PROPERTIES OF BIOCOMPOSITES FROM WASTE EGGSHELL AS FILLERS

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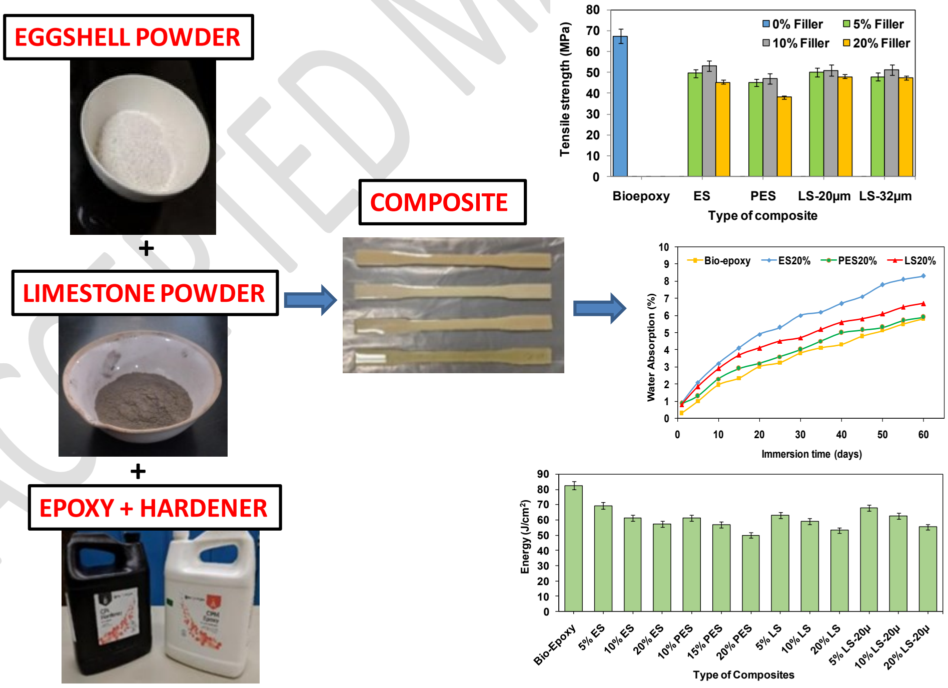
Graphical Abstract



Abstract

In recent years there has been a heightened concentration on the industrial subsectors that are the primary contributors to environmental pollution. Filler materials made from mineral limestone, which is composed of calcium carbonate ($CaCO_3$), are utilized in the production of polymer composites in order to lower production costs and improve the qualities of some of the composites. On the other hand, eggshells are typically regarded as waste despite the fact that they contain significant amounts of $CaCO_3$ in addition to certain organic membranes. The purpose of this research is to investigate the use of thermal and chemical treatments to produce purified eggshell powder with the interest of utilizing waste eggshell as an alternative to limestone. Polymer composites were developed using bio-epoxy resin with various quantities of eggshell powder (ESP), purified eggshell (PES), and limestone powder (LSP) fillers (5%, 10%, and 20% weight). Eggshell could be utilized as filler in bio-epoxy composites, which could then be employed in applications that require a lower cost but a greater tensile and flexural modulus.

Keywords: Biocomposites, Filler, Sustainability, Water absorption

1.Introduction

Agricultural wastes are among of the most developing challenges in the food sectors all over the world. This is due to the fact that economic and environmental considerations are at play. But, if there are new applications that can be found for these waste materials, this problem may turn out to be an opportunity for the environmentally friendly society. Research has been concentrated on developing efficient solutions for the correct management of agricultural wastes (Papargyropoulou *et al.,* 2014, Gertsakis and Lewis 2003) in order to preserve the quality of the environment. One alternative that calls for the use of unprocessed resources and fresh energy is the production of brand-new goods. Thus, in order to reduce the demand for new items, there should be as little waste as possible. The second choice is to find new uses for previously used resources. Waste is being generated by households at an increasing rate, which is leading to landfills reaching capacity. Several different kinds of waste materials have the potential to be repurposed, recycled, and converted into items that are valuable and useful.

In order to attain sustainability, it is essential to prioritize the recycling of old resources into new goods (Martin-Luengo *et al.,* 2011). Eggs from chickens are a common ingredient in foods that are processed in factories. At the moment, eggs are utilized in the creation of a wide range of goods, including cakes, salad dressings, and quiches. The production of these goods generates several daily tons of waste eggshells as a by-product, which in turn results in significant disposal expenditures around the globe (Sivakumar *et al.,* 2022). While eggshells include significant concentrations of calcium carbonate ($CaCO_3$) (between 92 and 95% by weight), they are often thrown away in landfills, which results in an annual cost of $100,000 for a single egg processing factory in the United States (Cree and Rutter 2015 , Abdulrahman *et al.,* 2014). Eggshell trash contributes to organic pollution (Laca 2017) and is produced on a yearly basis at a rate of around 8 million metric tons across the globe. This material is disposed of as rubbish in landfills without undergoing any sort of preparation. The eggshell makes up around 10% of the overall egg's weight, and it is possible to reclaim this material and put it to use in a variety of different contexts. It is common knowledge that composite materials are gaining attention in a variety of applications, most notably the plastics sector, because of their low cost, low weight, and increased mechanical qualities. As a platform for the development of novel biomaterials, eggshell waste is taken into consideration in this review (Faridi and Arabhosseini 2018). Components for machines, plastic toys, electrical packaging, automotive and aerospace parts are some of the potential applications for eggshell polymer composites. According to the published research, a number of different composite materials were produced using waste eggshell for use in a variety of applications. These applications include the improvement of the thermal conductivity of polyaniline material (Ghani *et al.,* 2012), the use of absorbent material in active packaging (Ummartyotin *et al.,* 2016), and the utilization of heterogeneous catalyst in the production of biodiesel (Sulaiman and Ruslan 2017). This brought to light an interest in doing more research and expanding the scope of potential uses of eggshell for developing new environmentally friendly materials with cheaper costs (Quina *et al.,* 2017). The matrix's principal roles are to shield the fillers and reinforcements from the effects of the environment while also acting as a stress transfer mechanism between them. While the load-bearing component of a composite is the filler material that is used in the composite (Karaduman *et al.,* 2018). The overall performance of composites is determined by a number of criteria, including the kind of fiber and resin used the volume proportion of filler and resin, the structure of the fibers, and the compatibility of the fibers with the matrix (Boukhoulda *et al.,* 2006). More importantly, waste eggshell has been utilized as a substitute for mineral limestone in a variety of applications.

Eggshell powder was subjected to thermal and chemical treatments in this investigation in order to generate pure eggshell powder and eliminate the organic membrane that was attached to it. For the production of bio-epoxy composites with varying amounts of filler, a process known as solution mixing was utilized. At varying filler percentages, the material's physical properties, including density and water absorption, as well as its mechanical and thermal properties, including tensile and flexural strengths/modulus and Charpy impact strengths. These results suggest that eggshells may be used as a replacement for conventional fillers in bioepoxy composites.

2. Relavance of the research

This research provides a method for purifying and reusing waste eggshell for bio-epoxy composites and evaluates the mechanical and thermal properties of bio-epoxy/eggshell composites as its primary contribution. Many reports on eggshell polymer composites have been published in the past, although most of these experiments employed crushed eggshell rather than shells in their natural state.There is a lack of research on eggshell purification to enhance the concentration of calcium carbonate by removing the organic membrane.

3.Methodology

3.1 Materials

The raw eggshell was acquired from a restaurant in Chennai, India, while the limestone powder was acquired from sakthi merchants in India. Table 1 lists the chemical composition of eggshell. Bio-epoxy resin and hardener were acquired from JK Traders, Chennai, India, for composite fabrication. This epoxy was composed of 31% bio-based material. Resin and hardener were combined in a ratio of 100:40.

Table 1. Chemical composition of Eggshell powder (ESP)

Chemical compound	Ca	Al	Si	K	Cl	Fe	Zn	Zr	P
%	90.45	2.34	5.60	0.83	0.32	0.1	0.04	0.02	0.3

3.2 Processing of ESP

The eggshell was washed and then it is allowed to dry at 105°C for 24 hours before being pulverized in a ball mill at 50 revolutions per minute for 24 hours in a container. 5 balls with a 25 mm diameter, 10 balls with a 20 mm diameter, and 15 balls with a 12 mm diameter were used in the ball mill during this procedure. Using the sieving machine, the ground powders were sieved to various sizes (32µm and 20µm mesh size) in order to acquire powders with distinct particle sizes. This apparatus utilized vertical and circular vibrations to generate three-dimensional sieving motions. Powder was sieved for six hours in ten separate portions. All sieves were frequently cleaned in an ultrasonic bath due to the repeated clogging of the 20 m sieve very thin pores by larger particulates in the samples.

3.3 Purification process of ESP

Eggshell particles that had been sieved were heated in air at temperatures ranging from 500 to 900^0C for varied durations of time in order to remove the membranes (0.5 to 2 h).The limestone($CaCo_3$) transformed to Calciumoxide (CaO) and carbon dioxide is produced. Next, produced CaO with addition of water is transformed into hydrated lime $Ca(OH)_2$. The addition of CO_2 turns calcium hydroxide back into limestone, which is ideally pure $CaCO_3$. The sample of purified limestone is heated at 105°C for 12hours to eradicate all water particles.

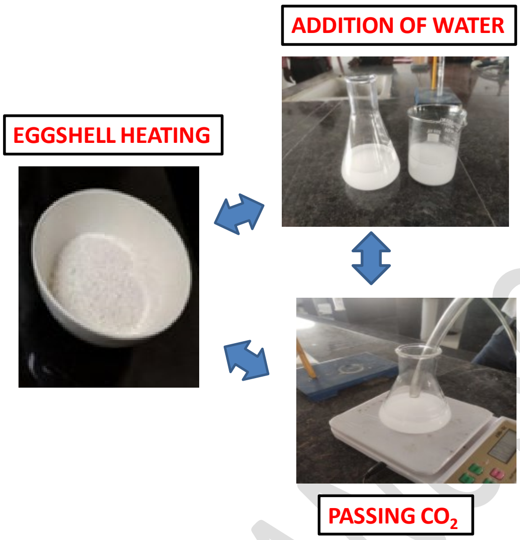


Figure 1. Process of eggshell purification

3.4 Specimen preparation

Composites were manufactured in accordance with ASTM specifications, as depicted in Figure 2. The bio epoxy and filler particles were initially combined and agitated. As soon as the mixture was devoid of air pockets, the hardener was added and it was poured into a silicon mould. Following the solution solidification, composite samples were then extracted. The values of additives utilized in bio composites are shown in Table 2.

Figure 2. Sample preparation (a) Egg shell powder (b)Epoxy resin& Hardener (c)Composites

Table 2. weight of filler and epoxy for composites

S.No	Mix Id	Size of Filler (µm)	Description
1	Bio epoxy	-	100% Bio epoxy without filler
2	ES5	32	5% ES+95%Epoxy
3	ES10	32	10% ES+90%Epoxy
4	ES20	32	20% ES+80%Epoxy
5	PES5	32	5% PES+95%Epoxy
6	PES10	32	10% PES+90%Epoxy
7	PES20	32	20% PES+80%Epoxy
8	LS5	32	5% LS+95%Epoxy
9	LS10	32	10% LS+90%Epoxy
10	LS20	32	20% LS+80%Epoxy
11	LS5-20µm	20	5% LS+95%Epoxy
12	LS10-20µm	20	10% LS+90%Epoxy
13	LS20-20µm	20	20% LS+80%Epoxy

* ES-Brown egg shell powder, PES- Purifies egg shell powder, LS- Limestone powder

4. Test properties

4.1 Tensile strength test

Tensile tests were performed on dog-bone shaped composite samples of standard dimensions 150mm x 20mm x 3mm (lxbxt) in accordance with the ASTM D638-14 standard. The tests were performed at room temperature with gauge lengths of 50 mm and a strain rate of 5 mm/min. The impact of filler kind and proportion was studied. Tensile characteristics of eggshell, limestone, and pure eggshell were investigated at three different filler loadings (5%, 10%, and 20 wt.%). Tensile strength was computed by taking average of three specimens.

4.2 Flexural strength test

The bioepoxy composites were subjected to three point bend tests utilizing an Instron 3366 testing equipment in accordance with the ASTM D790-17 standard. The strength value was calculated using the Equation 1.

Cross head speed = $ZL^2/6d$-------------(1)

Z - Constant (0.01)

L - Span(mm)

d - Thickness (mm)

4.3 Charpy test

The impact characteristics of polymeric materials can be used to determine their toughness. In general, toughness goes up with the ability to absorb energy. Charpy impact test was done with an Instron Model 450 MPX impact tester. The tests were done according to the standard ASTM D6110-18. The specimen holder held test samples that were 55 mm long, 10 mm wide, and 7.5 mm height. At room temperature, five samples of each composite composition were tested. Using equation 2, the average amount of energy absorbed per unit area (Ei) was found.

$$Ei = Ea \, / \, (b \times d) \text{ ----------(2)}$$

Ea - total energy absorbed (J/cm^2)

b - width (mm) and

d - thickness (mm)

4.4 Water absorption test

The inclusion of fillers (eggshell powder, refined eggshell powder, and limestone powder) may change the water absorption properties of epoxy composites since these additives have a high affinity for water. Test samples were immersed in a water container after being cut into rectangular specimens with dimensions of 25.4mm x 76.2mm x 5mm, as per code (ASTM D570 - 98(2018)). Samples were dried for 3 hours at 40ºC prior to immersion in water for 24 hours in order to evaluate the water absorption properties of the composites. The weights of samples were recorded at every 24 hours until the samples were 95% saturated condition. The excess water from the surface of the sample was wiped away with a paper towel and weighed to the closest 0.0001g. The rate of water absorption for the samples is determined using the Equation 3.

Water Absorption (%) =((Wt−Wo)/ Wo) x100 ---------------- (3)

Wo- Initial dry weight

Wt - Final weight (days)

5. RESULTS AND DISCUSSION

5.1 Tensile strength

The tensile strength values for all composite specimens with and without fillers are shown in Figure 3. The lack of filler components resulted in a maximum tensile strength of 67.5 MPa for the pure bio-epoxy. When 5% eggshell, pure eggshell, and limestone were added with the bio-epoxy, the tensile strength was lowered by 10.03%, 27.2%, and 14.6%, respectively. Tensile strengths reduced by 4.16%, 18.10%, and 15.21% for eggshell, pure eggshell, and limestone, respectively, when 10% fillers were added, but by 18.25%, 32.7%, and 21.7% when 20% fillers were used. The reason for the reduction in strength may be due to agglomeration of filler particles in the composites which hindered load transfer from the matrix to the fillers. Fractures can easily occur and spread as a result of this tendency (Song and Youn 2005). Generally, composites containing eggshell fillers outperformed pure eggshell and limestone in terms of tensile strength. These amino acids may aid in the bonding of bio-epoxy and organic membranes, which have been shown to bind effectively to eggshell particles. Because of the larger effective surface area, composites with 20µm limestone fillers had somewhat greater tensile strengths than composites with 32µm limestone fillers. The tensile modulus is depicted in Figure 4 depicts for several fillers. Bioepoxy composite without fillers had the lowest tensile modulus of 2.50GPa. Tensile modulus increased gradually as filler percentage increased for all filler material. When compared to Bio epoxy composites, the specimen with 20% of eggshell, purified eggshell, and limestone increased the modulus value by 69%, 94.20%, and 65.59% respectively.The inclusion of tougher limestone particles than the polymer matrix was linked to the increase in stiffness with filler increases.

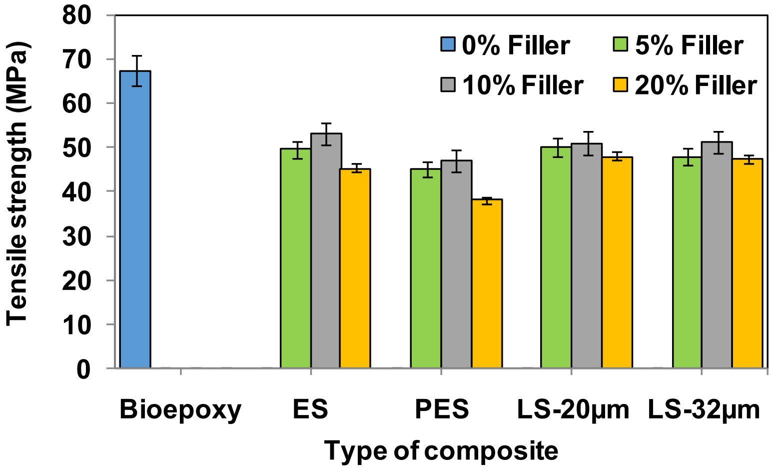


Figure 3. Tensile strength with fillers for different composite

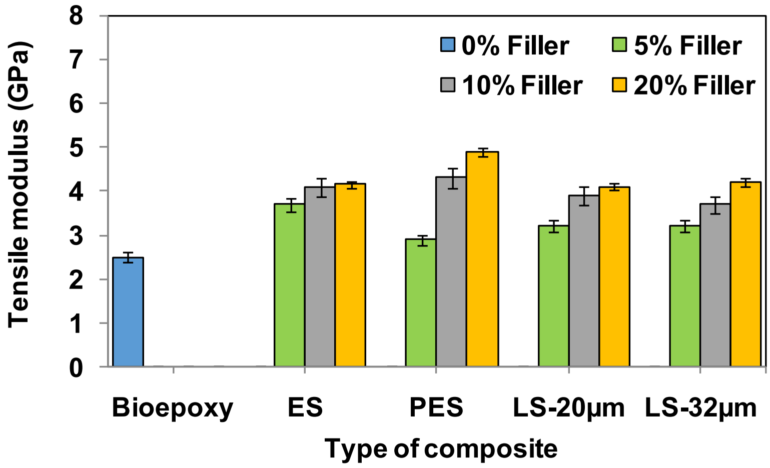


Figure 4. Tensile modulus with fillers for different composite

5.2 Flexural strength

Figure 5 depicts the flexural strength of bio-epoxy composite materials of various kinds (eggshell, pure eggshell, and limestone) and filler loadings. The highest flexural strength of the pure bio-epoxy was 884.5 MPa, which was equivalent to the manufacturer's figure of 92.7 MPa (Golakiya 2020). In general, eggshell particle-containing composites exhibited the highest flexural strengths, but when compared to pure bio-epoxy composites, they dropped by 12.4%, 15.7%, and 35.6% at 5, 10, and 20% wt.%, respectively. Reduced particle agglomeration may come from lower filler loadings, suggesting improved load transmission to the filler particles from the matrix. Pure eggshell and limestone fared equally well, with limestone outperforming both. With respect to pure epoxy, the composites with pure eggshell powder as filler the flexural strength was reduced as 25.1% at 5% ESP, 32.03% at 10% ESP and 35.77% at 20% ESP respectively. Likewise the composites with limestone filler the flexural strength was reduced as 21.25% at 5% LSP, 28% at 10% LSP and 32.54% at 20% LESP respectively.

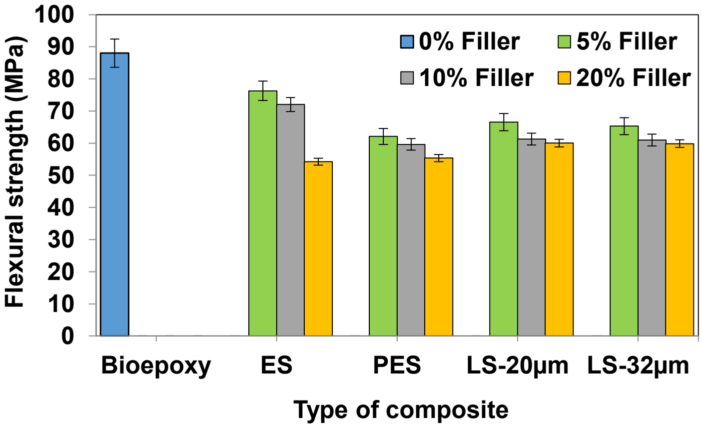


Figure 5. Flexural strength of composite specimens

The flexural modulus values for composites specimens is shown in Figure 6. For pure bio epoxy the value is 3.95Gpa. Compared to pure bio epoxy composite, the modulus value increased with addition of 20% filler ESP by 61.5% , PES by 37.28%, LSP by 35.26% respectively. This increase in modulus might be attributed to the inclusion of harder limestone particles, which boosted the stiffening effect in the composites (Qiu et al., 2000).

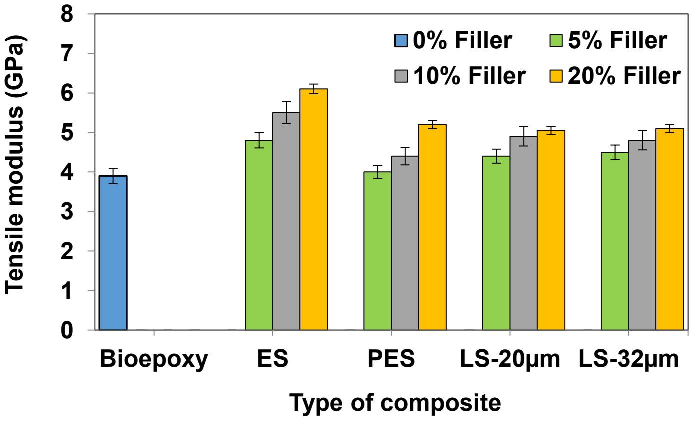


Figure 6. Flexural modulus of composite specimens

5.3 Charpy impact strength

Figure 7 shows the results of the Charpy impact toughness test. Impact test findings revealed a progressive decrease in impact energy with increasing filler content for all three fillers (eggshell, purified eggshell and limestone). This might be owing to a larger tendency for agglomeration at higher filler loadings, which results in weak interfacial areas upon impact. According to (Toro *et al.,* 2007), whenever a crack develops after an impact, it spreads to the weak interfacial regions. It is evident that with addition of filler material increases, impact intensities tend to diminish progressively. Pure bio-epoxy had an impact strength of 82 J/cm^2, which was lowered by 15%, 24%, and 32% for eggshell; 24%, 30%, and 38% for purified eggshell; and 21%, 26% and 34% for limestone fillers with 5%, 10%, and 20% wt. Since larger particle sizes result in greater stress concentration, limestone particles with 20µm sizes demonstrated higher impact strengths than 32µm sizes, as is common. Bio-epoxy composites with 20µm limestone fillers had 5.1%, 6%, and 5% greater impact strengths than 32µm fillers at 5%, 10%, and 20%, respectively. Additionally, eggshell fillers demonstrated a small improvement in impact strengths for the same filler loadings in pure eggshell and limestone composites.

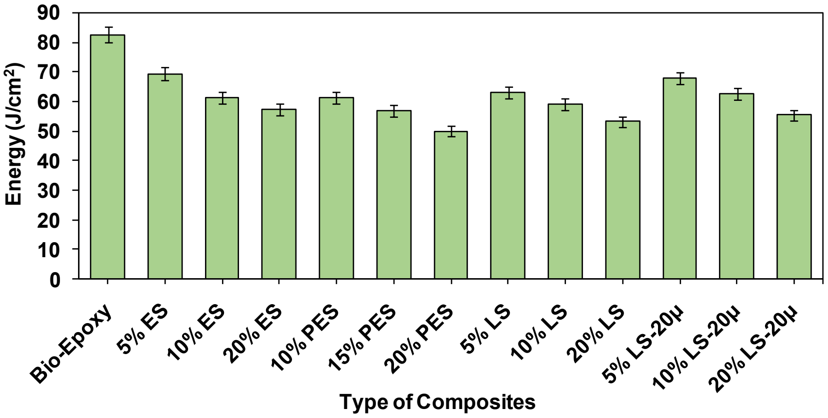


Figure 7. Charpy impact strength of composite specimens

5.4 Water absorption of bio-epoxy composites

Figure 8 show bio-epoxy composites with different fillers have different water absorption properties. The results revealed that the specimen ability to absorb water increased rapidly between days 0 and 20, and then reduced until they were saturated after 60 days in water. The ratio of water absorbed by pure eggshell, purified eggshell, and limestone fillers, as well as bio-epoxy with 20 wt. Water absorption was shown to be lowest for pure bio-epoxy, which had no $CaCO_3$ fillers. Composites loaded with unrefined eggshell and limestone fillers absorbed less water than their shell-filled counterparts. This may be because the membranes of eggshells contain amines, amides, and carboxylic acids, which provide surface functional groups (Zhang *et al.,* 2010). The hydrophilic nature of these short-chain functional groups means that they readily form hydrogen bonds with water molecules (Golakiya 2020). The water absorption rate of pure bio-epoxy composites was 5.65 wt.% after 65 days, whereas the water absorption rate of composites containing 20 wt.% of eggshell fillers was 43% higher. Water absorption testing revealed that composites made with 20 wt.% of purified eggshell and limestone fillers were equivalent to bio-epoxy composites at both the beginning and conclusion of the test.

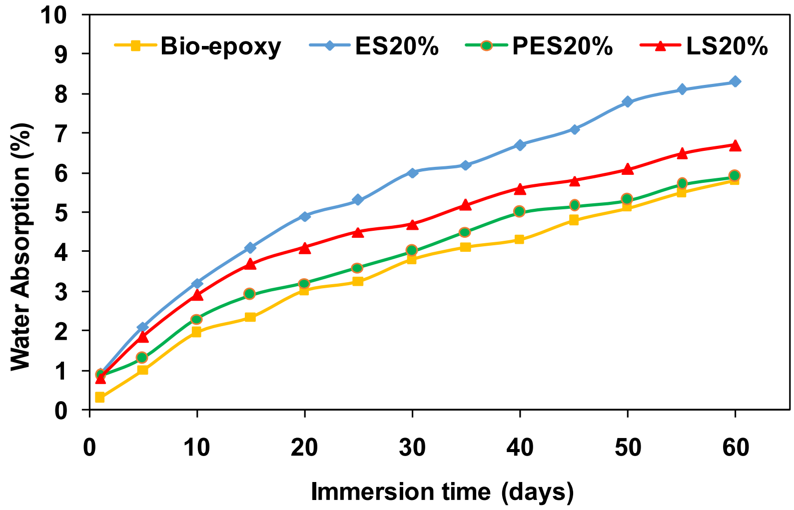


Figure 8. Rate of water absorption at 20% filler addition

Composites with greater filler loadings exhibited greater water absorption, and this was the case across all three filler types. It's possible that this is because of the increased quantity of water-absorbing filler particles. It is more difficult to achieve uniform filler dispersion in the epoxy matrix at large filler loadings because agglomeration is more likely to develop as a result of electrostatic interactions between micro particles (Ervina *et al.,* 2016). Moreover, the problems of attaining a homogenous dispersion at high filler loading may increase the void content in composites, which in turn raises the water absorptivity of the composites. Figure 9 shows the water absorption of bio-epoxy and bio-epoxy with 5, 10 and 20 wt. % eggshell as filler. The water absorption of bio-epoxy composites was found to be 5.75 wt.%, increasing by 2.15%, 15.44%, and 44.23% when 5, 10, and 20 wt.% of eggshell fillers were used. Figure 10 displays the results of water absorption testing for pure bio-epoxy and bio-epoxy containing 5, 10, and 20 wt.% purified eggshell, whereas Figure 11 depicts the same testing for bio-epoxy and bio-epoxy having 5%, 10%, and 20 wt.% limestone. The water-absorption properties of pure bio-epoxy were not significantly altered by the addition of 5 wt.% purified eggshell or limestone fillers. By using pure eggshell at a loading of 10 wt.% and limestone at a loading of 20 wt.%, the composites water absorption rates rose by 6.10 and 16.19%, respectively. Overall, water absorption was lower than eggshell filled composites due to the absence of membranes, and it was similar for pure eggshell and limestone at all filler percentages.

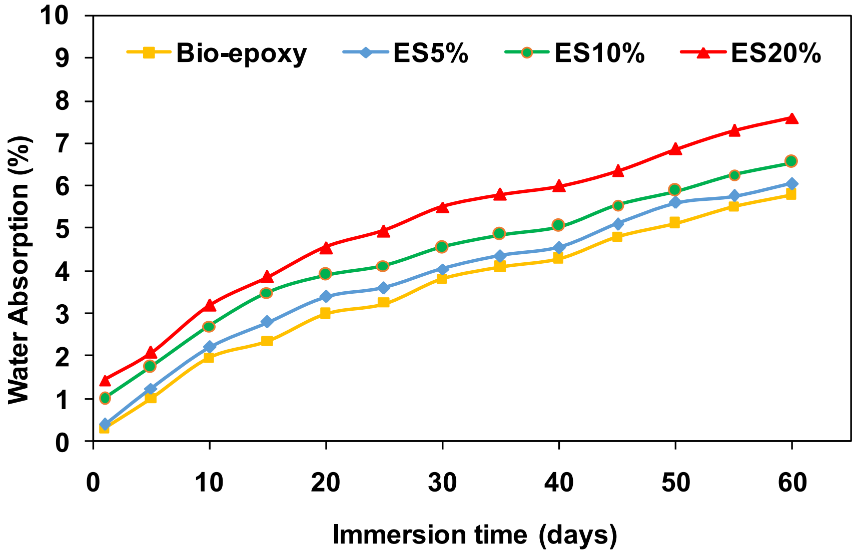


Figure 9. Water absorption for composites with ESP

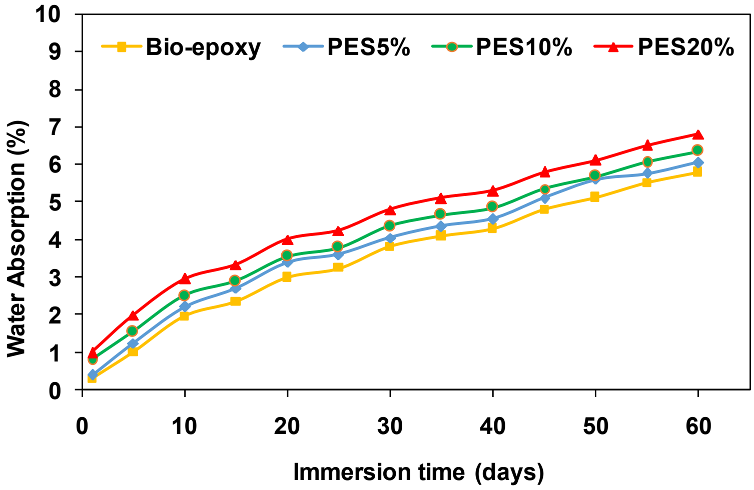


Figure 10. Water absorption for composites with PESP

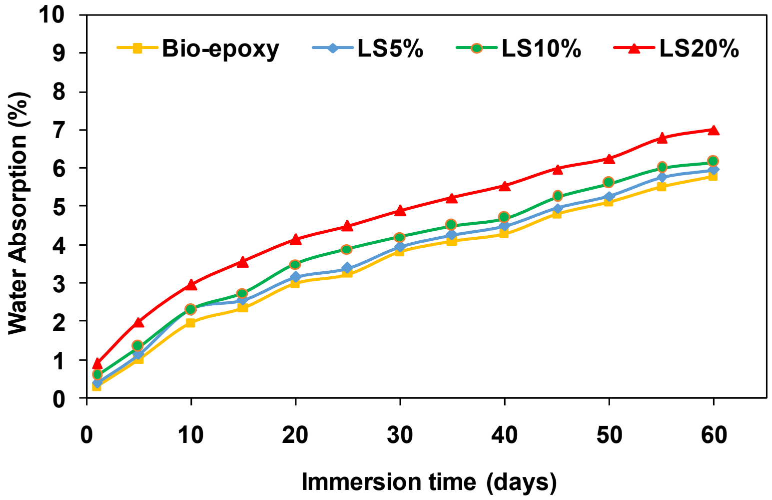


Figure 11. Water absorption for composites with LSP

Figure 12. WA comparison of composites with 20 µm & 32 µm fillers

6. Conclusions

Eggshells that have undergone efficient thermal and chemical treatments can be used to make composite materials, which have the potential to be of use to our society in terms of both the environment and the economy. In this body of work, one approach was provided for recovering pure CaCO3 from discarded eggshell and using it as filler in the production of new composite materials. Throughout the course of this research, the following sources were utilized to produce the fillers: unpurified eggs hell, purified eggshell, and mineral limestone. A solution mixing method was utilized in order to include the fillers into the bio-epoxy composite.

- When the addition of filler materials was raised from 5% to 20% for each of the three different filler types, the overall tensile and flexural strengths saw a drop (eggshell, purified eggshell and limestone). Yet, in comparison to the pure bio-epoxy, the tensile and flexural modulus improved when the filler loadings were increased. Eggshell should be added to the bio-epoxy in amounts of no more than 10% for composites that will be used in tensile applications, and no more than 5% for composites that will be used in flexural applications.

- The Charpy impact energy reduced as the filler content increased for all three different fillers. It's possible that this is because of the existence of agglomeration and voids, both of which are formed during manufacture at larger filler loadings.
- After 65 days in water, pure bio-epoxy composites had absorbed 5.75 wt.% water; bio-epoxy containing 20 wt.% eggshell had absorbed 44.23%, bio-epoxy specimen with purified eggshell at 20% absorbed 16.19% and limestone filler at 20 wt.% had absorbed 16.09% hgher water.

As a conclusion, eggshell has the potential to serve as an alternative to mineral limestone in the role of filler material in the plastics sector.

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