

## The Effect of Seashells as Filler in Epoxy Composites

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### ABSTRACT

The presence of seashell wastes is generalized in seashores. Sometimes, these wastes must be removed to provide clean beaches and obtain quality signs. It is possible to use these wastes as bio-filler for polymer matrices. Therefore, the primary purpose of this research is to study the mechanical properties and oil absorption of various seashells, namely, clams, cockles, and mussels. These three types of seashells are used as filler in an epoxy matrix. The performance of the seashells was investigated at 10wt%, 20wt%, and 30wt%. Calcium carbonate ( $\text{CaCO}_3$ ) is the main constituent of seashells and one of the most commonly used inorganic fillers in the polymer industry. Cockle has the highest amount of  $\text{CaCO}_3$ , followed by clam and mussel. The results disclose that adding the seashells as filler can improve tensile strength if the optimum filler loading is not exceeded. 10wt% of cockles in epoxy composites is reported as the best composition to achieve the highest tensile strength. Mussels and cockles absorb more oil in the epoxy composites at their various weight percentages. Besides, all seashells showed the highest oil uptake at 10wt% filler loading. Lower filler loadings lead to the absorption of more oil by the composites.

**Keywords:** *Seashells, epoxy composites, tensile properties, oil absorption*

### INTRODUCTION

Waste seashells have become a severe environmental crisis because most aquaculture wastes are abandoned annually in landfills or directly along the coastline. These can be a source of environmental nuisance and serious health hazards because the remaining organisms' matters can quickly become a breeding place for the harmful microorganisms which induce microbial decomposition and generate obnoxious odors [1]. While using the recycled waste of shells can offer environmental advantages by converting them to powder form. The foremost advantage of recycling shells is the prevention of the disposal of residue shells in landfills [2]. The seashell, mainly composed of calcium carbonate ( $\text{CaCO}_3$ ), can be used as a filler in a

polymer matrix. Fombuena [3] and Gopal [4] recognized that producing new polymer products focuses on new challenges of the growing environmental concerns and the development of new bio-based and biodegradable materials. Moreover, there needs to be more concern about the product with a balanced cost and performance. Incorporating fillers in a polymeric matrix is a fast and cost-effective way of achieving the desired properties.

Epoxy resin, categorized as a thermoset composite, is commonly used because of its excellent mechanical properties, low absorption, and good adhesion with various fillers. Adding filler to the epoxy purposely reduces the cost and enhances the mechanical properties. It is due to the epoxy brittleness and lack of thermal stability. Hence, incorporating an alternative filler from the waste, like seashells, has achieved spectacular attention without compromising serviceability and ecological requirements [5]. The powders obtained from the waste shells have been increasingly employed in industrial applications to exhibit their potential applications. In addition, Sophia [5] confirmed that the high cost of commercial calcium carbonates limits their usage, although they are a commonly utilized filler. Hence, this study is an effort to fill the research gap in utilizing waste shell powders as valuable bio-based fillers.

This study investigates the effect of employing three types of seashells: clam, cockle, and mussel as fillers in epoxy composites. It was concluded that the types of seashells and the filler loading amount (10wt%, 20wt%, and 30wt%) affect the tensile properties. In addition, the oil absorption of epoxy/seashell composites was determined. The absorbed oil content by the composites with different seashell types and loading amounts revealed the potential of utilizing the epoxy composites as absorbent materials. However, the oil absorption can lead to damage to the composites. Therefore, it is crucial to understand the limitations of these composites.

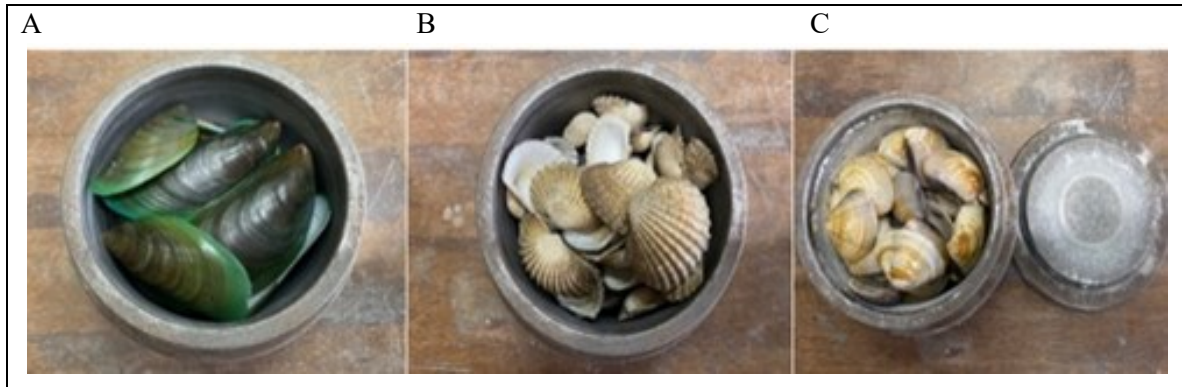
## EXPERIMENTAL

### *Materials and Methods*

The three different types of seashells (Figure 1), cockle, clam, and mussel, were used as filler in the epoxy with a variety of loading contents of 10wt%, 20wt%, and 30wt% to form the epoxy composites. The epoxy resin was crystal clear of bisphenol A supplied by HH Saintifik Enterprise from Jinhua Guangdong, China. The shells were collected from the seacoast at Perlis (cockle and clam) and Johor (mussel). At first, the shell was cleaned using a brush and then washed with water. After washing, it was dried in the sunlight for five days. The dried shell was then broken into small pieces using a grinding machine. The ground powder was sieved through a sieve shaker to obtain a size of 79–90 microns.

Mo *et al.* [6] stated that an additional grinding operation is required when using seashells in powdered form. When using seashell waste as aggregates, crushing is required to obtain a more rounded shape of the seashell with smaller fractions. It improves the bonding with the matrix and reduces the voids within the aggregates. The mixture of epoxy resin and hardener (ratio of 3:1) was then poured into the paper cup containing the previously measured seashell powder. A stirrer was used to stir the mixture. 5 to 10 min of stirring was required to confirm that the epoxy and seashells were uniformly mixed. The mixtures were then poured into a silicon mold of dumbbell shape and allowed to cure at room temperature for 24 h.

Afterward, the dumbbell-shaped sample with dimensions of 19mm × 165mm × 1mm, according to the ASTM D638, was removed from the mold.



**Figure 1:** Three types of seashells: a) mussels, b) cockles, c) clams (original look before grinding)

### ***Tensile Test and Oil Absorption Test***

Several tests, such as tensile and absorption, were conducted on the obtained composites. The tensile test was performed by Instron 5569 Universal Testing Machine with a cross-speed ahead of 10 mm/min to identify the mechanical properties of the composites. Also, the absorption ability of the epoxy composites in oil was determined. The type of oil was only used cooking oil. This was used to measure the amount of oil absorbed under specified conditions focusing on the type of seashell and the different filler percentages. The composites were weighed with a precision 0.001 before being placed in the oil. At the end of the immersion period (28 days = four weeks), the composites were removed from the oil; the surface oil was removed using tissue paper. Then, the wet composites were weighted to determine wet values. The oil absorption percent was calculated using Equation 1 [7]:

$$M(\%) = (m_t - m_o) / m_o \times 100 \quad \text{Equation 1}$$

Where  $m_o$  and  $m_t$  denote the dry weight and the weight after time "t," respectively.

## **RESULTS AND DISCUSSION**

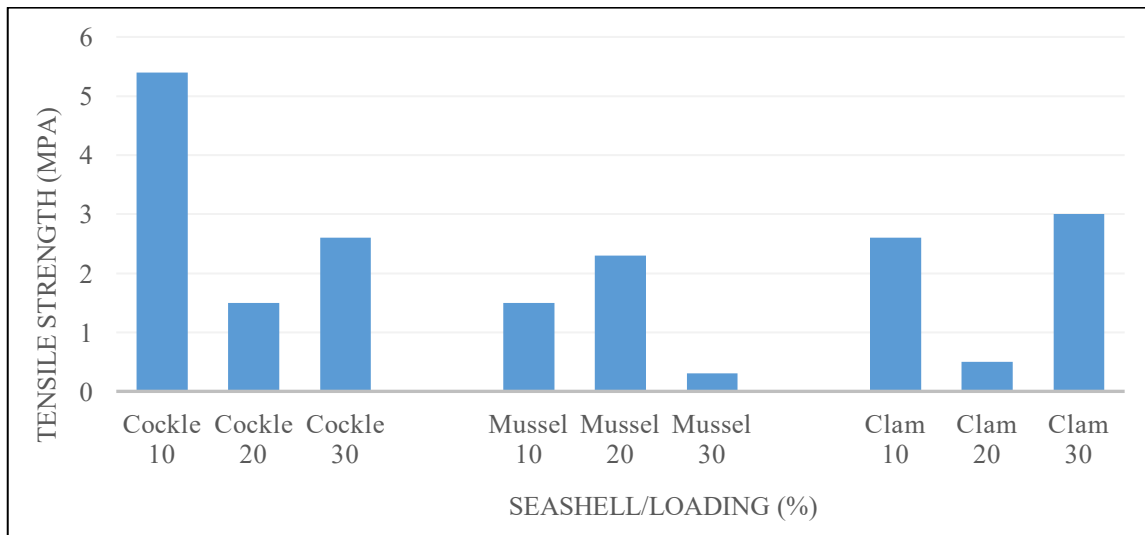
### ***Physical Features of Seashells***

A seashell is a hard and protective outer layer. As shown in Figure 1, the three different types of seashells are dissimilar. The mussel shell is longer than it is wide and wedge-shaped or asymmetrical. The exterior color of the shell is often dark greenish, blackish, and brownish. The interior color is silvery. At the same time, the cockle has a rounded and heart-shaped shell with a slightly ribbed texture. The color is almost

white/beige with a blackish or brownish tone. Clams are also similar to cockles, circular and oval-shaped, but without ribs. It has a very smooth external surface with yellowish and white color.

### *Tensile Properties*

The tensile test is performed to study and compare the tensile properties of all filled epoxy/seashell composites, not the neatness of the epoxy. It also can reveal the potential of  $\text{CaCO}_3$  obtained from organic shell waste to be dispersed into the polymer matrix since filler dispersion is crucial in the composites. Two tensile properties were evaluated: tensile strength and elongation at break. Figure 2 indicates the tensile strength of the epoxy/seashell composites with the seashell loading of 10wt%, 20wt%, and 30wt%. At 10wt% loading of the cockle, the highest value of tensile was observed. However, a drastic decline to 1.523 MPa and a gradual increase to 2.597 MPa was noticed after adding cockle filler with loadings of 20wt% and 30wt% into the epoxy, respectively. The 10wt% epoxy/cockle composite had the optimum filler loading. It is because of the strong polymer and filler interface adhesion for an effective stress transfer and the desirable particle dispersion between the epoxy and the seashell filler [8]. The 20wt% epoxy/cockle composite exhibited the lowest tensile strength, which can be due to the excessive addition of the cockle filler. This led to a non-uniform distribution of the cockle filler in the epoxy molecule [8], which caused the agglomeration.



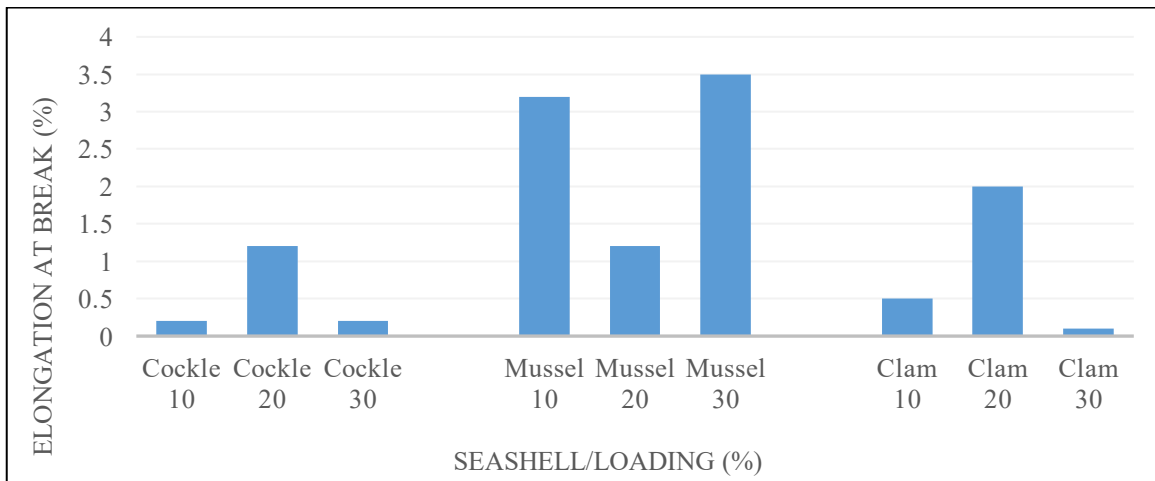
**Figure 2:** Tensile strength of the epoxy/seashells composites

Also, it can be seen clearly that the loading amount of 20wt% was an optimum loading in the mussel epoxy composites. Then, the tensile strength decreased dramatically at the 30wt% loading. Adding the seashell filler diminished the strengthening effect incorporated into the epoxy matrix. It is proven that adding the filler cannot continuously improve the rigidity or strengthen the polymer material with an optimal filler loading. Also, it is attributed to the poor interfacial adhesion of filler-matrix and particle aggregation [9].

The 30wt% epoxy/mussel composites exhibited the lowest tensile strength among the other epoxy/mussel composites because of the poor distribution and interfacial adhesion of the mussel filler within the epoxy, which can increase the brittleness as the filler content increases [10]. Besides, the excessive addition of the seashell filler into the matrix leads to agglomeration in the polymer matrix and a reduction in tensile strength. This is mainly due to stress concentration at the particle/matrix boundary region, which causes the weakening of the particle/matrix interaction.

The epoxy/clam composites showed the highest tensile strength at 30wt% of clam loading, while the lowest was at the 20wt% of clams. It can be concluded that 30wt% of clam was an optimum loading amount in the epoxy composites. The fillers can strengthen the filler/matrix interface, which gives the filler a better capability to support the transferred stress from the matrix [11]. There was a decrease in tensile strength as the filler content was increased from 10wt% to 20wt%. The lack of interaction between the clam filler and epoxy matrix restricts the load transfer from the epoxy to the seashell filler, which causes a reduction in the tensile strength of the composites [12].

The elongation at the break of the epoxy/seashell composites is shown in Figure 3. The cockles loading of 10wt% and 30wt% in the epoxy composites exhibited the lowest elongation at break percentage. The elongation at break decreased because adding the filler into the epoxy increased the stiffness of the composite. As the stiffness of the material increased, the ductility decreased. Besides, agglomeration was possible when the filler was added to the epoxy. Agglomeration can function as a stress raiser, leading to a catastrophic failure during elongation. The lowest percentage of elongation at break for the epoxy/mussel composites was demonstrated at the 20wt% loading of the mussel filler. It is due to the reason that according to Adeosun *et al.* [13], the composites with the highest tensile strength exhibit the lowest ductility.



**Figure 3:** Elongation at break of the epoxy/seashells composites

Adding seashell filler particles into the matrix can weaken the intermolecular forces at the matrix/filler interface. The composite increased elongation at break percentage for the composite by increasing the mussel loading from 20wt% to 30wt% because of the composite ductile state. The composite might be in a ductile state due to the non-homogeneous mixing of the epoxy and the mussel powder during the preparation process of the composites.

Among the composites, the 20wt% epoxy/clam composite had the highest elongation at break, while the composite with 30wt% of clam showed the lowest elongation at break. The most ductile composite was the composite with 20wt% loading of clams. The addition of clams reduced the impact strength of the composites. Abinash *et al.* [14] revealed that it reduces the brittleness of the composites. It is due to the uneven distribution of clam powder during the preparation process of the composites. Then, the 30wt% epoxy/clam composite had the lowest elongation at break percentage due to the reduction of deformability at the filler/matrix interface. Since the matrix became rigid as a result of adding the fillers. Increasing the filler content forms weaker interfacial regions between the matrix and filler. Therefore, the elongation at break is reduced [11]. It is also reported that the higher filler content can increase the broken polymer chains [9].

In general, filling a polymer with  $\text{CaCO}_3$  particles significantly influences the mechanical properties of the polymer [15]. Uniform filler dispersion within the polymer matrix is required to prevent the formation of cracks triggered by the presence of high contents of filler agglomerates. Furthermore, it is critical to increase the material's impact toughness. Although, there are some irregularities possibly caused by the poor interfacial interaction between  $\text{CaCO}_3$  shell particles and the polymer matrix. By comparing the three types of seashells used as filler in epoxy composites, the epoxy/cockle composite had the highest tensile strength at 10wt% of filler content. It was followed by the composite with the 10wt% of clam. The lowest tensile strength was for the composite with 30wt% mussel content. It is reported by Kumar *et al.* [16] that the  $\text{CaCO}_3$  present in the seashell particle can absorb 20% more impact energy attributed to the interface de-bonding. It is concluded that adding the seashell as a filler into the epoxy matrix can enhance the mechanical properties of the composites. The filler dispersion and the filler/matrix interaction are the key factors influencing the mechanical properties of the composites [3]. Good dispersion is needed to obtain balanced properties in the composites.

Norazlina *et al.* [17] discovered that the calcium carbonate obtained from the seashell can improve the mechanical properties of the composites. The enhanced mechanical properties of a composite, such as tensile strength, as a result of adding a seashell filler to the matrix, are supported by the findings of Ginting *et al.* [18]. The overall properties of the composites containing a seashell as filler can be affected by the size, content, and shape of calcium carbonate. According to Fombuena *et al.* [3], the seashell is mainly composed of calcium carbonate in the form of calcium oxide (CaO), more than 94% of which was proved by XRF. This indicates that seashell is an attractive biosource of high-purity calcium carbonate.

Soffian *et al.* [19] reported the chemical composition of  $\text{CaCO}_3$  in Malaysia's clams, cockles, and mussels. As shown in Table 1, the cockle has the highest amount of  $\text{CaCO}_3$  (98.7%), followed by the clam (96.8%). The mussel has the lowest amount of  $\text{CaCO}_3$ , which is 95.6%. The higher  $\text{CaCO}_3$  content can increase the tensile strength and stiffness of the composite while reducing the ductility of the composite.

Kumar [16] confirmed that the calcium carbonate gives the shell stiffness and strength, and the protein between these mineral sheets provides some compliance and enables the shell to develop energy-



dissipating micro-cracks making it much harder to break. Also, the drop in interfacial bonding leads to weakness in the transverse direction.

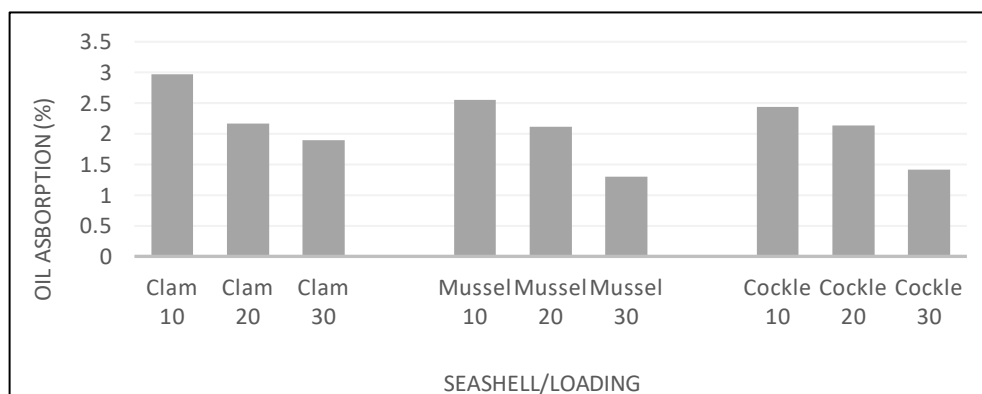
**Table 1:** Calcium carbonate ( $\text{CaCO}_3$ ) content in seashells [19]

Seashell	$\text{CaCO}_3$ content (%)
Clam	96.8
Mussel	95.6
Cockle	98.7

### Oil Absorption Tests

The oil absorption test investigates the possibility of submerging a composite in oil since all seashells have their whole life in water. When a composite is soaked in oil, the oil diffuses into the composite. Then, it can damage the composite structure from the inside. Therefore, it can diminish its mechanical properties. Once a composite has contact with an organic solvent, it swells to various degrees depending on the nature of the liquid. The absorption of any medium in natural filler mainly occurs due to the presence of fine pores and hydrogen bonding sites in the natural filler, the gaps and flaws at the interface, and the void formed during the formation process of epoxy composites. The absorption of the different seashell composites with 10wt%, 20wt%, and 30wt% seashell loading after 28 days of oil immersion is presented in Figure 4.

Theoretically, the oil capacity increased rapidly for the first few hours; then, it increased gradually until it finally became a plateau in which the system reached the equilibrium conditions. Only a tiny increase in the oil sorption capacity was observed near the equilibrium stage. The mechanism of oil sorption by the organic filler can be through absorption, capillary action, adsorption, and a combination of these processes [20]. The oil diffused from the bulk liquid and interpenetrated into the sorbent due to the concentration gradient and the capillary pressure existing within the pores of the composite.



**Figure 4:** Oil absorption percentage of the seashells at different loading

Comparing the seashells, the cockle, and the mussel absorbed more oil than a clam. According to Ginting [18], poor distribution of the seashell powder into the matrix results in a composite with looser porosity and higher oil absorption. Also, the oil molecules can easily penetrate and enter the empty spaces between the filler and matrix. Farahana [21] stated that the presence of  $\text{CaCO}_3$  also influences the absorption of carbonate-contained shells. As the filler loading increases, the formation of the filler agglomerates in the composites increases the oil absorption due to the difficulties in achieving a homogeneous dispersion of the filler.

All the studied composites showed high oil uptake at low seashell loading. However, it decreased when the loading increased to 30wt% for all seashell types. It is found that the higher the filler content, the higher the percentage of swelling for epoxy composites [22]. Also, the swelling percentage can be affected by polymer relaxation [23]. From Fickian diffusion, polymer relaxation is the stretching of polymer molecules by the diffusion of water molecules. Therefore, a redistribution of void and free volumes occurs that can affect the liquid absorption in the polymer.

The oil uptake and the consequent swelling percentage of the composites are related to several characteristics of the oil and the composites filled with seashells. The swelling ability of a polymer is mainly attributed to its affinity for the oil as the swelling medium [20]. The size and structure of the oil molecules are also the factors influencing the sorption. As the filler, the seashells also play an essential role in improving oil absorption or function as a resistance to prevent absorption. Swelling can result in polymer relaxation and weakened adhesion forces caused by the surrounding oil.

The seashell effectively reduced the oil absorption since it filled the micropores with its smaller size particles. Besides, adding the fillers restricts polymer mobility [16]. Although, the oil absorption can lead to a decrease in the end-use applications of these composites. Therefore, by understanding these composites' limitations and benefits, seashells have a promising potential to be employed in the plastic industry and especially in formulating plastic products. Their innovative application as absorbent materials for the oil spill in seawater also needs to be considered.

## CONCLUSION

Replacing conventional mineral fillers with recycled ones is the most cost-effective way to overcome severe environmental issues. Incorporating different seashells gave different results on tensile properties and oil absorption. Cockle enhanced the tensile strength of the epoxy composites compared to mussel and clam. The mechanical properties of the composites did not significantly change with the seashell content. However, they depended on the optimum loading and the type of seashell. The tensile strength was directly related to the filler/matrix adhesion quality. Considering the oil absorption, the cockle and the mussel absorbed more oil than the clam. Furthermore, the shell waste can be further processed to be utilized as the filler of polymer composites. These utilizations of shell wastes shed light on the industrial production of high-value-added products.



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## AUTHOR'S CONTRIBUTION

Nor Azwin was a supervisor for Final Year Project, who designed the research idea. Suk Lum and Khairulnisa carried out the research and the laboratory test and wrote the original draft. Lastly, Nor Azwin anchored the review and revisions and submitted the article.

## CONFLICT OF INTEREST STATEMENT

The authors agree that this research was conducted without any self-benefits or commercial or financial conflicts and declare the absence of conflicting interests with the funders.

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