



CHARACTERIZATION OF *Anadara granosa* AS A POTENTIAL SOURCE OF CALCIUM CARBONATE FOR GLASS IONOMER CEMENT FORMULATION

(Pencirian *Anadara granosa* Sebagai Sumber Kalsium Karbonat yang Berpotensi untuk Formulasi Simen Kaca Ionomer)

Nur'Izzah Md Nasir, Norhazlin Zainuddin*, and Francis Thoo Voon Wai

Department of Chemistry, Faculty of Science,
Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

*Corresponding author: norhazlin@upm.edu.my

Received: 6 October 2022; Accepted: 18 December 2022; Published: 22 February 2023

Abstract

Glass ionomer cements (GIC) are produced via acid-base reaction between calcium fluoroaluminosilicate glass powders and freeze-dried polyacrylic acid powder. Shells from *Anadara granosa* or commonly known as cockle, consist of >90% calcium carbonate (CaCO_3), have been utilized as the source of CaCO_3 by incorporating it as part of glass components for production of GIC. The main objective of this research is to investigate the effect of *Anadara granosa* shells in setting reaction of GIC using FT-IR spectroscopy. Two types of GIC were synthesized, GIC-A (analytical grade CaCO_3) and GIC-B (replacing CaCO_3 with the shells). FT-IR spectra showed the setting reaction for both GICs with the occurrence of cross-linking between polyacrylate chain and metal ion from the glass by gradual conversion of COOH at $1690\text{-}1700\text{ cm}^{-1}$ into $\text{COO}^-\text{M}^{n+}$ at $1550\text{-}1600\text{ cm}^{-1}$. For compressive strength, GIC-B showed a lower compressive strength compared to GIC-A at 1-day aging time. However, it reached similar value as GIC-A after 28 days aging time. In conclusion, *Anadara granosa* shells can be utilized for Ca aluminosilicate glass in GIC production where it exhibited similar setting properties and compressive strength as GIC from glass synthesized using commercial CaCO_3 .

Keywords: *Anadara granosa*, glass ionomer cement, calcium carbonate, calcium fluoroaluminosilicate

Abstrak

Simen kaca ionomer (GIC) dihasilkan melalui tindak balas asid-bes di antara serbuk kaca kalsium fluoroaluminosilikat dan serbuk asid poliakrilik kering sejuk beku. Cengkerang dari *Anadara granosa* atau kebiasaannya dikenali sebagai kerang ini mengandungi >90% kalsium karbonat (CaCO_3), telah dimanfaatkan sebagai sumber kalsium karbonat dengan menggabungkannya sebagai sebahagian daripada komponen kaca untuk menghasilkan GIC. Objektif utama kajian ini adalah untuk menyiasat kesan cengkerang *Anadara granosa* dalam tindak balas pengerasan GIC menggunakan spektroskopi FT-IR. Dua jenis GIC telah disintesis, GIC-A (CaCO_3 gred analisis) dan GIC-B (menggantikan CaCO_3 dengan cengkerang). Spektrum FT-IR menunjukkan bahawa tindak balas pengerasan bagi kedua-dua GIC berlaku dengan kehadiran rangkai silang antara rantai poliakrilat dan ion logam daripada kaca dengan pertukaran COOH secara beransur-ansur pada $1690\text{-}1700\text{ cm}^{-1}$ kepada $\text{COO}^-\text{M}^{n+}$ pada $1550\text{-}1600\text{ cm}^{-1}$. Untuk kekuatan mampatan, GIC-B menunjukkan kekuatan mampatan yang lebih rendah berbanding GIC-A pada masa penuaan 1 hari, namun, ia mencapai nilai yang sama seperti GIC-A selepas masa penuaan 28 hari. Kesimpulannya, cengkerang *Anadara granosa* boleh

digunakan untuk kaca Ca aluminosilikat dalam penghasilan GIC di mana ia mempamerkan sifat pengerasan dan kekuatan mampatan yang sama seperti GIC daripada kaca yang disintesis menggunakan CaCO_3 komersial.

Kata kunci: *Anadara granosa*, simen kaca ionomer, kalsium karbonat, kalsium fluoroaluminosilikat

Introduction

Blood cockle is a bivalve marine mollusc from the species *Anadara granosa* which is mostly used as a source of protein-rich food. Countries such as Malaysia, Indonesia, and Thailand are known for their extensive cockle industry [1]. The production of cockle in Malaysia is great and keeps increasing year by year. However, the shells are treated as waste with an unpleasant smell and are often just dumped in landfill or the sea [2-3]. From early 2000 until now, studies on seashells as a source of calcium carbonate, CaCO_3 are widely explored, especially in the medical field such as for bone and dental applications [4-11]. CaCO_3 in cockle shell consists of three polymorphs known as calcite, aragonite, and vaterite. Researchers are more interested in aragonite polymorph due to its biocompatible properties [12]. Aragonite has osteoregenerative potential and can be used for bone substitution [13]. On the other hand, calcite has good thermodynamic stability. Calcite nanoparticle is considered as an extremely effective material in biomedical due to their shape, non-toxic properties, and it is also easily metabolized by all cells. Calcite with nanostructure could supply calcium sources to retain Ca ions in the supersaturation state in the enamel minerals. Hence, calcite has great potential in preventing tooth erosion thereby it could be used for dental hypersensitive treatment [14]. While vaterite, less commonly occurs in nature because it is the least thermodynamically stable polymorph. Vaterite can rapidly transform into calcite and aragonite in an aqueous solution [15].

In dental applications, calcium hydroxide has been considered the gold standard for pulp capping materials for decades to stimulate the formation of tertiary dentin. Blood cockle shells are expected to be an alternative pulp protective material for initiating dentin tissue deposition so that the healing process can occur by the formation of reactionary dentin [16]. The cockle shell is also claimed to have anti-inflammatory properties as well as good stability due to calcite polymorph [17]. Researchers have also prepared zirconia stabilized by

CaO known as calcia-doped zirconia using CaO derived from cockle shells for dental application [18]. The study was done by comparing the CaO from cockle shells with the commercial CaO and the research concluded that the calcia-doped zirconia with the CaO derived from cockle shells may be used as an alternative to the current zirconia available in the market for dental application due to its physical and mechanical properties. Apart from that, their flexural and compressive strength are also comparable with the commercial type. Cockle shell is also being studied as hydroxyapatite paste as a remineralization agent, to which the result showed that it can increase tooth enamel surface hardness with nearly the same effect as CPP-ACP (commercial GC Tooth Mousse®) paste [19]. Another study has applied CaO in the glass formulation derived from clamshell for the production of glass ionomer cement, GIC. The physical and mechanical properties of GIC derived from soda lime glass and clamshell improved with the addition of hydroxyapatite [20].

Even though studies using clamshell as CaCO_3 source in GIC had been done previously, the studies only focused on the influence of hydroxyapatite existence. In this study, the GIC was prepared using Ca aluminosilicate glass derived from cockle shell and the setting reaction was thoroughly investigated using FT-IR spectroscopy. A comparison study with a similar formulation of glass ionomer using analytical grade CaCO_3 was done to determine the suitability of the cockle shell as the CaCO_3 source in the synthesis of GIC for dental application.

Materials and Methods

Materials

Silicon dioxide, SiO_2 and calcium fluoride, CaF_2 were purchased from Sigma-Aldrich Co., US. Aluminium oxide, Al_2O_3 , and calcium carbonate, CaCO_3 were purchased from Fisher Scientific, US, and phosphorus pentoxide, P_2O_5 from Acros Organics, US. All chemicals were analytical-grade reagents with more than 99% purity. *Anadara granosa* shells were obtained

from a fresh market at Lumut, Perak, Malaysia. These cockle shells were used as an alternative source to CaCO_3 . A medical-grade freeze-dried poly(acrylic acid) was supplied by Advance Healthcare, Kent, England with a molecular weight of $\sim 30,000$. Throughout the experiment, analytical-grade ethanol was used to dehydrate the cement. In addition, liquid nitrogen was employed to terminate the setting reaction in GICs.

Preparation of *Anadara granosa* shells powder

Anadara granosa shells were washed thoroughly and immersed in water to remove surface impurities. The shells were then dried in an oven at 110°C . Heat treatment was applied to the shells at 400°C for 2 hours. The shells were then crushed using stainless steel pounder and ball mill for 24 hours. After that, the ground shells were sieved to less than $45\ \mu\text{m}$ particle size.

Preparation of glasses

Two Ca aluminosilicate glasses, glass GIC-A (analytical grade CaCO_3) and GIC-B (CaCO_3 from *Anadara granosa* shells), with similar formulations were synthesized. Weight percentages of each composition were 16.60% alumina, 16.91% calcium oxide, 37.57% silica, 16.68% phosphorus pentoxide, and 12.24% calcium fluoride. All chemical compositions (SiO_2 , Al_2O_3 , CaCO_3 , and CaF_2) were homogenized by using a ball mill unit for 6 hours before melting. Phosphorous pentoxide was only added to the mixture just before the melting process to avoid hydration as it is a highly hygroscopic material. Approximately 30 g of the mixture in an alumina crucible was melted in a furnace at 1500°C for 2 hours. The molten mixture was poured immediately into the water for shock quenching to produce non-crystallized glass frits. The glass obtained was air-dried before placing it in an oven for overnight drying at 37°C . It was then ground by dry milling in a rotary ball mill and sieved to $\leq 45\ \mu\text{m}$ particle size.

Preparation of glass ionomer cement (GIC)

The preparation of GIC was done according to ISO 9917-1:2007 Dentistry Water Based Cements Part 1: Powder/liquid acid-base cements 2007 [21]. The glass powder was mixed with freeze-dried poly (acrylic acid), PAA and distilled water on a glass slab using a stainless-steel spatula in a weight ratio of 3:1:1. The GIC was then

inserted into a cylinder mold with a dimension of $4.0\ \text{mm} \times 6.0\ \text{mm}$. Then, the GIC together with the mold was placed in an incubator at 37°C for 1 hour. After that, the samples were transferred into containers with deionized water and left for a certain period according to their aging times studied. The aging time was from 5 minutes to 28 days. Liquid nitrogen and ethanol were applied to the GICs with aging time of less than 1 hour to terminate the setting reaction by dehydrating the GIC.

Setting reaction study of GIC

The setting reaction of GIC was studied at several time intervals: 5 minutes, 15 minutes, 30 minutes, 1 hour, 6 hours, 1 day, 7 days, and 28 days. Samples with time intervals ranging from 5 minutes to 1 hour were set in an incubator at 37° . GICs with aging time of more than 1 hour were placed in the incubator at 37°C for 1 hour then it was transferred into a sample bottle containing deionized water and kept in the incubator for the remaining aging period. For GICs less than 1 hour of aging time, liquid nitrogen and ethanol were used to terminate the reaction and dehydrate the GICs. The GICs were then ground to a fine powder for the FT-IR analysis.

Characterizations of *Anadara granosa* and GIC

The *Anadara granosa* shell was characterized by energy dispersive x-ray (EDX), thermogravimetric analysis (TGA), and X-ray diffraction (XRD), while GIC samples were characterized using Fourier transform infrared spectroscopy (FT-IR), and compressive strength test.

Energy dispersive X-ray

Elemental analyses of *Anadara granosa* shells in powder form were determined using an energy dispersive X-ray analyzer (FEI-Quanta 200, The Netherlands) directly linked to a scanning electron microscopy, SEM operated with environmental mode at 15 kV and relative humidity of 96%- 99%.

X-ray diffraction

XRD is a non-destructive technique for qualitative analysis. XRD was used to compare the XRD pattern of *Anadara granosa* shells with the analytical grade CaCO_3 . The analysis was conducted from 4° to 90° by

using a 2 θ goniometer X-ray powder diffractometer (PANalytical X'pert-Pro MPD PW 3040), operated at Cu-K α radiation ($\lambda = 0.15406$ nm). The diffractogram was scanned at a scan rate of 2° min⁻¹.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to analyze the thermal decomposition of *Anadara granosa* shells by using Mettler-Toledo thermogravimetric analyzer. Shell in powder form with particle size ≤ 45 μ m was placed in a 40 μ l alumina crucible and subjected to heating in the range of 25 to 1000 °C at 10 °C/min under the flow of nitrogen gas at 50 ml/min.

Fourier transform infrared (FT-IR) spectroscopy

FT-IR Spectroscopy is a non-destructive method for both qualitative and quantitative analysis. In this study, FT-IR was used to study the setting reaction of GIC from aging time of 5 minutes to 28 days. Perkin- Elmer FT-IR spectrometer coupled with UATR accessory was used to record FT-IR transmittance spectra. Approximately 0.001 g of sample was used and scanned within the wavenumber of 280 cm⁻¹ to 4000 cm⁻¹.

Compressive strength test of GIC

Compressive strength of the GIC was done according to ISO7489:1986 specifications [22, 23] with the dimension of 6.0mm $\times$ 4.0mm cylindrical-shaped cement. GIC samples were tested at 1, 7, and 28 days. The test was performed using Instron 4082 Universal Testing Machine with a 1kN load cell at a crosshead of 1mm/min until the cement fractured. Five specimens of each GIC were tested. The mean compressive strength and standard deviation of GIC were calculated.

Results and Discussion

Energy dispersive X-ray (EDX) of *Anadara granosa* shell

Table 1. shows the weight percentage of the composition of *Anadara granosa* shell. It was found that the major component of the shell was CaCO₃ with the presence of a small amount of other metal oxides such as Na₂O, Al₂O₃ and SiO₂. The presence of a small amount of sodium oxide may come from the sodium content of seawater during the *Anadara granosa* growth in the sea [9]. The percentage of CaCO₃ in *Anadara granosa* powder was 97.53%. Other oxides were all detected in very small amounts in the sample. Moreover, the result in this study is in good agreement with the findings of previous studies. Previous studies in Malaysia reported that *Anadara granosa* shells were composed of 98.7% CaCO₃, 0.05% Mg, 0.9% Na, 0.02% P and 0.2% of other elements (Fe, Cu, Ni, Zn, B, and Si) [24, 25].

Table 1. The weight percentage of *Anadara granosa* shell

Composition	Percentage in Weight (%)
Na ₂ O	0.73
CaCO ₃	97.53
Al ₂ O ₃	1.76
SiO ₂	0.07

X-ray diffraction analysis

XRD analysis shows that *Anadara granosa* shell exhibited similar XRD patterns as analytical grade calcium carbonate as shown in Figure 1. The diffraction lines for *Anadara granosa* shells were well matched with pure analytical grade CaCO₃ and thus indicates that it is suitable to be utilized as a source of CaO in the synthesis of Ca aluminosilicate glass.

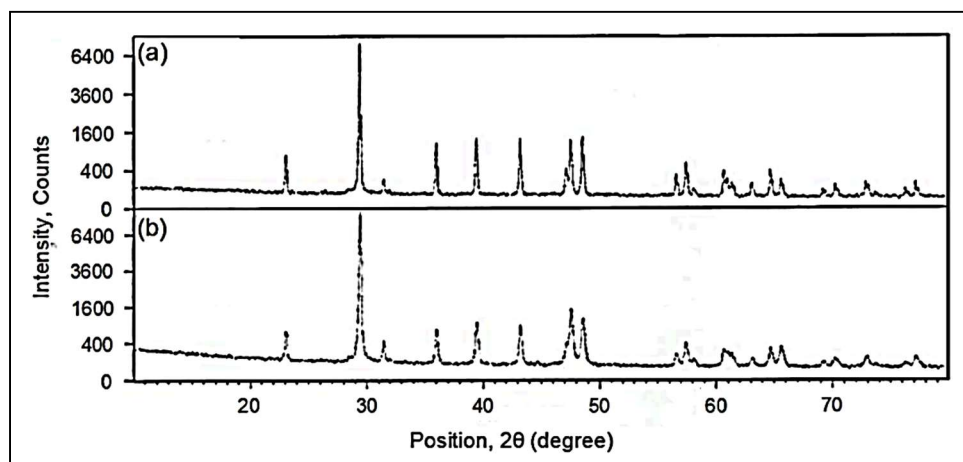


Figure 1. XRD pattern for (a) analytical grade CaCO_3 ; (b) *Anadara granosa* shells powder

Thermogravimetric analysis

From XRD analysis, it is found that the main component of *Anadara granosa* shell is CaCO_3 . Generally, CaCO_3 will undergo thermal decomposition when the heating

temperature is more than 550 °C. In this experiment, the *Anadara granosa* shell was heated up to 1000 °C, hence the calcium carbonate in *Anadara granosa* shell was expected to decompose to calcium oxide eventually.

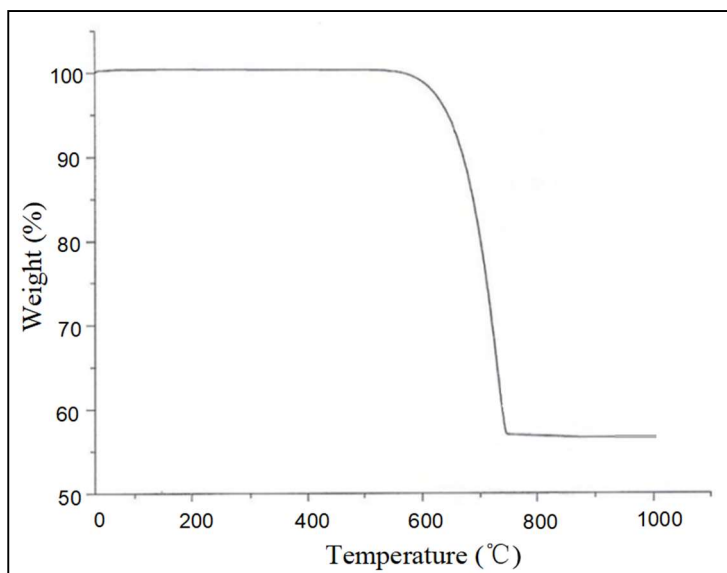
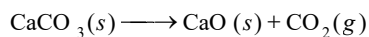


Figure 2. TGA decomposition graph of *Anadara granosa* shell

Based on the thermal decomposition curve in Figure 2, single-stage decomposition with an onset decomposition temperature of 508.6 °C was observed. The single decomposition step suggested calcium carbonate only undergoes a reaction in which bound carbon dioxide was released upon heating. At 508.6 °C, calcium carbonate in *Anadara granosa* shells started to

decompose and evolve into carbon dioxide. The offset temperature of 768.3 °C indicated the ending of the decomposition process and calcium oxide together with trace metals constituted the residue.

The process of decomposition of CaCO_3 to CaO can be presented using the equation shown below:



(eq. 1)

Based on the equation, it shows that 1 mol of CaCO_3 will produce 1 mol of CaO. The percentage of calcium

carbonate in *Anadara granosa* shells can be calculated as below:

$$\text{Percentage (\%)} \text{ of } \text{CaCO}_3 \text{ in } \textit{Anadara granosa} = \frac{\text{CO}_2 \text{ weight loss}}{\text{Mr CO}_2} \times \frac{\text{Mr CaCO}_3}{\text{Mass of } \textit{Anadara granosa}} \quad (\text{eq. 2})$$

Based on the formula above, 98.68% of calcium carbonate was found in *Anadara granosa*. This result agrees with the percentage of CaCO_3 obtained from the EDX analysis. According to a previous study, the total mineral content of cockle shells in west coast Malaysia comprises 98.7% of calcium carbonate and an insignificant amount of trace metals [24]. A high percentage of calcium carbonate in the shells suggested that it is suitable to be utilized as a source of calcium carbonate for the synthesis of Ca aluminosilicate glass.

Setting reaction of GIC-A and GIC-B by using FT-IR spectroscopy

The setting reaction of GIC-A and GIC-B were studied by using FT-IR spectroscopy. Generally, setting reaction in GIC involves the formation of metal polyacrylate and silica gel repolymerization. Figure 3 shows the FT-IR spectra of GIC-A (analytical grade CaCO_3), and GIC-B (CaCO_3 from shells) in the range of 2000 cm^{-1} to 600 cm^{-1} for setting time from 5 minutes to 28 days. Both GICs show similar trends in FT-IR spectra.

The formation of metal polyacrylate takes place between carboxylic part ($-\text{COOH}$) of polyacrylic acid with metal ions such Al^{3+} and Ca^{2+} from the glass particle. This reaction is known as cross-linking reaction and produced $\text{COO}^-\text{M}^{n+}$ species in the GIC. In FT-IR spectroscopy, $\text{COO}^-\text{M}^{n+}$ is assigned as asymmetric vibration of $(\text{COO}^-)\text{Ca}^{2+}$ and $(\text{COO}^-)\text{Al}^{3+}$ with respect to Ca^{2+} and Al^{3+} present in the glass [26]. From Figure 3,

the absorption band of COOH at wavenumber 1730 cm^{-1} is observed at 5 minutes aging time and at the same aging time, a shoulder peak corresponds to the cross-linking absorption band, $\text{COO}^-\text{M}^{n+}$ at wavenumber 1620 cm^{-1} also appeared. As the aging time increased, the absorption band of COOH began to disappear and the intensity of the $\text{COO}^-\text{M}^{n+}$ band increased. The disappearance of COOH band is due to the cross-linking between the PAA and the glass proceeds to a higher extent with aging time. It is also found that the absorption bands of COOH group for GIC-A and GIC-B slightly shifted to lower wavenumbers from 1745 to 1720 cm^{-1} .

As the aging time increased from 5 minutes to 28 days, the intensity of the absorption band of COOH decreased while $\text{COO}^-\text{M}^{n+}$ absorption band increased gradually. This suggests that the cross-linking of carboxylate group, COO^- by metal cations occurred to a greater extent and corresponded to progressive proton removal from carboxyl groups. At 28 days of aging time, there was still a shoulder band at 1700 cm^{-1} corresponding to the unreacted COOH of PAA. COOH group of PAA did not undergo complete ionization as PAA is generally a weak acid. Furthermore, the remaining protons were strongly attracted by electrostatic forces due to greater ionization of polyacrylate chains as setting reaction continued. Due to strong binding forces, protons on the unionized COOH group were hard to be replaced by metal cations for cross-linking [26].

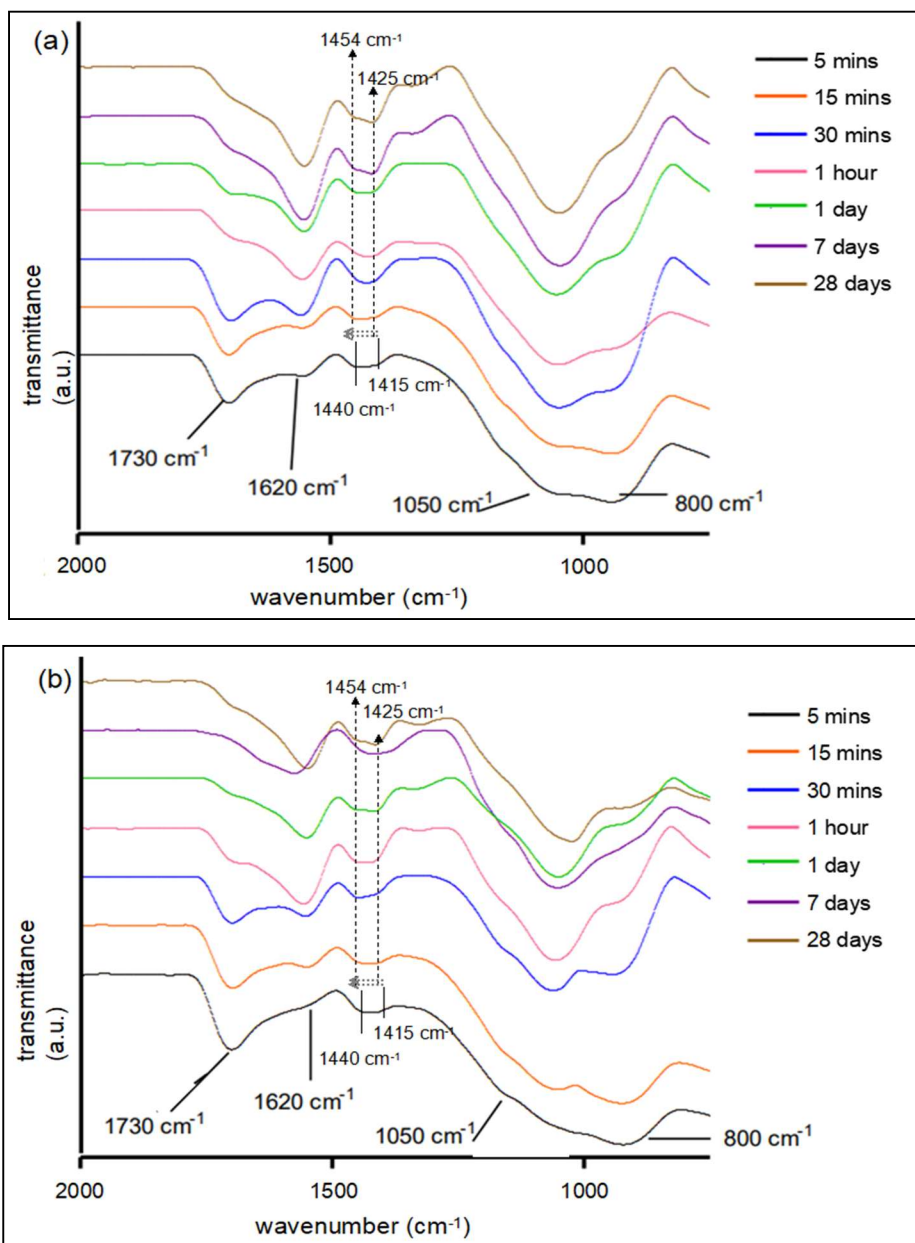


Figure 3. FTIR spectra for (a) GIC-A and (b) GIC-B from 5 minutes to 28 days aging time.

Another reaction in the setting of GIC is repolymerization of silica network of the glass. FT-IR spectra showed changes in the region of 1200 to 800 cm^{-1} which corresponded to the changes from Si-OH (800 cm^{-1}) to Si-O-Si (1050 cm^{-1}). At the early aging time, Si-O-H band from the formation of silica gel was easily observed as compared to Si-O-Si band which remained obscure. This is in line with the setting mechanism which suggests that the proton ionized from COOH

group of PAA had displaced metal cations in the silicate network and formed Si-O-H. At a later setting reaction, an absorption band with a shoulder corresponding to Si-O-Si gradually appeared. Meanwhile, the diminishing absorption band of Si-O-H was observed. Next, two weak bands were observed at 1440 cm^{-1} and 1415 cm^{-1} associated with scissors and bending vibrations of $-\text{CH}_2$ and $-\text{CH}-\text{C}=\text{O}$ groups respectively. Both bands were slightly shifted to a higher wavenumber from 1440 cm^{-1}

to 1454 cm^{-1} for $-\text{CH}_2$ and from 1415 cm^{-1} to 1425 cm^{-1} for $\text{CH}-\text{C}=\text{O}$. This may be due to the cross-linking reaction where the angle of $\text{CH}-\text{C}=\text{O}$ bonding was altered for calcium ion and aluminum ion to cross-link with the polyacrylic acid on the surface of the glass. This interaction caused the $-\text{CH}_2$ bond near the $\text{CH}-\text{C}=\text{O}$ to vibrate and altered the position of $-\text{CH}_2$ bending [27]. Due to the higher energy needed to vibrate these species, the absorption bands shifted slightly higher wavenumber in the cement. In conclusion, the study of setting reaction of GICs by using FT-IR spectroscopy

indicates that the setting mechanism involves both cross-linking reaction and silica gel repolymerization occur concurrently.

Degree of cross-linking (DCL)

Cross-linking of PAA by metal cations resulted in the formation of cement matrix due to gelation of PAA. The degree of cross-linking (DCL) was calculated according to a previous study by Matsuya et al. [29] using FT-IR spectroscopy. The DCL between polyacids chains was calculated from the formula:

$$\text{DCL} = \frac{\text{Abs}(\text{COO}^- \text{M}^{n+})}{\text{Abs}(\text{COOH}) + \text{Abs}(\text{COO}^- \text{M}^{n+})} \quad (\text{eq. 3})$$

where Abs refer to FTIR absorbance with respect to specific wavenumber.

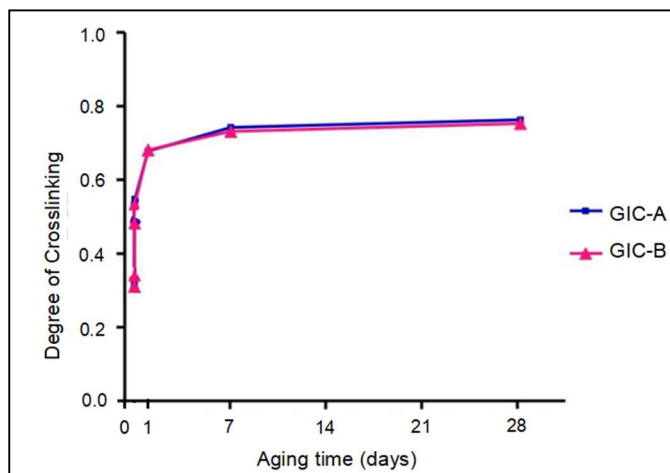


Figure 4. Degree of cross-linking for GIC-A and GIC-B

Figure 4 shows the rapid increment of DCL value within 1 hour followed by gradual increment up to 28 days for both GIC-A and GIC-B. A similar finding was reported previously by Matsuya et al. [29]. The DCL value for GIC-A and GIC-B increased drastically within 1 hour of aging time with DCL values of 0.5473 and 0.5344, respectively. The increase in DCL suggests that a greater extent of the cross-linking reaction occurred between polyacrylate chains and metal cations from the glass. This finding also suggests that there is a high amount of metal cations released during glass degradation where

these metal cations then cross-link with the polyacrylate chain. There was only a slight increment in DCL values for longer aging time (7 to 28 days) from 0.7426 to 0.7631 for GIC-A and 0.7316 to 0.7528 for GIC-B. The fact that the DCL still increased up to 28 days suggests that the cross-linking reaction continues with time after the initial setting [30]. This is probably caused by continuous release of ions from the glass and the change in conformation of PAA [31,32]. Change in PAA chain conformation provided accessibility for cross-linking sites at carboxylate group. Previous study by Cattani-

Lorente et al. [33] suggested slow additional cross-linking to be another factor other than the role of silica gel phase which contributed to the strengthening of cement.

In addition, as the setting reaction proceeded, the polyacrylate matrix became rigid and highly viscous which rendered free carboxylic groups from forming ionic bonding with metal cations [27]. Therefore, the intensity of FT-IR absorption bands for COOH and $\text{COO}^-\text{M}^{n+}$ and DCL values for both cement types were not significantly changed. In conclusion, the setting study of GIC-B which was produced from the *Anadara granosa* shell showed a similar setting mechanism as GIC-A from analytical grade CaCO_3 .

Compressive strength of GIC

The effect of maturation of cement was examined on compressive strength for GIC-A and GIC-B. Previous studies had reported maturation of cement which involved additional cross-linking between polyacrylate matrices [31, 33]. A minimum aging time of 24 hours is needed as GICs are weak and sensitive to desiccation and moisture contamination at the early setting stage. Loss of water will cause shrinking and crazing of cement surface while hydration will result in the leaching of matrix-forming ions upon disintegration. Figure 5 shows the mean values (MPa) and standard deviations obtained for the compressive strength of GIC-A and GIC-B from 1 day to 28 days of aging time.

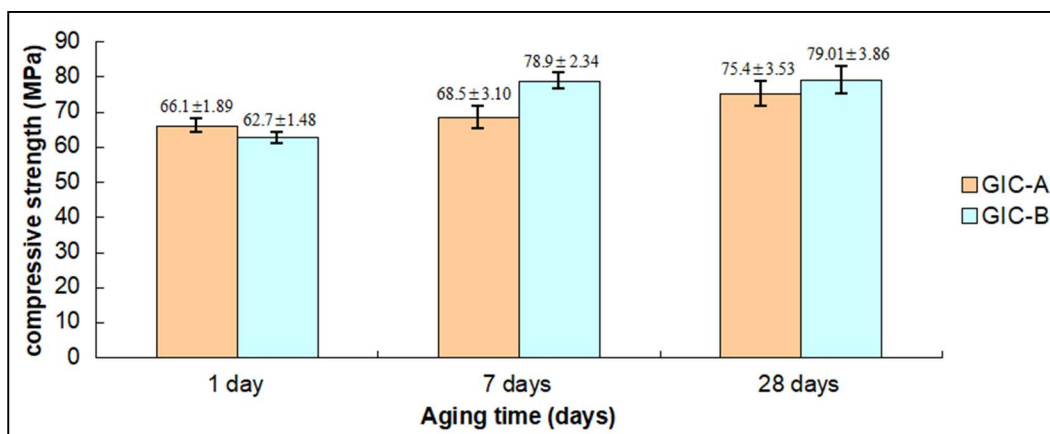


Figure 5. Compressive strength of GIC-A and GIC-B cements at 1 day to 28 days aging time

Figure 5 shows that at 1 day of aging time, GIC-B exhibited slightly lower compressive strength than GIC-A with the value of 62.7 MPa and 66.1 MPa, respectively. The lower compressive strength of GIC-B than GIC-A at 1-day aging time may be due to the presence of sodium in *Anadara granosa* shell in the glass. Lohbauer [34] stated that the incorporation of sodium into glass resulted in an adverse effect on solubility, hydrolytic stability, and mechanical properties of the set cement. The high mobility of sodium in silicate glass increased its tendency to be released from the glass and readily exchanged with protons during the setting reaction [35]. Since sodium was not strongly bound to carboxylate group as COO^-Na^+ hence, it was ionized readily into the aqueous phase.

When aging time increased from 1 day to 7 days, there was an increase in the compressive strength for GIC-B from 62.7 MPa to 78.9 MPa. Previous studies stated that commonly GIC does not reach its maximum strength at 24 hours after setting reaction [36]. For both GICs, the compressive strength increased slightly from 7 days to 28 days of aging time which is consistent with the findings from FT-IR spectra (Figure 3) as well as DCL (Figure 4). Based on Figure 5, both GICs exhibited almost similar compressive strength at 28 aging time with a value in the range of 75.0 - 79.0 MPa.

Conclusion

In this study, the high percentage of CaCO_3 in *Anadara granosa* shells indicates that they can be used as a source of CaCO_3 in dental glass. The setting reaction and

compressive strength of GIC made from *Anadara granosa* shells show similar results as GIC from analytical grade CaCO_3 . Therefore, this study has revealed the potential of *Anadara granosa* shells for dental cement formulation.

Acknowledgments

The authors are grateful for the financial support from the Ministry of Higher Education (MOHE), Malaysia (Fundamental Research Grant Scheme FRGS/1/2013/SG06/UPM/02/2), and the Chemistry Department, Faculty of Science, UPM for the equipment and laboratory.

References

1. Jaji, A.Z., Md Zuki, A.B.Z., Mahmud, R., Yusof, M.L., Mohamad, M.N.H., Isa, T., Fu, W. and Hammadi, N.I. (2017). Synthesis, characterization, and cytocompatibility of potential cockle shell aragonite nanocrystals for osteoporosis therapy and hormonal delivery. *Nanotechnology, Science and Applications*, 10: 23-33.
2. Fu, W., Mohd Noor, M. H., Mohamad Yusof, L., Tengku Ibrahim, T. A., Keong, Y. S., Jaji, A. Z. and Abu Bakar Zakaria, M. Z. (2017). In vitro evaluation of a novel pH-sensitive drug delivery system-based cockle shell-derived aragonite nanoparticles against osteosarcoma. *Journal of Experimental Nanoscience*, 12: 166-187.
3. Summa D., Lanzoni, M., Castaldelli, G., Fano, E. A., & Tamburini, E. (2022). Review: Trends and opportunities of bivalve shells' waste valorization in a prospect of circular blue bioeconomy. *Resources*, 11(48); 1-16
4. Yang, E. I., Yi, S. T., and Leem, Y. M. (2005). Effect of oyster shell substituted for fine aggregate on concrete characteristics: Part I. Fundamental properties. *Cement and Concrete Research*, 35(11): 2175-2182.
5. Ballester, P., Mármol, I., Morales, J., and Sánchez, L. (2007). Use of limestone obtained from waste of the mussel cannery industry for the production of mortars. *Cement and Concrete Research*, 37(4): 559-564.
6. Mohamed, M., Yusup, S., and Maitra, S. (2012). Decomposition study of calcium carbonate in cockle shell. *Journal of Engineering Science and Technology*, 7(1): 1-10.
7. Asmi, D., and Zulfia, A. (2017). blood cockle shells waste as renewable source for the production of biogenic CaCO_3 and its characterisation. *IOP Conference Series: Earth and Environmental Science*, 94: 012049.
8. Ghafar, M. S. L., Hussein, M. Z., Rukayadi, Y. and Zakaria, M. Z. A. B. (2017). Synthesis and characterization of cockle shell-based calcium carbonate aragonite polymorph nanoparticles with surface functionalization. *Journal of Nanoparticle*, 2017: 1-12.
9. Mailafiya, M. M., Abubakar, K., Danmaigoro, A., Chiroma, S. M., Abdul Rahim, E. Mohd Moklas, M. A. and Zakaria, Z. A. B. (2019). Review: Cockle shell-derived calcium carbonate (aragonite) nanoparticles: A dynamite to nanomedicine. *Applied Science*, 9(2897): 1-25.
10. Sainudin, M. S., Othman, N. H., Ismail, N. N., Wan Ibrahim, M. H. and Rahim, M. A. (2020). Utilization of cockle shell (*Anadara granosa*) powder as partial replacement of fine aggregates in cement brick. *The International Journal of Integrated Engineering*, 12(9): 161-168.
11. Syafwandi, and Cerra, R. A. (2021). The effect of substitution of coarse and fine aggregates with shells of blood clams and cement with fly ash and the additional of superplasticizer against the compressive test. *International Journal of Transportation and Infrastructure*, 4(2): 148-156.
12. Chen, J. and Xiang, L. (2009). Controllable synthesis of calcium carbonate polymorphs at different temperatures. *Powder Technology*, 189(1): 64-69.
13. Akilal, N., Lemaire, F., Bercu, N. B., Sayen, S., Gangloff, S. C., Khelfaoui, Y., Rammal, H., Kerdjoudj, H. (2019). Cowries derived aragonite as raw biomaterials for bone regenerative medicine. *Materials Science and Engineering: C*, 94: 894-900.
14. Tram, N. X. T., (2020). Synthesis and characterization of calcite nano-particle derived from cockle shell for clinical application. *ASEAN Engineering Journal*, 10(1): 49-54.

15. Ni, M., and Ratner, B. D. (2008). Differentiation of calcium carbonate polymorphs by surface analysis techniques – an XPS and TOF-SIMS study. *Surface and Interface Analysis*, 40(10): 1356-1361.
16. Praja, H. A., Dhaniar, N., Santoso, R. M., Putri, D., Annisa Salsabila A. P., Veda Sahasika A. N., Soetojo, A. and Saraswati, W. (2022) Calcium carbonate of blood cockle (*Anadara granosa*) shells induced VEGF-A expression in dentin pulp complex an in vivo study. *Malaysian Journal of Medicine and Health Sciences*, 18(SUPP6): 24-30.
17. Al Omari, M. M. H., Rashid, I. S., Qinna, N. A., Jaber, A. M. and Badwan, A. A. (2016). Chapter 2: Calcium carbonate. Book title: Profiles of drug substances, excipients, and related methodology. Elsevier, 41: pp 2-445.
18. Hussein, A. I., Che Mat, A. N., Abd Wahab, N. A. A., Rahman, Husein, A. and Ab-Ghani, Z. (2020). Synthesis and properties of novel calcia-stabilized zirconia (Ca-SZ) with nano calcium oxide derived from cockle shells and commercial source for dental application. *Applied Science*, 10(5751): 1-13.
19. Nugroho, J. J., Natsir, N., Trilaksana, A. C., Rovani, C. A., and Atlanta, M. M. (2019). The increase of tooth enamel surface hardness after application blood cockle shells (*Anadara granosa*) paste as remineralization agent. *International Journal of Applied Pharmaceutics*, 11(4): 26-29.
20. Wan Jusoh, W. N., Matori, K. A., Mohd Zaid, M. H., Zainuddin, N., Ahmad Khiri, M. Z., Abdul Rahman, N. A., Abdul Jalil, R. and Kul, E. (2021). Incorporation of hydroxyapatite into glass ionomer cement (GIC) formulated based on alumino-silicate-fluoride glass ceramics from waste materials. *Materials*, 14(954): 1-14.
21. International Organization for Standardization (2007). Dentistry-water-based cements Part 1: Powder/liquid acid-base cements (ISO 9917-1:2007). Retrieved from <https://www.iso.org/standard/45818.html>
22. Genebra (1986). International organization for standardization. ISO7489. Dental glass polyalkenoate cements.
23. Mallmann, A., Ataíde, J. C. O., Amoedo, R., Rocha, P. V. and Jacques, L. B. (2007). Compressive strength of glass ionomer cements using different specimen dimensions. *Brazilian Oral Restorative*, 21: 204-208.
24. Awang-Hazmi, A. J., Zuki, A. B. Z., Noordin, M. M., Jalila, A., and Norimah, Y. (2007). Mineral composition of the cockle (*Anadara granosa*) shells of West Coast of Peninsular Malaysia and its potential as biomaterial for use in bone repair. *Journal of Animal and Veterinary Advances*, 6(5): 591-594.
25. Hoque E, Shehryar M, Islam K. N. (2013). Processing and characterization of cockle shell calcium carbonate (CaCO₃) bioceramic for potential application in bone tissue engineering. *Journal Materials Sciences Engineering*, 2(4): 2-6.
26. Tomlinson, S. K., Ghita, O. R., Hooper, R. M. and Evans, K. E. (2007). Investigation of the dual setting mechanism of a novel dental cement using infrared spectroscopy. *Vibrational Spectroscopy*, 45(1): 10-17.
27. Crisp, S., M. A. Pringuer, M. A., Wardleworth, D. and Wilson, A. D. (1974). Reactions in glass ionomer cements: II. An infrared spectroscopic study. *Journal of Dental Research*, 53(6): 1414-1419.
28. Md Nasir, N. I., Zainuddin, N., Wan Yunus, W. M. Z. and Matori, K. A. (2014). The influence of modified sodium montmorillonite as filler on the performance of glass polyalkenoate cement. *Malaysian Journal of Analytical Sciences*, 18(3): 572-583.
29. Matsuya, S., Maeda, T. and Ohta, M. (1996). IR and NMR analyses of hardening and maturation of glass- ionomer cement. *Journal of Dentistry Restorative*, 75(12): 1920-1927.
30. Hill, R. G. (1993). The fracture properties of glass polyalkenoate cements as a function of cement age. *Journal of Materials Science*, 28(14): 3851-3858.
31. Crisp, S. and A. D. Wilson (1974). Reactions in glass ionomer cements: I. Decomposition of the powder. *Journal of Dental Research*, 53(6): 1408-1413.
32. Crisp, S. and A. D. Wilson (1974). Reactions in glass ionomer cements: III. The precipitation reaction. *Journal of Dental Research*, 53(6): 1420-1424.

33. Cattani-Lorente, M. A., Godin, C. and Meyer, J. M. (1994). Mechanical behavior of glass ionomer cements affected by long-term storage in water. *Dental Materials*, 10(1): 37-44.
34. Lohbauer, U. (2010). Dental glass ionomer cements as permanent filling materials? – properties, limitations and future trends. *Materials*, 3(1): 76-96
35. De Barra, E. and Hill, R. G. (1998). Influence of alkali metal ions on the fracture properties of glass polyalkenoate (ionomer) cements. *Biomaterials*, 19(6): 495-502.
36. Cattani-Lorente, M. A., Godin, C. and Meyer, J. M. (1993). Early strength of glass ionomer cements. *Dental Materials*, 9(1): 57-62.