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Effect of green clam shells powder addition on properties biodegradable films of polyvinyl alcohol (PVA)

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Abstract

This paper presents an experimental study of the addition of green clam shells powder (GCSP) to the biodegradable film properties of polyvinyl alcohol (PVA). To get GCSP, the green clamp shell was immersed in a 50% NaOH solution for 2 hours, blended until the particle size passed 100 mesh, then heated at a temperature of 500 ºC for 2 hours. The Biodegradable film characteristic was investigated by the addition of GCSP (2, 4, 8, and 10 %wt) in PVA suspension. PVA/GCSP biodegradable films were prepared by a casting solution method. The GCSP functional group's molecular chemical bond and structural analysis were tested using Fourier Transform Infrared (FTIR) and X-Ray Diffraction (XRD). To obtain the mechanical properties of biodegradable films, a tensile test was carried out. The results of the FTIR and XRD test showed that the alkali treatment or/and the calcination process affected the GCSP grain structure. SEM micrographs showed that the grain structure of GCSP which was treated with alkali or/and the calcination process had a more uniform and homogeneous size. The addition of GCSP to PVA was able to increase the tensile strength of the biodegradable film. Overall, the optimal addition of GCSP was 10 wt.% which was calcination treated in a PVA matrix with tensile strength, elongation at break, and Young's modulus of 170 MPa, 18%, and 1184 MPa, respectively.

Keywords: biodegradable film, green clam shell powder, polyvinyl alcohol.

1 Introduction

The very wide use of plastic in various fields of life supported by low production costs has encouraged the plastics industry to continue to develop plastic products and their derivatives[1-4]. It is estimated that the annual production of conventional plastics (petrochemicals) reached nearly 300 million tons in 2018[5]. Petrochemical-based plastics, (e.g. polyolefin, polyester, polyamides, etc.) have been widely used as packaging materials, due to their unique characteristics: they are available in large quantities and at low cost, exhibiting favorable properties (good mechanical strength, improved barrier properties, heat seal ability) and applicability in industrial processing[6, 7].

However, its widespread use has caused serious environmental pollution problems mainly due to the high number of single-use plastic items that reach 50% of the total mass of plastic produced [8] and less than 10% of the total amount of plastic waste that has been recycled, while the rest is thrown away and turned into the garbage so that it has the potential to cause environmental pollution.

Researchers have been actively working on developing biodegradable polymers to protect the global environment from plastic waste. Biodegradable polymers are currently classified into the following groups and are chemically synthesized polymers such as polylactic acid, polyvinyl alcohol, microbial produced polymers such as polyhydroxybutyrate copolymers and natural product-derived polymers such as acetyl cellulose.

Polyvinyl alcohol (PVA) is one of the import polymer and is available in the form of powders, fibers and films. It is well-known, water soluble polymer which is widely used as paper coating agents, adhesives and films [9] ; in fact, PVA is the only polymer with 2 exclusively carbon atoms in the main chain that is regarded as biodegradable. PVA has advantages over other biodegradable polymers, including lower cost due to its versatility in being able to be processed from aqueous solutions or suspensions as well as from melt by blow extrusion and injection molding [10, 11].

Film formed from PVA which are water soluble have been used for many years for packaging applications where the contents must be dispersed in water. Examples of such packaging applications for these materials include pesticides used as water sprays, caustic cleaners or detergents dissolved during use, and process chemicals such as pigments, dyes or carbon black dispersed in water. PVA film also been used as laundry bags for hospitals. These bags protect the hospital staff and dissolve in the wash [12].

The biodegradable materials composed entirely of PVA, however, lack the strength and rigidity to withstand the stress. To improve the mechanical properties of materials, GCSP blended with PVA as potential biodegradable polymers, due to GCSP lowers costs and PVA provides excellent mechanical properties for the materials [13]. PVA has excellent compatibility with GCSP and blends are expected to have good film properties. Several such blends have been developed and tested for biodegradable packaging applications and appear to have potential for use [14]. Polyvinyl alcohol (PVA) was chosen as a blending combination to GCSP to improve product properties as it is the most biodegradable vinyl polymer [15].

Sources of calcium are found in several foods and beverages including milk, meat, eggs, fruits, vegetables, fish and several types of seafood [16, 17]. Seafood is one of the foods with high calcium levels, for example shellfish [18]. Clam shells have more calcium than shellfish meat [19], but are not used properly. Clam shells contain calcium carbonate (CaCO3) which has the potential to be used as bioceramics for several tissue engineering applications [20]. Kiranda, et al [21] state that CaCO3 as a raw natural mineral is the largest source in the manufacture of calcium compounds commercially and is used in various applications such as biomedical, industrial, and nanotechnology. One type of shellfish that is commonly cultivated and consumed is green clam (*Perna viridis*).

In this study, the effect of calcination (HH) and alkali treatment (AA) on the physical properties of green clam shells was carried out by XRD and FTIR tests. Then by varying the number of volume fractions, it was carried out to determine the tensile properties of the PVA/green clam shell biodegradable film.

2 Materials and Methods

2.1 Materials

Polyvinyl alcohol (PVA) with density of 1.32 g/cm^3 was supplied by Chang Chun Petrochemical Co. Ltd. Green clam shells *(Perna viridis)* were collected from a seafood restaurant in Bengkulu City, Indonesia (Fig. 1). A 50% solution of sodium hydroxide (NaOH) is obtained by adding a certain amount of distilled water to the NaOH solution.

Fig. 1. Green clam shell

2.2 Preparation of green clam shell powder

The procedure for making green clam shell powder (GCSP) includes being washed with clean water to remove dirt on the clam shells, soaked them in a 50% sodium hydroxide solution for 2 hours to remove dirt still remaining on the shells, washed again with clean water and drying under sunlight. Then the shells were put into a blender to obtain shell powder and filtered using a 100 mesh sieve for uniformity in the size of the shell powder. The result of sifting is a white powder. Furthermore, the calcination process was carried out by heating the shell powder at a temperature of 500^{o}C for 2 hours, as shown in Fig. 2.

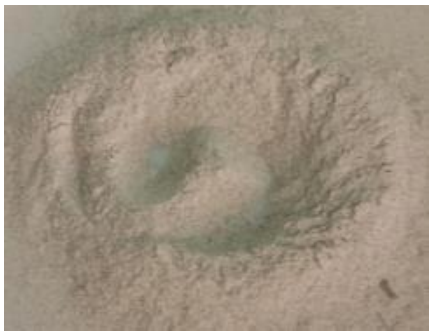

Fig. 2. Green clam shell powder (GCSP)

2.3 Preparation of PVA/GCSP composite

The biodegradable films were prepared using casting process, which consists of dehydrating a film genic solution applied on a support. Then, 2.5 g of PVA were poured into a round bottom flask with 50 ml deionized water, and then it was stirred with high speed (>1000 rpm) in a constant temperature of water bath at 95^{o}C for 10 min. 2.5 g of green clam shell was first dissolved in 50 ml deionized water and was stirred using glass rod for few seconds before adding to the round bottle flask. The blend was stirred for another 10 min. Then the GCSP were added slowly and continued with stirring for 10 minutes (>1000 rpm).

The mixtures were cast onto a glass plate which was placed on a leveled flat surface. Care must be taken to remove bubbles that are a by-product of the preparation. Before drying in the oven at 90°C for 30 minutes, the biodegradable film was dried at room temperature for 12 hours. The films were then peeled off and reserved, as shown in Fig. 3.

2.4 Morphology studies

Morphology study was done at the surface of the sample using a Scanning Electron Microscopy (model Perkin Elmer) to observe the GCSP and PVA distribution and GCSP aggregation. The test specimens were attached to the aluminum holder with double-sided tape and sprayed with gold (10 nm thickness) to eliminate the effect of electron filling on the Polaron SC 515 sputter coating. Image of SEM micrograph for sample were taken at certain magnification.

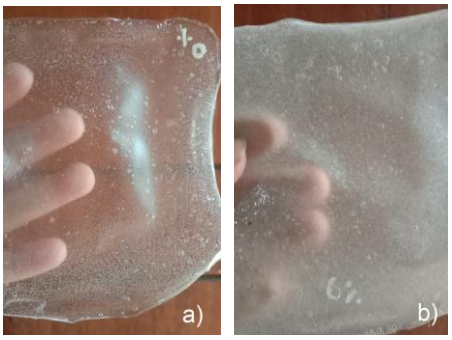

Fig. 3. Biodegradable film. a) PVA; b) PVA/GCSP

2.5 Fourier transforms infrared radiation (FTIR)

The FTIR spectra was recorded on a Shimadzu type 8400S FTIR spectrometer. The wave range was from 4000 to 400 cm^{-1} at a resolution of 16 cm^{-1} and a scan of 10. A quantity of 2 mg of FPF powder sample was mixed with 98 mg of potassium bromide (KBr) prior to being compacted into thin pellets with a hydraulic press.

2.6 X-Ray diffraction (XRD)

The XRD was used to calculate the crystallinity index (CI) of fibers by means of the empirical Segal equation (1) [22].

$$CI(\%) = \frac{(I_{002} - I_{amp})}{I_{002}} x100\% \quad (1)$$

Where CI is crystallinity index, I_{002} is the maximum intensity of 002 lattice diffraction plane at a 2θ of between 22° and 23° and I_{amp} is the intensity diffraction at an angle 2θ close to 18° representing amorphous materials in cellulose fibers. A Rigaku miniflex 600 X-ray diffractometer employing Cu Kα (λ = 1.54) radiation with a current of 30 mA and a voltage of 30 mA was used. All samples were scanned in the range of 5-40° of 2θ and the scanning speed was 2°/min.

2.7 Mechanical test

Tensile strength, elongation at break, and young's modulus were evaluated for each film using the Instron 3366 testing machine. Six dumbbell-shaped specimens (ASTM D638) were cut from each film, as shown in Fig. 4. Each specimen had a width of 12 mm. The average thickness of the specimen was about 0.09 mm. The thickness of the films was measured with thickness gauge. The mean standard deviation within the films was about 10% of the average thickness. The gauge length and grip distance were both 15 mm. Crosshead speed was 50 mm/min and load cell was 10 kN.

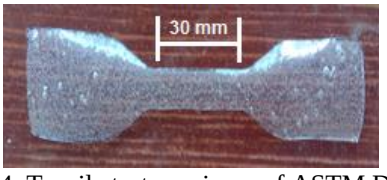

Fig. 4. Tensile test specimen of ASTM D638

3 Results and Discussion

3.1 FTIR analysis

Fig. 5 shows the comparison on XRD pattern of derived CaO from scallop shell and prepared $CaTiO_3$. Derived calcined scallop shell exhibits the reflections at 2θ: 18.97 and 37.39° that are corresponding to the presence of CaO and the reflection at 17.87° and 34.18° as indication of $Ca(OH)_2$. The data representing the incomplete conversion of Ca-containing in the scallop shell during the calcination. Furthermore, the prepared CaTiO3 express the formation of TiO2 in composite form with Ca in the form of CaTiO3 by some reflections as indication of anatase formation [23].

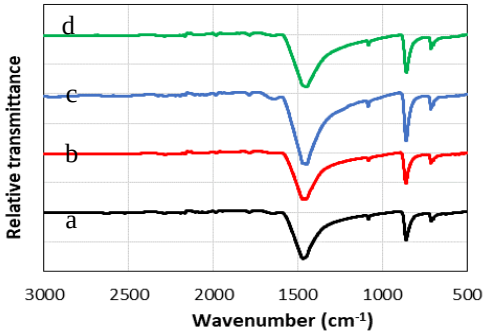

Fig. 5. The FTIR patterns of a) raw GCSP; b) Calcination GCSP; c) Alkali treatment GCSP; d) Alkali treatment + Calcination GCSP

3.2 XRD analysis

Fig. 6 shows the X-ray diffractogram graph of raw GCSP and after treatment. Based on Fig. 6a, it can be seen that the XRD pattern shows that the decomposition of GCSP which is calcination treated at 500°C for 2 hour produces a sharper spectrum indicating that the crystallinity of the shells increases, as shown in Fig.s 6b and 6d. Meanwhile, GCSP which were treated with alkali at 50% NaOH solution for 2 hour tended to have no effect on the crystallite of the shells, as shown in Fig. 6c. The conclusion that can be drawn from this XRD test is that calcination treated green clam shells tend to be more influential than alkali treatment to increase the crystallinity index (CI) value.

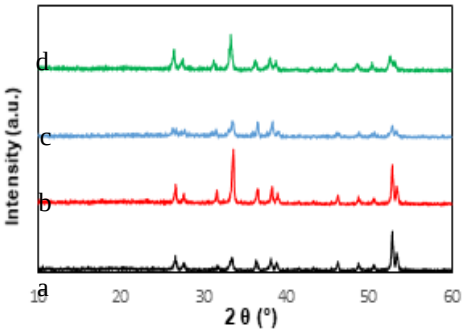

Fig. 6. The XRD patterns of a) raw GCSP; b) Calcination GCSP; c) Alkali treatment GCSP; d) Alkali treatment + Calcination GCSP.

The results of the calculation of the crystallization index of green clam shells are presented in Table 1.

Table 1. The crystallization index of GCSP

Specimens	I_{002} (cm^{-1})	I_{amorf} (cm^{-1})	Crystalinity Index (%)
RM	68	6	91,18
HH	256	12	95,31
AA	84	8	90.48
HA	174	12	93,10

From Table 1 it can be seen that the alkali treatment of green clam shells has the effect of lowering the crystallinity index. Not so with calcination treated which has the effect of increasing the crystallinity index, both on the raw material shell (RM) and on the alkali treated shell (AA). The highest crystallinity index value was obtained in calcination treated shells (HH), which was 95.31% or an increase of 4.5% compared to raw material shells (RM).

3.3 SEM micrograph.

SEM micrographs of the raw GCSP and after treatment are shown in Fig. 7. In general, it can be seen that GCSP has almost the same structure in all types of GCSP. The raw GCSP shown in Fig. 7a has a very variable grain size that indicates that not all shells are powdered. Meanwhile, the alkali treated of GCSP (Fig. 7b) appears to have a more homogeneous grain size, although some are still larger. The grain size was more homogeneous in calcination treated of GCSP (Fig. 7c) and alkali-calcination (Fig. 7d). Therefore, it can be concluded that the calcination is effective in uniform the size of the powder grains. Mukminin, et al. [24] reported that calcination treated at 900°C for 4 hours gave a uniform and homogeneous distribution of hermit crab shell sizes.

3.4 Tensile properties

The tensile test results of the biodegradable film are shown in Fig. 8-10. Based on Fig. 8 and 10, it can be seen that the addition of GCSP to the biodegradable film increased the tensile strength and young's modulus in all specimens. The highest tensile strength and young's modulus were obtained from the biodegradable film added with 10% GCSP weight fraction which was given calcination (HH), which was 170 MPa and 1184 MPa, respectively.

The results of this tensile test have the same trend as the results of the XRD test, which shows that calcination treated (HH) GCSP has the highest crystallization index. Research conducted by Ariawan, et al [25] showed the same trend that an increase in the crystallinity index of salacca zalacca fiber increased the flexural strength of salacca zalacca fiber-reinforced HDPE composites. Meanwhile, based on Fig. 9, the addition of GCSP to the biodegradable film tends to decrease the elongation at break. The highest elongation at break was obtained at the addition of 2% by weight fraction of GCSP to the alkaline-treated biodegradable film in all specimens, which was 39%.

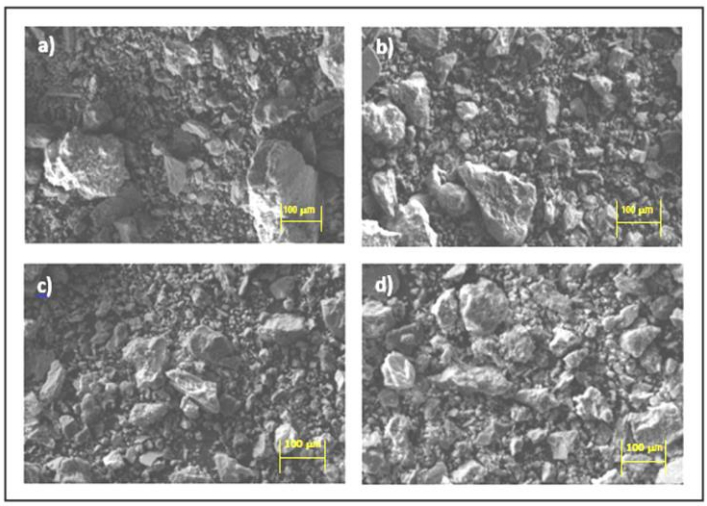

Fig. 7. Scanning electron micrographs of a) raw GCSP; b) Calcination GCSP; c) Alkali treatment GCSP; d) Alkali treatment + Calcination GCSP

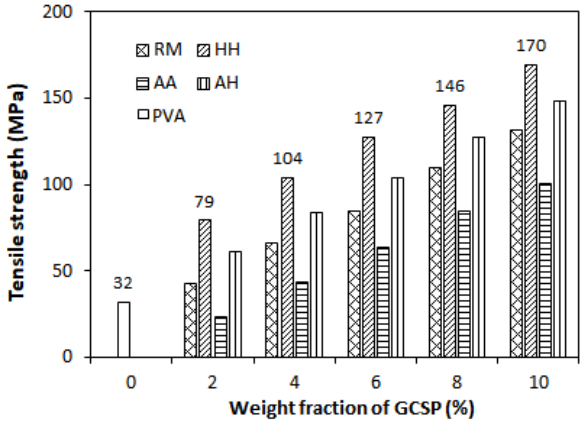

Fig. 8. The Tensile strength of biodegradable film

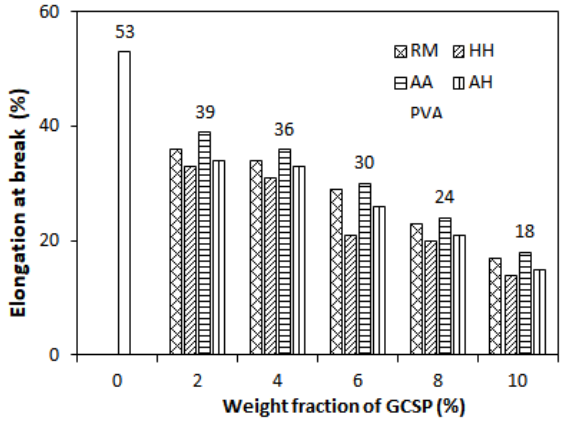

Fig. 9. The elongation at break of biodegradable film

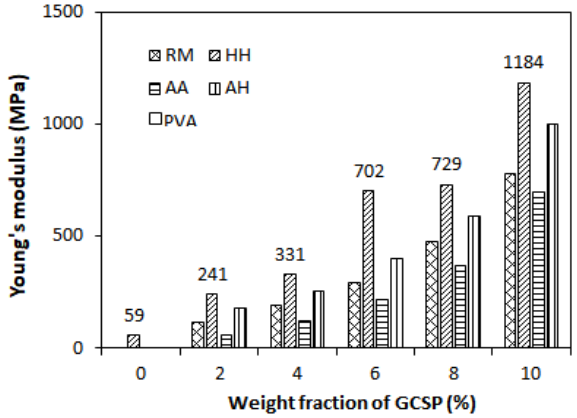

Fig. 10. The Young's modulus of biodegradable film

4 Conclusions

The results of the FTIR and XRD test showed that the alkali treatment or/and the calcination process affected the GCSP grain structure. The SEM micrographs showed that the grain structure of GCSP which was treated with alkali or/and the calcination process had a more uniform and homogeneous size. The addition of GCSP to PVA was able to increase the tensile strength of the biodegradable film. Overall, the optimal addition of GCSP was 10 wt.% which was calcination treated in a PVA matrix with tensile strength, elongation at break, and Young's modulus of 170 MPa, 1184 MPa, and 18%, respectively.

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