly for all composites. Composites with loadings of more than 10 wt. % may have decreased particle dispersion, increased particle agglomeration and increased the degree of filler-matrix debonding as shown in Figure 4 (c).

Figure 9 shows the flexural modulus of pure PLA and PLA composites with different amounts of calcium carbonate fillers. The flexural modulus increased up to the maximum filler content of 20 wt. % for both types of 32 µm fillers. The flexural modulus of pure PLA was 3.3 GPa, and significantly improved to 7.8 GPa and 5.7 for

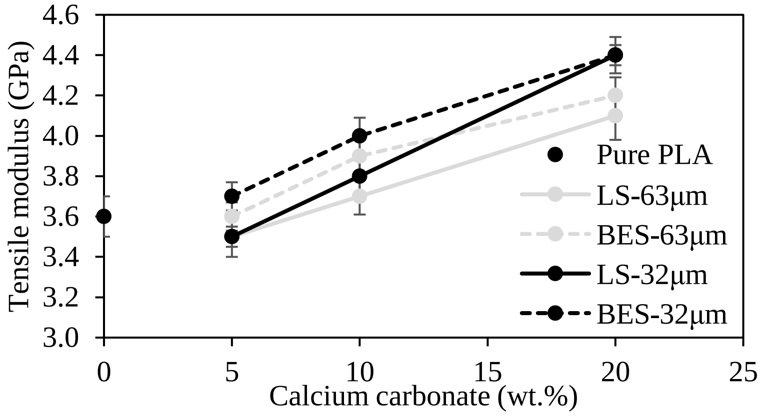

Figure 7. Effect of filler type and loading on the tensile modulus of LS and BES filled PLA composites.

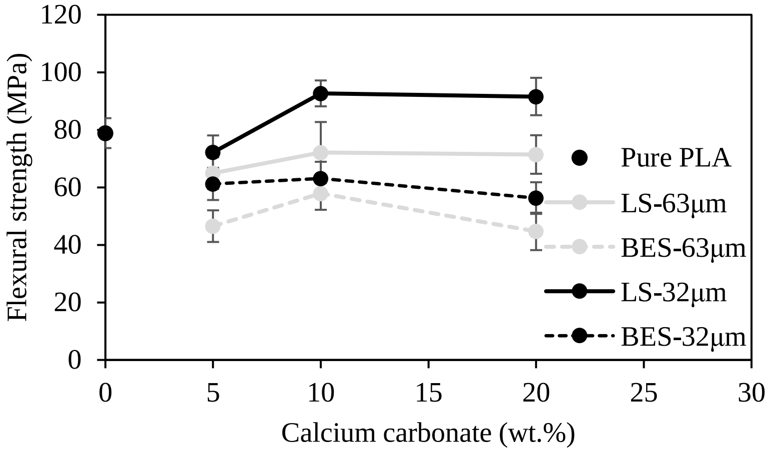

Figure 8. Effect of filler type and loading on the flexural strength of LS and BES filled PLA composites.

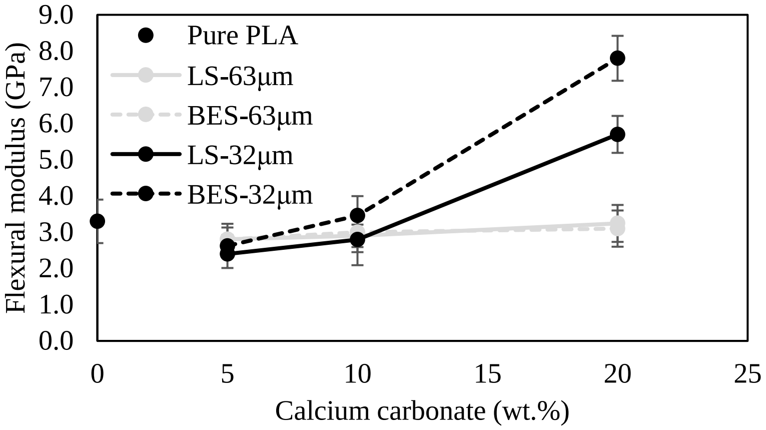

Figure 9. Effect of filler type and loading on the flexural modulus of LS and WES filled PLA composites.

BES-32 µm and LS-32 µm, respectively. The presence of calcium carbonate fillers increased the composite modulus in bending which suggests an improved resistance to deformation.

3.4 Conclusions

In this study, the effects of adding 5 to 20 wt. % conventional and eggshell derived $CaCO_3$ fillers to PLA was investigated. Water immersion tests and mechanical properties were conducted on the composites and compared to pure PLA. In general, for both particle filler sizes, the LS/PLA based composites absorbed less water than the BES/PLA composites, possibly due to the porous nature of eggshell particles as was depicted in the SEM micrograph. Overall, the mechanical properties were better for the smaller size filler particles. The tensile and flexural strengths decreased when the addition of filler materials were greater than 5 wt. % and 10 wt. %, respectively. However, the tensile and flexural modulus improved with the increase of filler loadings compared to the pure PLA. In conclusion, brown chicken eggshells could be used to fully or partially replace conventional limestone as a filler material for PLA composites.

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