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Biocomposites from (*Anadara granosa*) shells waste for bone material applications

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Abstract. The overall objective for this study is to determine the effect of biopolymer types and ratio on producing biocomposites derived from cockle (*Anadara granosa*) shells waste. In this study, two types of biopolymer were used i.e. sodium alginate and carboxymethyl cellulose. These biocomposites are meant for bone material applications. The processes involved in producing the biocomposites were pre-treatment of the cockle shells, formation of $CaCO_3$ in aragonite form and finally the synthesis of biocomposites. All samples have undergone physicochemical and mechanical analyses to determine their crystallinity, purity, functional group, surface morphology, elemental compounds and compressive strength using X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope (SEM), Electron Dispersive X-ray Analysis (EDX) and Universal testing machine (UTM). The $CaCO_3$-biocomposites have been prepared using different ratio of biopolymer and different types of biopolymers. The physicochemical properties of the biocomposites are not affected by the ratio and types of biopolymers. Yet, the ratio and types of biopolymers have influenced the mechanical properties of biocomposites. The biocomposite with lesser amount of biopolymer has denser structure and greater mechanical strength. Comparison between types of polymers revealed that biocomposite with carboxymethyl cellulose has greater mechanical strength compared to biocomposite with sodium alginate.

1. Introduction

Shellfish aquaculture mainly cockle (*Anadara granosa*) is one of the most important industries worldwide and generates abundant of shell wastes. In Malaysia, marine shells are mostly used in handicrafts industry to produce decorative stuffs like key chains. Shell wastes are mostly dumped in landfills without any post-treatment due to high cost of disposal procedure [1,2]. The abandoned shell wastes often cause unpleasant view to the landfills and give out nauseating smell.

In order to minimise the negative impacts on the environment, researchers around the world are studying on the transformation of cockle shell wastes into valuable products. For examples, it has been used as a potential aggregate replacement in concrete [3–5], as catalysts [6,7], drug delivery and bone materials [8,9]. In fact, seashells consist of high composition of calcium carbonate ($CaCO_3$) of more than 95% by weight [10–12]. $CaCO_3$ especially in aragonite polymorph crystal is suitable in bone tissue engineering as it is biocompatible, dense in nature, and can replace bone structure [13–15].

However, application of $CaCO_3$ alone as bone material has limitation due to inadequate in mechanical properties. Therefore, combining $CaCO_3$ with other polymer such as sodium alginate,

cellulose and polyvinyl alcohol could improve its mechanical properties while maintaining its biological properties [16–18]. The combination of $CaCO_3$ with natural sources polymer is known as biocomposite.

As to date, a few study on the formation of biocomposite derived from waste materials were done using cockle shell wastes [9,19], *Paphia undulates* shell wastes [20], and fish scale wastes [21]. Hence, this study is investigating the feasibility of producing $CaCO_3$-biocomposite derived from cockle shell wastes that suitable as bone material. This current study is focusing on the effect of biopolymer ratio which is sodium alginate and effect of biopolymer types which are sodium alginate and carboxymethyl cellulose on physicochemical and mechanical properties of $CaCO_3$-biocomposites.

2. Materials and Methods

2.1. Materials
The cockle shells used in this study were obtained from local market in Kuantan, Pahang. Sodium alginate was purchased from R&M (Malaysia) and carboxymethyl cellulose was purchased from Sigma Aldrich (USA). Deionized water (from Millipore Elix 5, USA) was used in the entire studies.

2.2. Pre-treatment of shell and synthesis of $CaCO_3$
The seashells were boiled in water for 15-20 minutes to remove the organic matters that attached on them. Then, the shells were dried in the oven at the temperature of 110 °C for 2 hours. The dried shells were then crushed by using grinder (Retsch ZM200, Germany) into $CaCO_3$ powder and sieved over a set of clean test sieve (Retsch AS200, Germany) with sizes between 63 and 71 μm.

2.3. Synthesis of $CaCO_3$-biocomposites
The biocomposites were synthesised according to the method of [22,23] with slight modifications. Five percent of sodium alginate was dissolved in deionised water and hydrated overnight. The sodium alginate solution was mixed with $CaCO_3$ powder in mass ratios of 1:0.3 and 1:1. The ceramic/sodium alginate mixture was kneaded using flat end spatula into a homogenous paste and subsequently moulded into silicone mould. Moulded green bodies were incubated at 60 °C for 24 h to remove moisture and water content. The experiment was repeated using different biopolymer which is carboxymethyl cellulose. Table 1 shows biocomposites that were produced in this study.

Table 1. Different types of samples produced in this study.

No	Type of Sample	Abbreviation
1	Raw shell powder	$CaCO_3$
2	Calcium carbonate-sodium alginate biocomposite with ratio 1:0.3	CA3
3	Calcium carbonate-sodium alginate biocomposite with ratio 1:1	CA10
4	Calcium carbonate-carboxymethyl cellulose biocomposite with ratio 1:0.3	CC3

2.4. Physicochemical and mechanical characterization of $CaCO_3$-biocomposites
The physicochemical analyses of biocomposites were done using X-ray diffraction (XRD), Fourier transform infrared (FTIR) and scanning electron microscope (SEM) along with energy dispersive X-ray (EDX). The XRD analysis was carried out using X-ray powder diffractometer (Rigaku MiniFlex II, Japan) in order to assess the phases, crystallinity and purity of the biocomposites. Scans were carried out in the range of 2θ range from 20°-80° with step size 0.02° at 1s step time. FTIR (Thermo Fisher Nicolet iS5, USA) with diamond attenuated total reflectance (ATR) system over a range of 400 to 4000 cm^{-1} was used to identify functional groups in the biocomposites. The morphology and elemental analysis of the biocomposites were observed using SEM along with EDX (Hitachi TM3030

Plus, Japan). The samples were sputter-coated with platinum to prevent charging during analysis process. The compressive strength was determined by crushing a biocomposite between two flat platens using a computer controlled universal testing machine with a ramp rate of 5 mm/min. Three identical specimens for each sample group were used in the compressive testing [24,25].

3. Results and discussion

3.1. Effect of $CaCO_3$ to sodium alginate ratio on properties of $CaCO_3$-biocomposite

Figure 1 shows the XRD patterns of sodium alginate powder, $CaCO_3$ powder, CA3 biocomposite and CA10 biocomposite. It is confirmed that CA3 and CA10 possessed aragonite polymorph when compared to PDF Card (No: 00-041-1475). Although both biocomposites contain sodium alginate, the peak that resembles sodium alginate did not show on the XRD patterns. It may due to very limited concentration of sodium alginate and it did not shown in XRD patterns. Furthermore, the XRD might not detect the sodium alginate due to the detection limit of XRD [26] and amorphous nature of sodium alginate [27]. Thus, it did not disturb the crystallinity and purity of $CaCO_3$. This finding is slightly different with [9] and [28] where the sodium alginate concentration in both studies are higher and there were sodium alginate peaks appeared on its XRD patterns.

Figure 2 illustrated the FTIR spectrum of sodium alginate, $CaCO_3$, CA3 biocomposite and CA10 biocomposite. It is observed that the bands of both biocomposites (Figure 2(c) and 2(d)) are identical to $CaCO_3$ band as indicated by carbonate (CO_3^{2-}) group bands appeared at 1790, 1490, 1170, 861, and 716 cm^{-1}. The spectra of both biocomposites did not contain any band that related to sodium alginate. This may due to the concentration of sodium alginate in the biocomposites are too low and the FTIR could not detect its presence. At the meantime, the IR spectrum of sodium alginate in Figure 2(a) shows a wide band at 3,430 cm^{-1}, which related to the characteristic absorption of hydroxyl groups. Whereas, bands that appeared at 1,615 and 1,418 cm^{-1} were attributed to the asymmetric and symmetric stretching vibrations of carboxyl groups (COO−), respectively. A band around 1,029 cm^{-1} (C–O–C stretching) was observed corresponding to its saccharide structure. The similar sodium alginate band is also observed in study that has been done by [29] and [9].
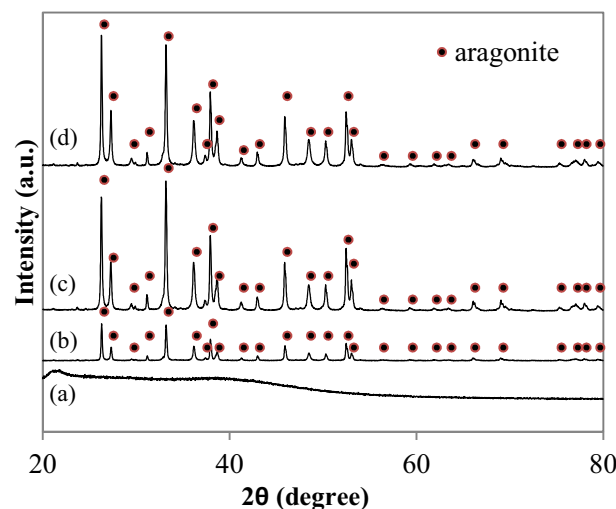

Figure 1. XRD patterns of (a) sodium alginate, (b) $CaCO_3$, (c) CA3 biocomposite and (d) CA10 biocomposite.
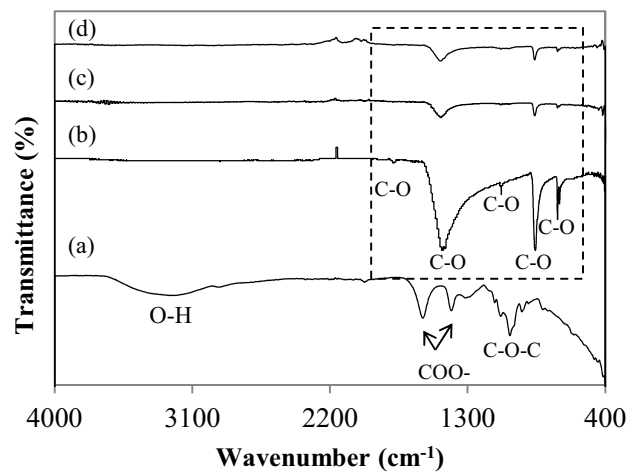
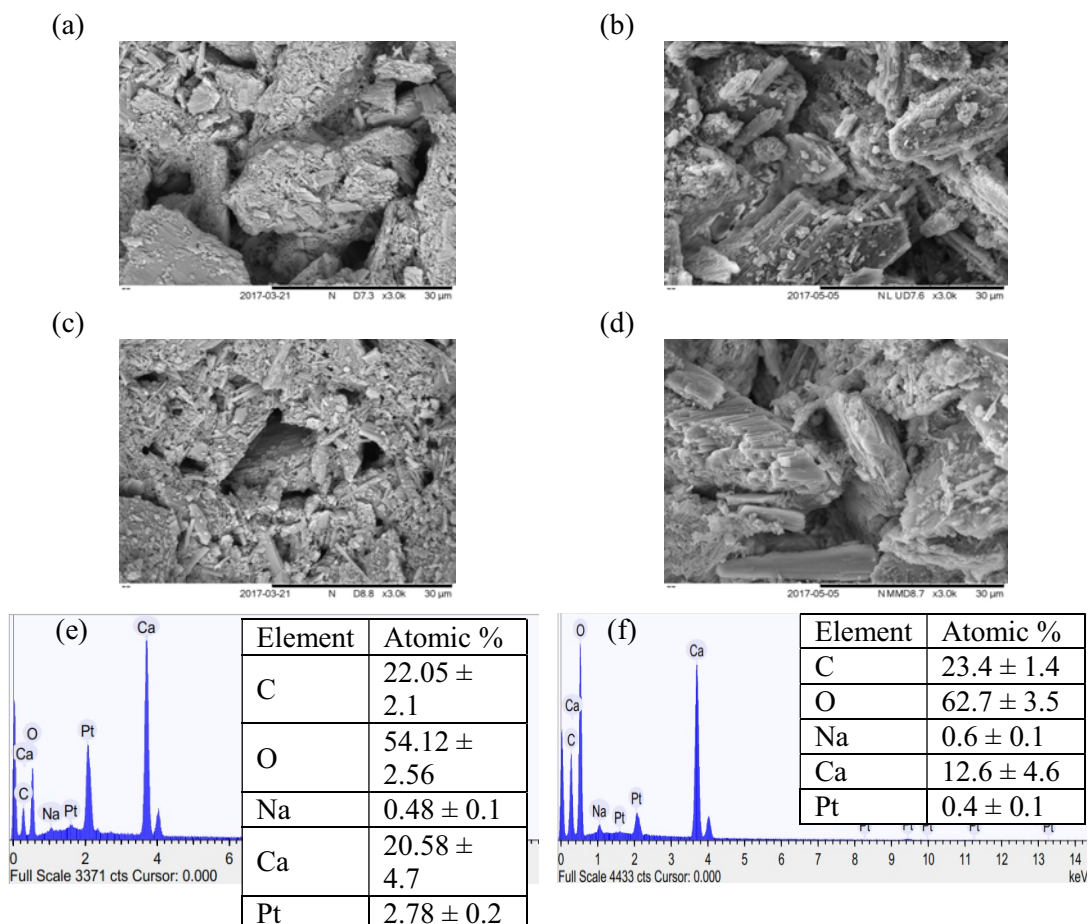**Figure 2.** FTIR spectra of (a) sodium alginate, (b) CaCO₃, (c) CA3 biocomposite and (d) CA10 biocomposites.

Element	Atomic %
C	22.05 ± 2.1
O	54.12 ± 2.56
Na	0.48 ± 0.1
Ca	20.58 ± 4.7
Pt	2.78 ± 0.2

Element	Atomic %
C	23.4 ± 1.4
O	62.7 ± 3.5
Na	0.6 ± 0.1
Ca	12.6 ± 4.6
Pt	0.4 ± 0.1

Figure 3. SEM micrographs and EDX analyses of CA3 (a - surface, c – cross section and e - EDX analysis) and CA10 (b - surface, d - cross section and f - EDX analysis) at 3000× magnification.

Figure 3 displays the SEM observation and EDX analysis of CA3 and CA10. It can be seen that the CaCO₃ in both biocomposites were agglomerated. This may due to the binding capability of sodium alginate [30,31] thus stacking the powders together. Although the powder particles have been

clumped, it still can be observed the lamellar structure of $CaCO_3$. This finding is correlated with [32] and [33] where $CaCO_3$ possessed lamellar structure.

Meanwhile, EDX analyses of both biocomposites show sodium (Na) element peak existed. The Na element proves that sodium alginate is presence in the biocomposites. This similar results was reported by [34]. The difference between CA3 and CA10 is the percentage of Na in the biocomposite. CA10 (Figure 3(f)) has higher percentage of Na compared to CA3 (Figure 3(e)) due to higher concentration of sodium alginate in CA10. From Figure 3, it can be observed that CA3 biocomposite has denser structure compared to CA10. This finding is proven by [22] where the density of biocomposite is increased when concentration of biopolymer decreased.

The compressive strength of CA3 and CA10 biocomposites were shown in Figure 4. The CA3 biocomposite which has lesser sodium alginate ratio exhibit higher compressive strength (243.3 MPa) compared to CA10 biocomposite (93.3 MPa). Increase in the concentration of biopolymer which in this study is sodium alginate has decreased the density of the biocomposite. This finding was supported by [22] and [25] where the compressive strength is inversely proportional with the amount of polymer. This result is correlated with SEM results in Figure 3 where the higher concentrations of sodium alginate in biocomposite make its morphology less dense. Kokubo et al. [35] reported, the compressive strength of human cortical bone is around 100-230 MPa. Thus, only CA3 biocomposite has passed the bone material properties.
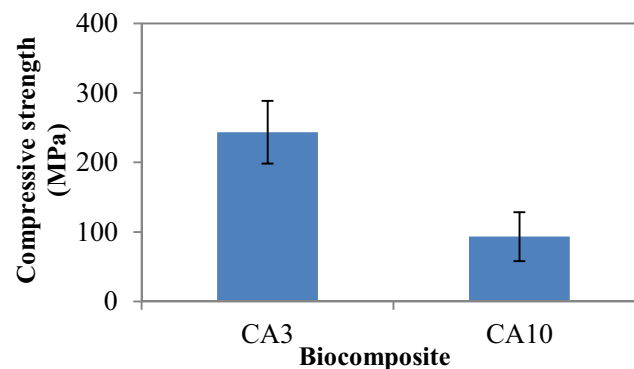

Figure 4. Compressive strength of (a) CA3 biocomposite and (b) CA10 biocomposite.

3.2. Effect of polymer types on properties of $CaCO_3$-biocomposites

Figure 5 shows the XRD patterns of carboxymethyl cellulose, sodium alginate, $CaCO_3$, CA3 biocomposite and CC3 biocomposite. The biocomposites, CA3 and CC3 both displayed aragonite crystal peaks by comparing with $CaCO_3$ pattern (Figure 5(c)). The CA3 biocomposite contained sodium alginate while CC3 contained carboxymethyl cellulose. However, there is no peak which resembles both biopolymers appeared on CA3 and CC3 patterns. This may due to the low concentration of both biopolymers in the biocomposites. Furthermore, XRD has detection limit around 5-10% [26]. Besides that, the XRD pattern of carboxymethyl cellulose (Figure 5(a)) and sodium alginate (Figure 5(b)) are broad and did not have sharp peak. This indicates that both are amorphous biopolymer [36].

Figure 6 shows the FTIR spectrum of carboxymethyl cellulose, sodium alginate, $CaCO_3$, CA3 biocomposite and CC3 biocomposite. It was observed that the bands appeared in both biocomposites spectrum are identical to $CaCO_3$ band as indicated by the CO_3^{2-} bond at 1790, 1480, 1130, 854 and 714 cm^{-1}. By comparing both biocomposites with carboxymethyl cellulose (Figure 6(a)) and sodium alginate (Figure 6(b)) spectrum, it can be seen that there is no band in the biocomposites (Figure 6(d) and 6(e)) that identical with the biopolymers. This may due to the detection limit of FTIR that could not detect the presence of carboxymethyl cellulose and sodium alginate in very low concentrations
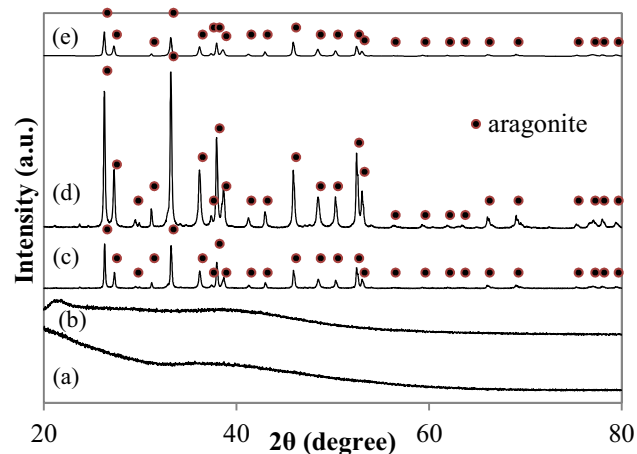
Figure 5. XRD patterns of (a) carboxymethyl cellulose, (b) sodium alginate, (c) CaCO₃, (d) CA3 biocomposite, (e) CC3 biocomposite.
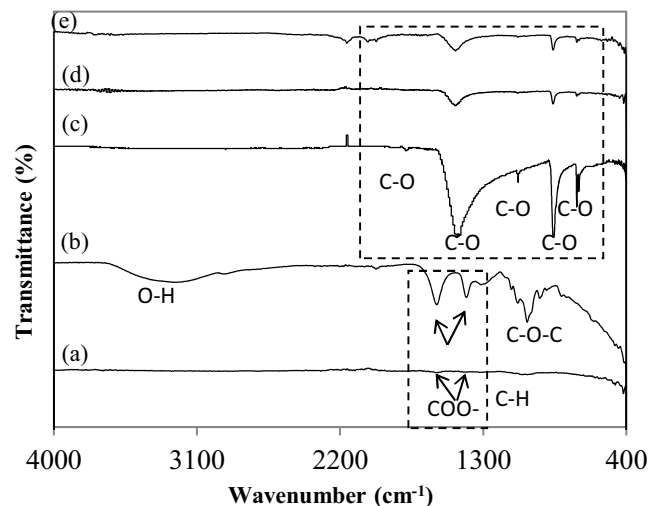

Figure 6. FTIR spectrum of (a) carboxymethyl cellulose, (b) sodium alginate, (c) CaCO₃, (d) CA3 biocomposite, (e) CC3 biocomposite.

Figure 7 shows the SEM observation and EDX analysis of CA3 and CC3 at 3000× magnification. The morphologies of CA3 and CC3 biocomposites are almost similar in term of density. This may due to the similar concentration of biopolymer used in both biocomposites. Meanwhile, EDX analyses show Na element peaks exist in both biocomposites. This Na element confirms that sodium alginate and carboxymethyl cellulose are presence in the CA3 and CC3, respectively. A study done by [34] stated that Na is representing sodium alginate in biocomposite as Na is one of the elements in sodium alginate. Meanwhile, [37] reported that Na in his study representing carboxymethyl cellulose as Na is also one of the elements in carboxymethyl cellulose. Both biopolymers are identified with Na element due to their chemical formula. Sodium alginate has chemical formula $C_6H_9NaO_7$ while carboxymethyl cellulose has chemical formula $C_8H_{15}NaO_8$. The atomic percentage of Na is similar due to same concentration of sodium alginate and carboxymethyl cellulose presence in both bio composites.
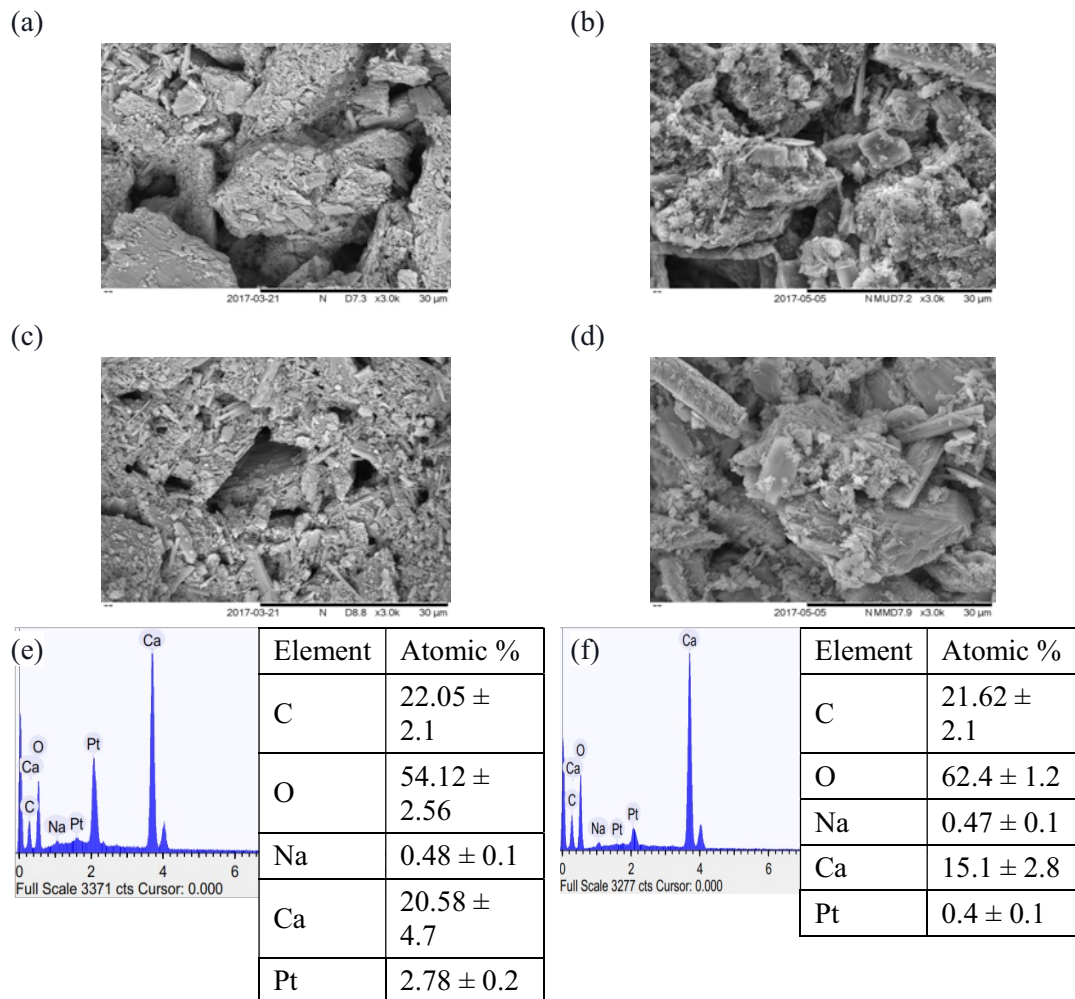
(a)

(b)

(c)

(d)

(e)

Element	Atomic %
C	22.05 ± 2.1
O	54.12 ± 2.56
Na	0.48 ± 0.1
Ca	20.58 ± 4.7
Pt	2.78 ± 0.2

(f)

Element	Atomic %
C	21.62 ± 2.1
O	62.4 ± 1.2
Na	0.47 ± 0.1
Ca	15.1 ± 2.8
Pt	0.4 ± 0.1

Figure 7. SEM micrographs and EDX analyses of CA3 (a - surface, c – cross section and e - EDX analysis) and CC3 (b - surface, d - cross section and f - EDX analysis) at 3000× magnification.

Figure 8 shows the comparison of compressive strength between CA3 and CC3. Both biocomposites consist of similar concentration of biopolymers. CA3 contained sodium alginate while CC3 contained carboxymethyl cellulose. However, the result shows CC3 exhibited higher compressive strength which is 343.3 MPa while CA3 possessed 243.3 MPa. According to [38], carboxymethyl cellulose acts as a skeleton in biocomposite because of the bridging effect of the molecules which contributes to improvement of the compressive strength of the biocomposite. Thus, biocomposite containing carboxymethyl cellulose has higher compressive strength compared to biocomposite with sodium alginate.
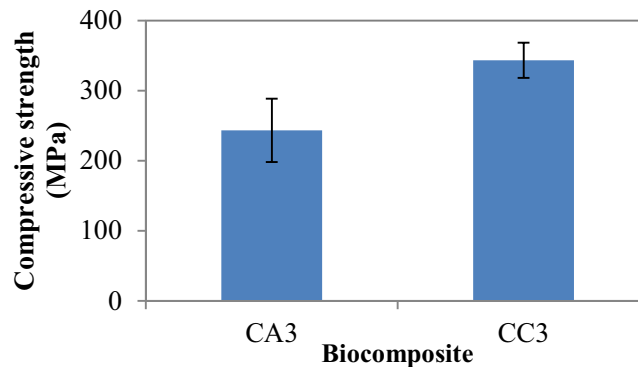
Figure 8. Compressive strength of (a) CA3 biocomposite and (b) CC3 biocomposite

4. Conclusions

$CaCO_3$-biocomposites have been synthesised using cockle shell wastes. Physicochemical analyses (XRD, FTIR, SEM/EDX) have proven that $CaCO_3$-biocomposites contained aragonite crystal. The $CaCO_3$-sodium alginate biocomposites show that the sodium alginate ratio in the system has affected the surface and cross section morphology and mechanical characteristics. Lower the amount of sodium alginate made the structure of biocomposite denser thus increased the compressive strength. Therefore, CA3 is better compared to CA10 in term of mechanical characteristic. Comparison between $CaCO_3$-sodium alginate (CA3) and $CaCO_3$-carboxymethyl cellulose (CC3) revealed that different types of biopolymers give out almost similar morphology but different in mechanical characteristics. The CC3 has greater mechanical strength compared to CA3.

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