



Development Process to Purify Waste Eggshells to Manufacture Epoxy Composites

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ABSTRACT

A filler material for polymers is calcium carbonate (CaCO_3) (CC) found in rocks. It is added to polymer materials to enhance properties of the matrix as well as to lower the cost of the end products. The breaking plant industry produces bulk quantities of discarded eggshells which can be regarded as a bio-filler candidate as they contain a high percentage of CC. The complex microstructure and strong bond between eggshell crystals and organic membranes have made the separation more difficult. Thermogravimetric analysis (TGA) showed a small weight loss in purified powders at 400-500 °C due to the presence of small amounts of other elements. Inductively coupled plasma mass spectrometry (ICP-MS) showed the percentage of CC increased from 88% in raw eggshells to 95 % after heating to 750 °C. Scanning electron microscope (SEM) showed eggshell powders had irregular geometries. The effects of heat treated 32 μm sized eggshell fillers (0-20 wt. %) in bio-epoxy composites were evaluated for tensile and flexural strengths. The best tensile and flexural strengths were obtained when raw brown eggshell (BES) were added at 10 wt. % and 5 wt. % loadings, respectively which slightly decreased the strengths by 10 % and 14 %, respectively compared to pure epoxy. However, the tensile and flexural modulus improved as the percentage of loadings increased for all filler types.

KEYWORDS: epoxy resin, eggshell purification, characterization, mechanical properties

1. INTRODUCTION

Conventional materials can be replaced by new composite materials due to certain advantages such as lower cost with better mechanical properties. Different types of filler materials such as calcium carbonate (CaCO_3) (CC), aluminum trihydrate (ATH), and barium sulfate have been added to polymers to improve various properties as composite materials. Overall, CC holds the largest market volume and is used mainly in plastic industries (Web-1).

Chicken brown eggshells (BES) are the byproduct of a food industry and have created a disposal problem. In the United States, companies (e.g. egg breaking plants) are paying \$100,000 per year to dispose of waste eggshells to landfills (Sonklar, 1999). However, eggshells have excellent mechanical properties that gives us reason to consider them as filler materials for epoxy polymers. Typically, eggshell contains 94-96 % CC with 3-4 % organic membranes (Yamamoto et al., 1996). Different methods such as plasma etching, acid treatment, and vacuum separation methods have been developed to remove this membrane effectively (Cusack et al., 2002). Recently, effects of eggshell powder on polymer composite materials were studied without removing this membrane (Zuiderduin et al., 2003; Pliya and Cree, 2015; Ang et al., 2016).

This study investigates the development of heat treatment process to extract pure CC from waste eggshells and further produce epoxy composites by addition of different weight percent of CC filler materials. The physical properties, morphology of fractured surfaces and mechanical properties of the composites containing limestone (LS) and purified eggshell (PES) were evaluated.

2. EXPERIMENTAL

2.1 Material

Raw BES were provided from a local hatchery, Maple Lodge Farms Hatchery division based in Stratford, Ontario, Canada while conventional limestone was obtained from Imasco Minerals Inc. Bio-epoxy resin and hardener for composite material preparation was purchased from Super Sap, a leading manufacturer of thermoset bio-epoxy systems located in Michigan, USA. Molds for the mechanical test specimens were made from a silicone rubber, Mold Max 10T.

2.2 Heat Treatment to Remove Organic Membrane

Initially raw BES were rinsed with water to remove precipitated solids and then coarse crushed using a ball mill to obtain a 32 micron powder. To remove the organic membranes from the eggshells, first, powder was heated to form pure CaO, at 750°C, in air, as shown in reaction 1 (Oliveira et al., 2013). Following this step water and CO₂ was added to the CaO to recover pure CaCO₃. However, as a byproduct, CO₂ is generated in this process, which can be stored and reused for reaction 3 in an industrial mass production scenario.

1. $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ (750°C)
2. $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$
3. $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ (drying at 105°C)

2.3 Composite Preparation

Composite samples were prepared using LS and PES powders both as filler materials. Initially, silicone based molds were prepared as per ASTM standard dimensions for tensile and flexural specimens. Epoxy was mixed with different percentages (5, 10, and 20 wt. %) of fillers using a magnetic stirrer. The operating temperature of stirrer was set to 30 °C with rotational speed of 60 rpm. After mixing all the ingredients for 30 minutes, the mixture was degassed in a vacuum furnace to a pressure of 28 in Hg for 30 minutes to remove air bubbles. The hardener was then added to the mixture, stirred for 5 minutes and the liquid solution was poured into the mold. After 24 hours of solidification, composite samples were removed from mold and post-cured at a temperature of 82°C for 30 minutes. The percentage of different fillers for LS and PES added to the bio-epoxy (BE) polymer are shown in Table 1.

Table 1. Filler loading types in bio-epoxy composites

| Composite | Bio-epoxy (wt. %) | CaCO ₃ (wt. %) |
|-----------|-------------------|---------------------------|
| BE | 100 | 0 |
| LS-5 | 95 | 5 |
| LS-10 | 90 | 10 |
| LS-20 | 80 | 20 |
| PES-5 | 95 | 5 |
| PES-10 | 90 | 10 |
| PES-20 | 80 | 20 |

2.4 Characterization of Materials

In order to characterize the calcination process, Thermo Gravimetric Analysis (TGA) was conducted using instrument TGA-Q5000 (TA instruments, USA). LS and PES powders with sample size of 40 mg were heated from 23 °C to 1000 °C with a ramp of 10 °C/min with continuous nitrogen injection. To detect the element distribution in PES powder, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis was performed using the digestion systems 'CEM Corporation Mars 6 microwave' and the samples were analyzed on 'Agilent 7700x ICP MS'. Initially the powder samples were digested in 65 % concentrated nitric acid at a temperature of 200 °C in a closed vessel microwave digest. The image morphology of BES, LS and PES powders were obtained by scanning electron microscopy (SEM) (JEOL JSM-6010LV). The operating voltage range of test was 7-10 kV. The particles were coated with gold to increase the conductivity.

2.5 Mechanical Characterization

The tensile properties of BE composites were determined according to the ASTM D638-14 test standard specifications. The specimen were made of a dog-bone shape with dimensions of 65 mm x 12.74 mm x 3.25 mm (l x w x t). The tensile tests were performed using an Instron 600LX with an Instron Advanced Video Extensometer, (model 2663-821). The crosshead speed was set to 5 mm/min with a load cell of 100 kN. Flexural, three-point loading strength tests were performed using an Instron universal testing machine (model 3366) equipped with a 10 kN load cell. The support span length to depth ratio was 16:1 as per ASTM D790-17 standard. The average tensile and flexure properties were determined from five tests on each material at room temperature and averaged.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric Analysis

The weight loss of BES, LS and PES at a temperature range of 23-920°C are shown in Figure 1. A very small weight loss can be observed in between 250-600°C due to the presence of water molecules in all samples and slight decomposition of organic membrane in BES. BES began to decompose at 600°C due to the decomposition of the organic protein into molecules such as CO and CO₂, while both LS and PES showed rapid weight losses after 660°C. A major weight loss is seen in the range of 600-850°C for all samples due to the decomposition of CaCO₃ to CaO.

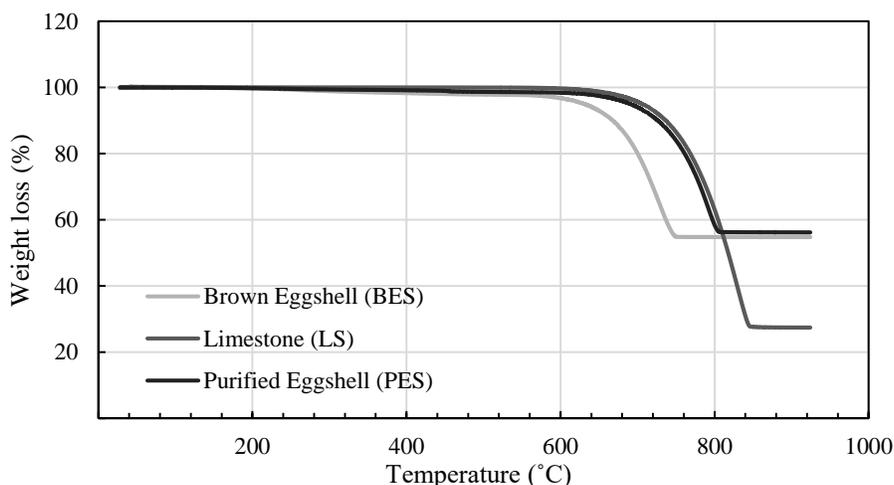


Figure 1: TGA analysis of BES, LS and PES powders

3.2 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Analysis

As Table 2 illustrates, the chemical sample of BES showed CaCO_3 was the most abundant component. Raw BES contained 87.5 ± 0.5 % CaCO_3 , which increased to 95.0 ± 0.5 % for PES after the heat treatment. This improvement is due to burning of protein and organic membrane in the eggshells. Small amount of MgO , P_2O_5 , Al_2O_3 , Fe_2O_3 , SiO_2 , and NiO were also found in the treated samples. Similarly, the as-received limestone was 99.9 % CaCO_3 .

Table 2. Chemical composition of PES and BES

| | Ca($\mu\text{g}/\text{gm}$) | % CaCO_3 | % MgO | % P_2O_5 | Al_2O_3 |
|-----|-------------------------------|-------------------|----------------|--------------------------|-------------------------|
| PES | 380000 | 95.0 | 1.0 | 0.8 | 0.05 |
| BES | 349000 | 87.5 | -- | -- | -- |

3.3 Scanning Electron Microscopy Analysis

Morphological structural of BES, LS and PES are outlined in Figure 2. As observed, all samples are irregular in shape with wide range of particle sizes due to the crushing processes. The organic membranes on the surface of the BES particles can be observed in Figure 2 (a) which is absent in the PES samples of Fig 2 (c).

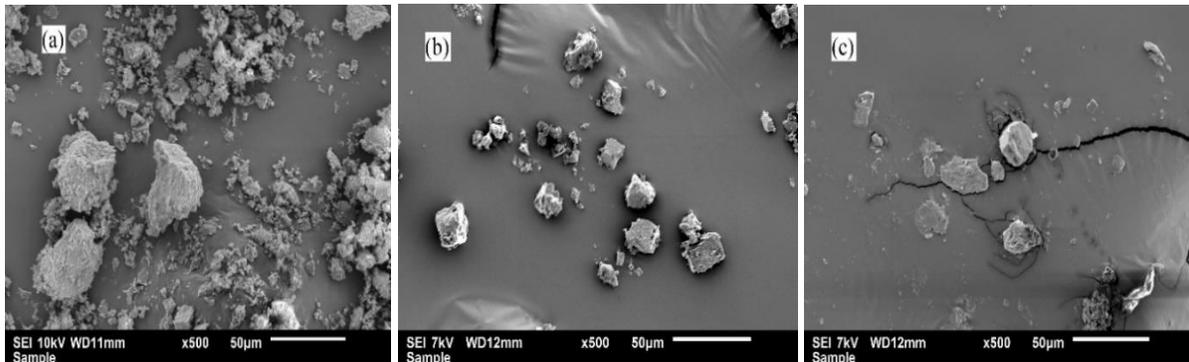


Figure 2: SEM images showing particle morphology of (a) BES (b) LS (c) PES

The tensile fractured surface morphologies of pure BE and composites containing LS and PES with different filler weight percentages are shown in Figure 3. The BE composite has smooth, flat surfaces due to the brittleness of the fracture as shown in Figure 3 (a). As the percentage of filler was increased for both types of fillers the fractured surfaces became rougher as a result of improved ductility. LS and PES particles bonded within the matrix can be seen in Figure 3 (b, c, d, e). At higher loadings, due to the higher density of CC particles, stress transformation between CC particles is predominant rather than the intended particle-to-polymer interaction (Salmah et al., 2013). This particle-to-particle interaction will create weaker filler-matrix interface and as a result holes can be observed in Figure 3 (b, c) due to some particles being extracted because of agglomerations.

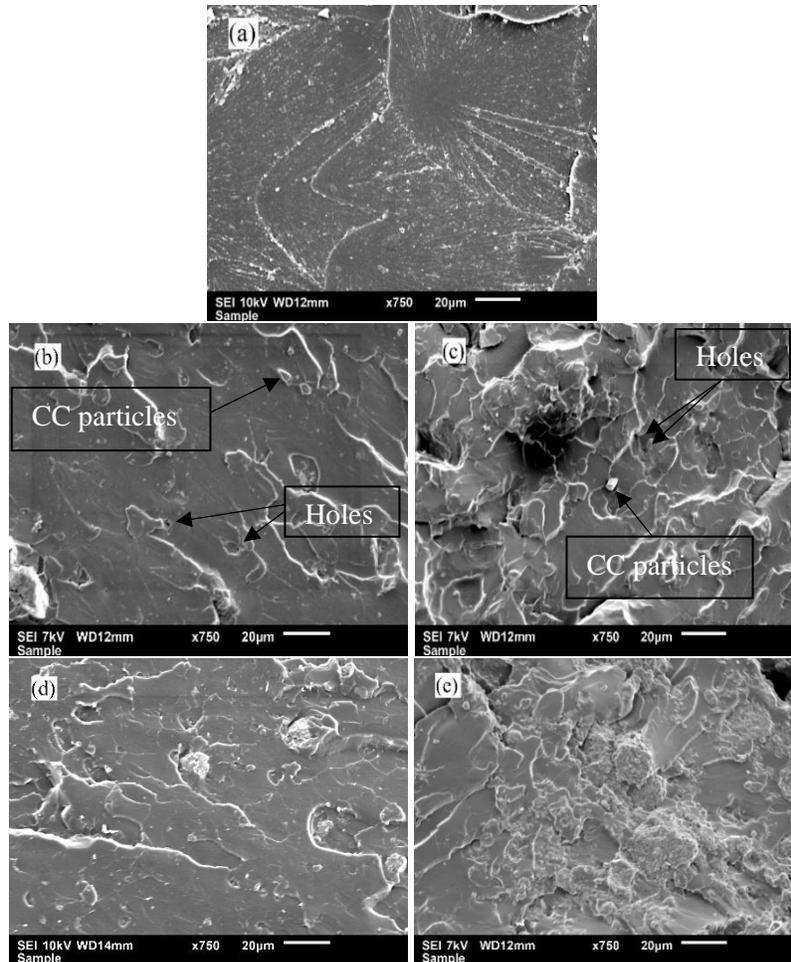


Figure 3: SEM fractured tensile surface of (a) BE (b) BE with 5 wt. % LS and (c) BE with 10 wt. % LS (d) BE with 5 wt. % of PES and (e) BE with 10 wt. % of PES

3.4 Mechanical Properties

The tensile strength of pure BE and BE with different types and amounts of filler loadings are shown in Figure 4. The pure BE showed the maximum tensile strength of 55.9 MPa which is due to the absence of any filler materials. The tensile strength reduced to 50.1 MPa, 47.1 MPa and 40.1 MPa when 5 wt. % of BES, LS and PES was mixed with the BE, respectively. Tensile strengths were highest when 10 wt. % fillers were added and reached 54.9 MPa, 48.0 MPa and 46.4 MPa for BES, LS and PES respectively, but decreased to 45 MPa, 44.3 MPa, and 37.2 MPa at 20 wt. %, fillers, respectively. The reduction in strength at higher filler loadings is due to particle agglomeration. Overall, composites with BES fillers showed higher tensile strength as compare to LS and PES. The decrease in tensile strength may be due to absence of organic membrane. (Hincke et al., 2012) showed that the soluble matrix proteins of calcitic biomaterials can modify crystal growth, and in this manner affect the macroscopic properties of the resulting composite. The nature of the interactions between the mineral phase and eggshell matrix proteins has been intensely investigated, but mechanistic details remain unknown (Hincke et al., 2012). Figure 5 shows the tensile modulus results for different fillers with different loadings. Pure BE showed the lowest tensile modulus of 2.5 GPa which increased steadily as the percentage of filler increased. The highest modulus was recorded to be 4.9 GPa for PES composites with 20 wt. % loading. The improvement of modulus with filler increment is attributed to the presence of harder CC particles.

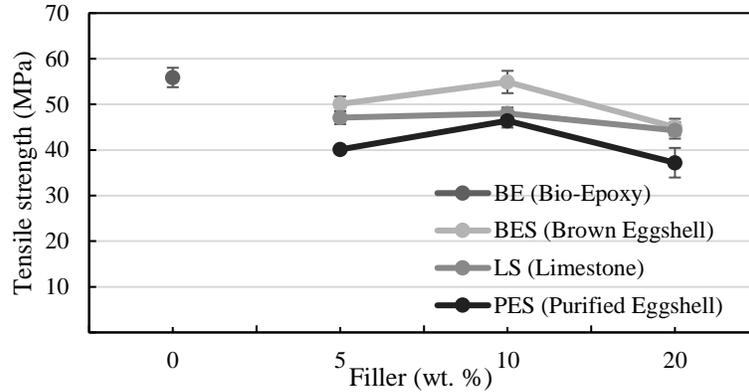


Figure 4: Effect of CC filler type and loading on tensile strength

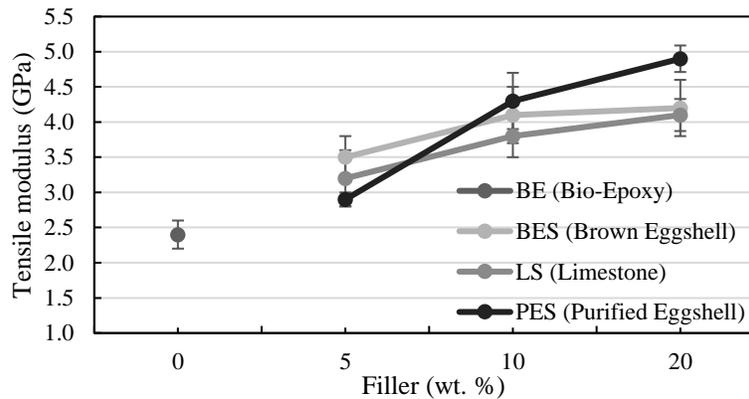


Figure 5: Effect of CC filler type and loading on tensile modulus

The flexural strength of the composite materials with different types of fillers are shown in Figure 6. The pure BE had a maximum flexural strength of 86.0 MPa. Generally, composites containing BES particles showed the highest flexural strengths of 74.4 MPa with 5 wt. % loading but decreased to 53.6 MPa when 20 wt. % fillers were added. At lower filler loadings, there may be less particle agglomeration which suggests better load transfer from the matrix to the filler particles. The LS and PES performed similarly with LS having slightly better strengths. The flexure modulus increased sharply from 3.8 GPa for BE to a maximum of 6.1 GPa for BES at 20 wt. % loadings and 5.2 GPa at 20 wt. % of PES (Figure 7). The presence of rigid CC particles, and strong bonding with the bio-epoxy tends to improve the resistance to deform in flexure.

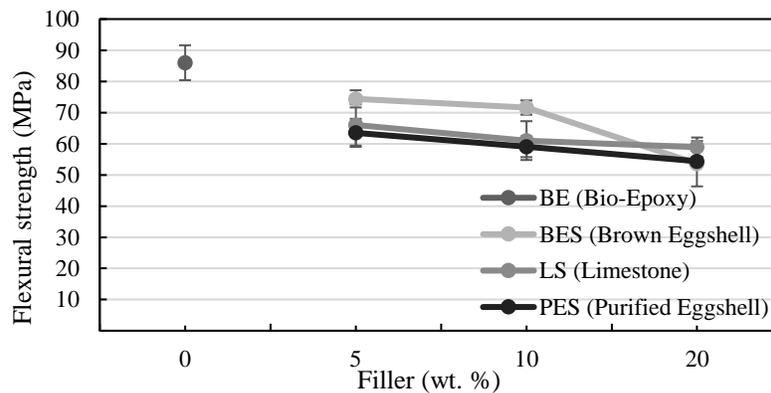


Figure 6: Effect of CC filler type and loading on flexural strength

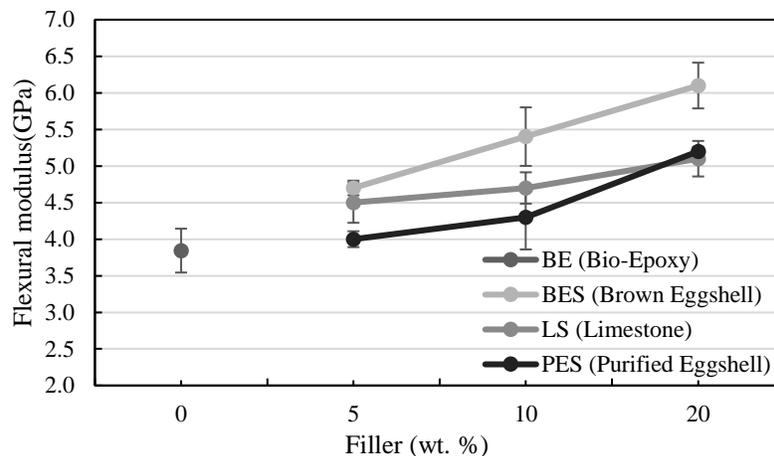


Figure 7: Effect of CC filler type and loading on flexural modulus

4. CONCLUSION

The effective treatment and utilization of bio-waste can benefit our society in both environment and economic ways. This article presents one way to recover pure CC from waste eggshells and to utilize it as a filler to make a new composite. ICP-MS analysis showed the PES contained slightly more CC than raw BES due to the removal of the organic membrane. Small weight loss can be observed in the TGA curve in between 250-600 °C due to present of organic membrane in the BES. SEM images of fracture tensile surface showed some holes at higher filler loading due to agglomerations of filler particles. Overall, the tensile and flexural strengths decreased when the addition of filler materials were increased for 5 wt. % to 20 wt. % for all three fillers (BES, LS and PES). However, the tensile and flexural modulus improved with the increase of filler loadings compared to the pure BE. For composites subjected to tensile and flexural applications, the addition of not more than 10 wt. % and 5 wt. % BES, respectively in this BE is recommended. In conclusion, brown chicken eggshells could be used to fully or partially replace conventional limestone as a filler material for plastic industries.

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