11th Canadian-International Conference on Composites

Characterization of Bio-Epoxy Waste Eggshell Composite

S. Owuamanam[1] and D.Cree[2]*
[1] Department of Mechanical Engineering, University of Saskatchewan, Saskatoon, Canada
[2] Department of Mechanical Engineering, University of Saskatchewan, Saskatoon, Canada
* Corresponding author (duncan.cree@usask.ca)

ABSTRACT

Low cost fillers such as limestone (LS) are added to polymers as an effort to reduce the overall cost of the polymer while improving/maintaining their properties. The effect of waste eggshell (ES) powder containing a high calcium carbonate ($CaCO_3$) content was used as a bio-filler (5-20 wt. %) in a bio-epoxy composite. Physical (ES and LS particle morphology and composite fractured surfaces), chemical (inductively coupled plasma mass spectrometry (ICP-MS) and X-ray diffraction (XRD)), and mechanical (flexural and Charpy impact) properties were evaluated. The average particle size was 5.01 ± 0.14 µm and 6.68 ± 1.57 µm for ES and LS, respectively. SEM showed ES and LS particle shapes varied and fractured surfaces were modified with the addition of fillers. XRD analysis indicated the presence of calcite, while ICP-MS showed 88 % ± 0.71 $CaCO_3$ in ES. The flexural strength was not significantly affected with 5 wt. % ES or LS in which both decreased by 10-11 %. The flexural modulus increased with an increase in filler loading and was maximum at a content of 20 wt. % for both ES and LS. The smallest decrease in Charpy impact energy was for the 5 wt. % loadings which decreased by 14 % and 9 % for ES and LS, respectively.

KEYWORDS: *eggshell, limestone, bio-epoxy, composite, mechanical testing*

1 INTRODUCTION

In recent years, there has been an increased use of polymer reinforced composites in (structural) applications due to their light weight, low cost, and high stiffness. This presents polymer composites as alternatives to metals in selected industrial, aerospace and automobile applications. Generally, epoxy is widely used over other thermoset polymers in various applications due to characteristic processing techniques, better performance at elevated temperature, and superior strength. Utilization of polymer materials produced from raw materials containing a percentage of bio-based content is encouraged as a way of promoting environmental sustainability. Bio-based epoxy resins can be obtained from renewable plant sources such as linseed oil, lactic acid, corn, soy-bean oil, pine and vegetable oils (Masoodi and Pillai, 2011).

Low cost fillers can be added to polymers in an effort to reduce cost, and improve or maintain their properties. Limestone (LS) derived from sedimentary rock is the most widely used inorganic filler for polymers due to their low cost, earthly abundance, high calcium carbonate ($CaCO_3$) content, and chemical stability up to 800 °C. Eggshells (ES) contain 94-96 % $CaCO_3$ content, 3-4 % organic matter and minor traces of magnesium and phosphorus (Boronat et al., 2015; Pliya and Cree, 2015). Large quantities of waste ES are disposed from egg breaking plants to landfills at a cost. For instance, companies in the United States of America spend approximately US $100,000 to dispose of ES annually (Web-1).

Diverting this waste to novel applications would reduce disposal costs and the negative effects on the environment. Several studies have been conducted on the use of waste materials with high $CaCO_3$ content as fillers for polymer composites. For instance, (Fombuena et al., 2014) reported a 47 % increase in flexural modulus with 30 wt. % loading while the Charpy impact toughness decreased by 84 % with 5 wt. % loading in GreenPoxy/ground seashell composites. Similarly, (Tiimob et al., 2016) reported approximately an 8 % increase in flexural strength and 11 % increase in flexural modulus when 5 wt. % filler (nano eggshells) was added to a Super Sap bio-epoxy.

This study investigated the use of a solution mixing method to produce bio-epoxy/$CaCO_3$ composite materials. The aim of this work was to evaluate the chemical composition, morphology, flexural strength and Charpy impact toughness properties of bio-epoxy resins containing ES and LS fillers.

2 EXPERIMENTAL

2.1 Materials

ES and LS were obtained from Maple Lodge Farms Hatchery, Ontario, Canada and Imasco Minerals Inc., respectively. The bio-epoxy with 31 % bio-based content was Super Sap CPM epoxy and CPL hardener as shown in Figure 1 (a) purchased from Entropy resins, San Antonio, CA. Silicone, Mold Max^{TM} 10T for making composite molds was purchased from Smooth-On Inc.

2.2 Eggshell Powder Preparation

The as-received ES were firstly washed with water and dried for 24 h at 105 °C to eliminate odor and contaminants. The ES were subsequently subjected to dry coarse crushing. Water was then added to the crushed shells and stirred, followed by a manual precipitation process to remove water and majority of organic membranes. The slurry mixture was dried at 105 °C for 24 h to obtain the powdered ES (Pliya and Cree, 2015). The ES were further ball milled in water for 6 h into fine powders using a small scale milling apparatus, thereby reducing the particle size. The particles were sieved with the aid of a vibrating sieve shaker machine (Ro-tap).

2.3 Composite Preparation

The composites were prepared using a solution mixing method with filler amounts of 5, 10, and 20 wt. % of ES/LS added as a replacement of bio-epoxy resin as outlined in Table 1. The mix ratio of resin to hardener was 100:40 (by weight) (Web-2). The required quantity of bio-epoxy resin was placed in a plastic beaker and the ES or LS of required weight percent was added to the resin. The solution was initially stirred using a magnetic stirrer for 1 h at 700 rpm at room temperature (23 °C) and further ultrasonic homogenized (Sonicator model FS-900N) for 5 min to further disperse the fillers. The mixture was degassed under vacuum (>28 inHg) for 30 min to evacuate air bubbles generated due to mixing. The required amount of hardener was poured into the mixture and hand stirred for 3 min and again degassed under vacuum for 15 min. The composition was gently poured into silicone rubber molds and allowed to cure for 24 h at room temperature and further post-cured at 82 °C for 40 min.

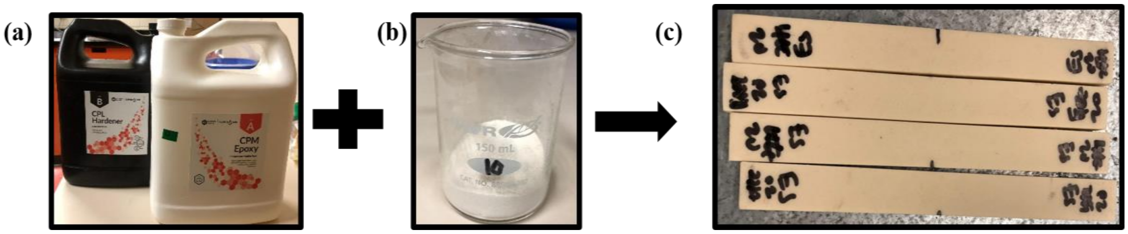

Figure 1: A photograph of (a) CPM epoxy and CPL hardener (b) $CaCO_3$ powder filler and (c) Cured flexural strength bio-epoxy/$CaCO_3$ composite specimens

Table 1 Composition of $CaCO_3$ fillers in bio-epoxy composites

Filler type	Filler (wt. %)	Resin (wt. %)	Hardener (wt. %)
	0	71.43	28.57
ES	5	67.86	27.14
	10	64.29	25.71
	20	57.14	22.86
LS	5	67.86	27.14
	10	64.29	25.71
	20	57.14	22.86

2.4 Material Characterization

Filler particle (ES and LS) morphology and fractured surfaces of flexural test were examined by scanning electron microscope (SEM) (model JEOL 6010). The images were taken at an operating voltage of 10 kV. The samples were sputter-gold coated to improve their conductivity. The as-prepared ES chemical composition was conducted to determine the calcite content. The powdered samples were digested using 65 % concentrated nitric acid at 200 °C in a closed vessel (CEM Corporation Mars 6 microwave digestion systems) and further analyzed in an inductively coupled plasma mass spectrometer (Agilent 7700x ICP-MS). The test was performed in triplicates and averaged. This analysis was performed to identify the phases present in ES and LS fillers. The crystalline phases of the ES and LS particles were analyzed by X-ray diffraction analysis (XRD) with Cu kα radiation (Rigaku Ultima IV Powder X-ray diffractometer) of wavelength $\lambda = 0.15406$ nm. The measurements were conducted at a diffraction angle of 2θ ranging between 20° and 50° at an operating voltage 40 kV and current of 44 mA with a step size of 0.02° and scan rate of 4.0°/min. After sieving, both filler particle size distributions were determined using a Malvern Mastersizer S (long bench) laser diffraction particle size analyzer according to ISO 13320:2003 standard. This was repeated three times to ensure reproducibility and the average particle size were reported.

2.4.1 Mechanical Characterization

The as-prepared composite response to three-point flexural tests was determined at 23 °C and relative humidity of 42 % using an Instron^{TM} universal testing machine (model 3366) according to ASTM D790-17 standard. The sample dimensions were 200 mm × 20 mm × 10 mm (l × w × t) with a span to depth ratio of 16:1. The load cell and cross-head speed used were 5 kN and 4 mm/min, respectively. The Charpy impact toughness was obtained using an Instron model 450 MPX series Impact Tester. The energy absorption test was performed on un-notched specimen of dimensions 55 mm × 13 mm × 3.2 mm (l × w × t) at 23 °C with a relative humidity of 38 % under the guidance of ASTM D6110-18. Both tests results reported are an average of five samples of each composite formulation.

3 RESULTS AND DISCUSSION

3.1.1 Scanning Electron Microscopy Analysis

Figure 2 presents similar micro-structures for both ES and LS. ES filler presented a rough and irregular morphology which may be due to grinding and ball milling processes. However, LS particles had less rough surfaces than ES and exhibited a rhombohedral-like morphology (arrow mark) which indicated the presence of calcite crystals (Boronat et al., 2015).

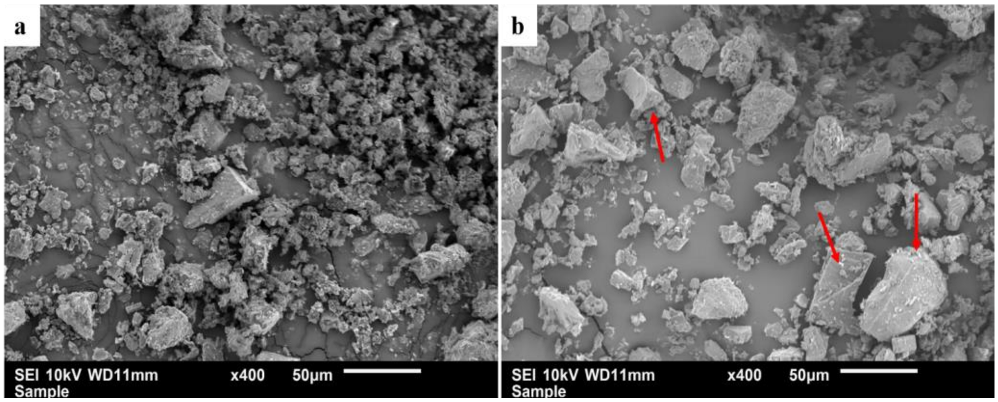

Figure 2: SEM images showing particle morphologies of (a) ES and (b) LS

The flexural fractured surfaces are shown in Figure 3. The fractured surface of the pure bio-epoxy resin presented a smooth, plate-like and cleavage surface suggesting brittle failure. It also showed fewer uninterrupted crack paths after initiation in comparison to the composites. The fractured surfaces of ES (Figure 3 (b)) and LS (Figure 3 (d)) composites containing 5 wt. % loadings presented a greater degree of roughness due to more interruptions of failure propagation as a result of filler inclusions. For 20 wt. % ES (Figure 3 (c)) and LS (Figure 3 (e)) loadings, the degree of roughness further increased. Possibly, at high filler contents, the filler induced higher stress concentrations, which resulted in further propagation of cracks and subsequently deteriorated the mechanical properties.

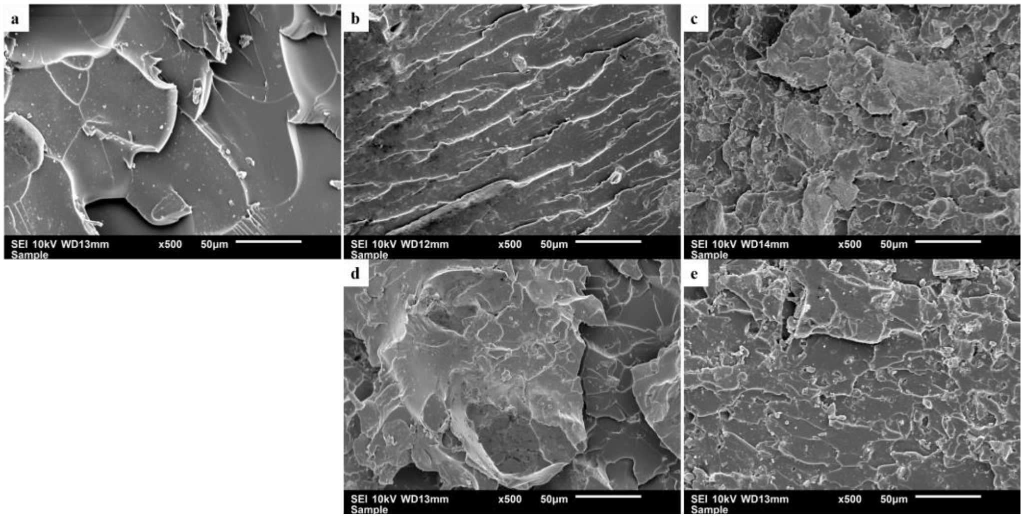

Figure 3: SEM flexural fractured surfaces of (a) pure bio-epoxy resin, (b) 5 wt. % ES loading, (c) 20 wt. % ES loading, (d) 5 wt. % LS loading and (e) 20 wt. % LS loading

3.1.2 Chemical Composition Analysis

Chemical analysis on the as-prepared ES confirmed a relatively high $CaCO_3$ content to be 88 % ± 0.71 with minor traces of magnesium (0.27 %) and phosphorus (0.13 %). Similarly, LS presents a $CaCO_3$ content of 99.9 %, as reported in the supplier's data sheet (Web-3). In comparison to LS, this slight difference was expected due to the organic matter contained in ES which is not present in LS. Although an effort was made to remove the organic membranes after each grinding process, the results showed some membranes remained. From chemical analysis, ES powders are anticipated to serve as an alternative to LS as filler materials in composites due to the comparable $CaCO_3$ contents.

3.1.3 X-ray Diffraction Analysis

Figure 4 illustrates the XRD pattern of the as-prepared ES and as-received LS. The diffraction peaks suggest a crystalline phase showing the main material of ES to be $CaCO_3$ phase in the form of calcite. The major XRD intensity peak was found at a 2θ angle of 29.4° while the minor peaks are 23.2°, 31.5°, 36.1°, 39.6°, 43.3°, 47.7°, and 48.7° for both ES and LS which was also reported in the literature (Tiimob et al., 2016). This analysis is consistent with the obtained ICP-MS result for ES.

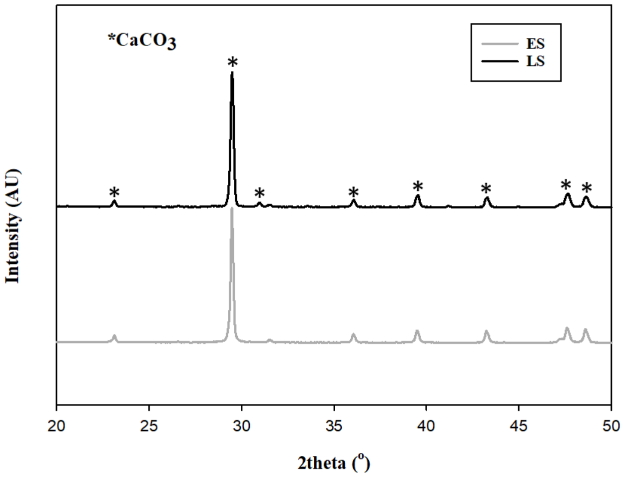

Figure 4: XRD diffraction patterns of ES and LS filler

3.1.4 Particle Size Analyses

The particle size distribution curve (PSDC) of ES and LS are illustrated in Figure 5. The average particle size of the sieved fillers were determined to be 5.01 ± 0.14 µm and 6.68 ± 1.57 µm for ES and LS, respectively. The particle size of LS filler was approximately 1 µm larger than ES filler, possibly due to the processing method of the waste eggshells.

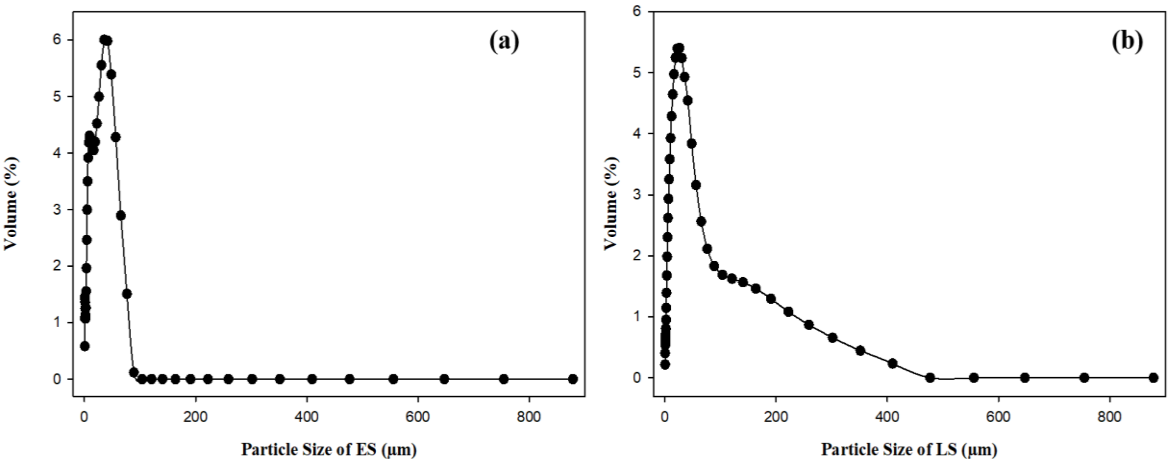

Figure 5: The particle size distribution curves for (a) ES and (b) LS

3.1.5 Mechanical Characterization Results

As shown in Figure 6, the highest flexural strength was obtained for pure bio-epoxy with a value of 95.74 MPa, in-line with the manufacturers data sheet (e.g. 92.7 MPa). Both filler types exhibited similar flexural behavior. For example, as the ES filler loading increased from 5, 10 and 20 wt. %, the flexural strength of the composites reduced by 10 %, 25 % and 40 %, respectively, while composites with LS fillers decreased by 11 %, 24 % and 38 %, respectively. The trend indicates higher flexural strengths for low filler contents. Depending on the end application of this composite, a 10-11 % flexural strength reduction when 5 wt. % could be acceptable. Further inclusion above 5 wt. % resulted in a more pronounced decrease below the flexural strength of bio-epoxy matrix. Although the powders were thoroughly mixed into the resin during composite processing, particulate fillers added in greater amounts (e.g. 10 and 20 wt. %) may tend to agglomerate due to electrostatic forces existing between the particles (DesRosiers Lachiver et al., 2006). Agglomerates serve as stress concentrators and tend to induce brittle failure (Rahman et al., 2012; Mohan and Kanny, 2018). The flexural modulus of both composites increased with increase in filler loadings. The flexural modulus of the pure bio-epoxy was 2.54 GPa similar to the manufacturers data sheet (e.g. 2.8 GPa). As the composite ES filler loading increased from 5, 10 and 20 wt. %, the flexural modulus increased by 8 %, 15 % and 15 %, respectively, while the LS filler composites increased by 11 %, 17 % and 19 %, respectively. This improvement may be attributed to the higher stiffness of the filler material compared to the bio-epoxy (McKeen, 2009).

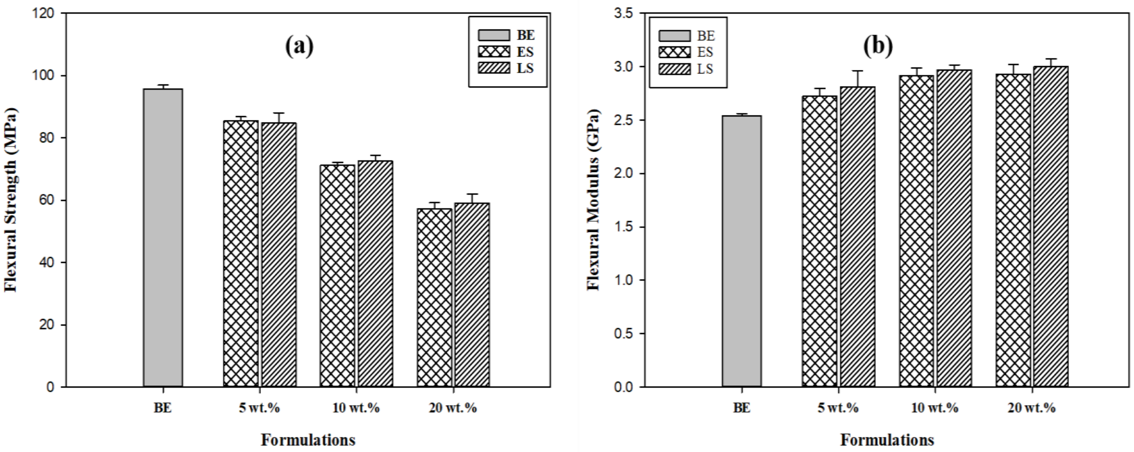

Figure 6: Effect of ES and LS filler loadings on the (a) flexural strength and (b) flexural modulus of bio-epoxy composites

Figure 7 shows the Charpy impact toughness results of bio-epoxy composites with various filler types and contents. The pure bio-epoxy had an impact energy of 8.21 kJ/m^2. The energy absorbed decreased with increase in filler contents for both fillers. As the ES filler loading increased from 5, 10 and 20 wt. %, the Charpy impact energy decreased by 14 %, 34 % and 44 %, respectively, while the LS filler reduced by 9 %, 31 % and 41 %, respectively. This decrease may be due to the presence of accumulated particles in the composites.

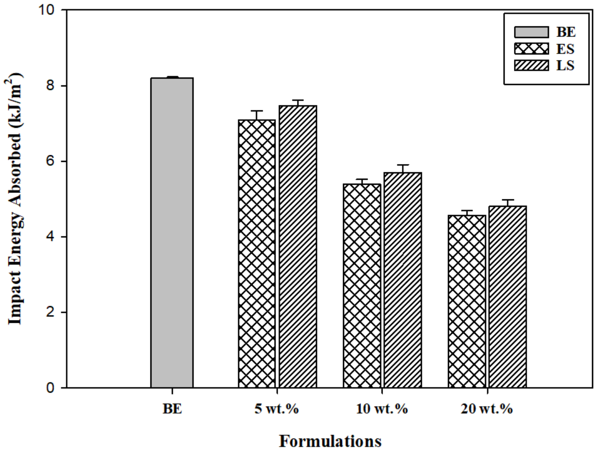

Figure 7: Effect of filler type and loadings on impact energy absorbed for bio-epoxy composites

4 CONCLUSION

In this study, SEM examination of the fillers presented similar structures with LS having less rough surfaces. The fractured flexural surface of pure bio-epoxy resin presented a smooth surface indicative of a brittle material, while ES and LS composites both exhibiting a greater degree of roughness with increase in filler loadings. Mass spectrometry analysis presented a lower $CaCO_3$ content for ES comparable to conventional limestone possibly due to the organic membrane remaining on the eggshells, while XRD analysis indicated the presence of $CaCO_3$ in the form of calcite for both ES and LS. The average particle size of LS was measured to be approximately 1 µm larger than ES. The mechanical tests conducted showed ES and LS fillers exhibited similar flexural strengths and Charpy impact toughness behaviors. For both mechanical properties, this study suggested filler loadings up to 5 wt. % would not have a great effect on the properties. From the results obtained, ES presented a promising approach to serve as a possible alternative to conventional mined LS used as fillers in bio-epoxy composites. Developing new purposes for waste eggshells may reduce the disposal to landfills.

5 ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) under the Discovery Grant (RGPIN 418729).

REFERENCES

Boronat, T., Fombuena, V., Garcia-Sanoguera, D., Sanchez-Nacher, L. and Balart, D. (2015). Development of a Biocomposite Based on Green Polyethylene Biopolymer and Eggshell. Materials and Design, 68, 177–185.

DesRosiers Lachiver, E., Abatzoglou, N., Cartilier, L. and Simard, J. (2006). Insights Into the Role of Electrostatic Forces on the Behavior of Dry Pharmaceutical Particulate Systems. Pharmaceutical Research, 23, 997–1007.

Fombuena, V., Bernardi, L., Fenollar, O., Boronat, T. and Balart, R. (2014). Characterization of Green Composites from Biobased Epoxy Matrices and Bio-fillers Derived from Seashell Wastes. Materials and Design, 57, 168–174.

Masoodi R. and Pillai K. M. Modeling the processing of Natural Fiber Composites Made using Liquid Composite Molding. in "Handbook of Bioplastics and Biocomposites Engineering Applications," Scrivener Publishing LLC, (2011), pp. 43–73.

McKeen, L. W. Introduction to Plastics and Elastomer. in "The Effect of Creep and Other Time Related Factors on Plastics and Elastomers," Elsevier Publishers, Burlington, MA (2009), pp. 1–31.

Mohan T. and Kanny K. (2018). Thermal, Mechanical and Physical Properties of Nanoeggshell Particle-Filled Epoxy Nanocomposites. Journal of Composite Materials, 52, 1–12.

Pliya P. and Cree D. (2015). Limestone Derived Eggshell Powder as a Replacement in Portland Cement Mortar. Construction and Building Materials, 95, 1–9.

Rahman, M., Zainuddin, S., Hosur, M. V., Malone, J. E., Salam, M. B. A., Kumar, A. and Jeelani, S. (2012). Improvement in Mechanical and Thermo-Mechanical Properties of E-Glass/Epoxy Composites using Amino Functionalized MWCNTs. Composite Structures, 94, 2397–2406.

Tiimob, B., Jeelani, S. and Rangari, V. (2016). Eggshell Reinforced Biocomposite - An Advanced “Green” Alternative Structural Material. Journal of Applied Polymer Science, 133, 1–10.

Websites:
Web-1: https://news.psu.edu/, consulted 2 January 2018.
Web-2: https://europe.entropyresins.eu/store/supersap-cpm-cpf-cpl/, consulted 2 November 2018.
Web-3: https://www.imascominerals.com/, consulted 5 November 2018.