ISSN 1027-5495. Functional Materials, 28, No.1 (2021), p. 106-113.
doi:https://doi.org/10.15407/fm28.01.106

Clamshell nanoparticles (Anadara granosa) as fillers in unsaturated polyester resin composites: Effect of fillers and molding pressure

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Received December 25, 2020

The purpose of this study was to determine the effects of clamshell nanoparticles (Anadara granosa) predominantly consisting of calcium carbonate and the molding pressure on unsaturated polyester resin composites. The method of applying clamshell nanoparticles uses a top-down method, nanoparticles are made directly by minimizing large-sized material through the stages of suspension, ultrasonication, and separation of nanoparticles using a membrane. Composites are made using the press method on two parallel plates. The results showed that clamshell nanoparticles had an average diameter smaller than 50 nm, crystallinity index of 99.06 %. The greatest tensile strength properties at 97:3 composition, 8.6 bar molding pressure at 30.947 MPa, the elongation at break at 100:0 composition, 6.89 bar molding pressure at 11.169 %, with the impact strength at 97:3 composition, 8.6 bar molding pressure at 12050 J/m^2.

Keywords: nanoparticle, top-down, ultrasonication, molding pressure.

Наночастинки грейферної раковини (Anadara granosa) як наповнювач ненасиченої поліефірної смоли: вплив наповнювачів та тиску формування. *M.H.S.Ginting, R.Hasibuan, M.Lubis, F.A.Winoto, R.C.Siregar*

Вивчено вплив наночастинок карбонату кальція, отриманого з раковини молюска на ненасичені композити поліефірних смол. При одержанні наночастинок грейферної оболонки використовується низхідний метод, наночастинки виготовляються безпосередньо шляхом мінімізації великогабаритного матеріалу через стадії суспензії, ультразвукової обробки та розділення наночастинок за допомогою мембрани. Композити виготовляються пресовим методом на двох паралельних пластинах. Результати показали, що наночастинки грейферної оболонки мали середній діаметр менше 50 нм, індекс кристалічності АС 99,06. Найвищі властивості міцності на розрив при складі 97:3, тиску при формуванні 8,6 бар при 30,947 МПа, подовження при розриві при складі 100:0, тиску при формуванні 100 фунтів на квадратний дюйм при 11,169 %, ударна міцність при 97:3, тиску при формуванні 125 фунт/кв·Дж/м^2.

Исследовано влияния наночастиц карбоната кальция, полученного из раковины моллюска (Anadara granosa), на свойства композитов из ненасыщенных полиэфирных смол. При получении наночастиц из раковины моллюска используется нисходящий метод, наночастицы производятся напрямую путем размельчения материала большого размера через стадии суспендирования, обработки ультразвуком и разделения наночастиц с помощью мембраны. Композиты изготавливаются методом прессования на двух параллельных пластинах. Результаты показали, что наночастицы двустворчатой оболочки имели средний диаметр менее 50 нм, индекс кристалличности АС 99,06 %. Наибольшие характеристики прочности на разрыв для состава 97:3, давления формования 8,6 бар при 30,947 МПа, удлинения при разрыве для состава 100:0, давления формования 6,89 бар при 11,169 %, с ударной вязкостью для состава 97:3, давления формования 8,6 бар при 12050 фунт/Дж·м^2.

1. Introduction

Unsaturated polyester resins are polymers that are rigid, brittle, have low mechanical properties so that, to make the product suitable for applications, appropriate fillers should be added. These fillers must have properties in conformity with polyesters, such as fiberglass. However, in the recent years fillers of natural origin were used, such as eggshells [1], Clamshell [2] and snail skins [3].

Clamshells contain calcium carbonate compound, $CaCO_3$ (carbonate group/CO_3) with 94–99 % of the total weight of the clam [4–7], as well as Mg 0.51 %, and silicates 0.078 %. It can be categorized, from its chemical composition, as mineral biomaterial filler [5]. It is hydrophilic, and is expected to be able to interact well with unsaturated polyester resins.

Research on unsaturated polyester composites filled with clamshell particles has been carried out, with the best tensile strength properties achieved at conditions 97:3 (wt. %) with 17.785 MPa and water absorption of 0.811 % [8]. This property can be improved by reducing the particle size to nanoparticles [9]. The mechanical properties of composites are known to be satisfactory if the fillers are evenly distributed on the matrix [1]. This distribution is influenced by the particle size. The smaller the particle size, the more homogeneous is the distribution of fillers and the better composites are produced, so, studies should be carried out on the clamshell-based nanoparticle fillers in unsaturated polyester composites.

Polyester composites of polyester nanoparticles filled with clamshell nanoparticles were made using the molding pressure method on two parallel plates. The mixture of unsaturated polyester-clamshell nanoparticles was enclosed in two parallel plate molds, at pressure 8.6 bar for 40 min [2, 10]. This method is easy and simple, so we used it for our research. The purpose of this study was to determine the effect of clamshell nanoparticle fillers and the pressure of molding unsaturated polyester resin composites.

2. Experimental

This study used clamshell as fillers, which were obtained by random selection from seafood restaurants around Percut Medan. The chemicals — unsaturated polyester resins and methyl ethyl ketone peroxide (Mekpo) — were purchased from CV Juntus Raya Medan.

Clamshell nanoparticles are made using the top-down method by reducing the large material directly into the size of the nanoparticles [9]. The clamshell is ground using a ball mill up to 170 mesh size [8]. Its was made through several stages — making the suspension of nanoparticle clamshell by adding a solution of Cocamidopropyl Betaine/Amphitol 24AB as a surfactant, then the ultrasonication process for 60 min resulting in a reduction in particle size [11] and separation of nanoparticle suspension using a dialysis membrane [12].

Unsaturated polyester resin with certain variations mixed with Mekpo catalyst at 1 wt. % of resin weight [13–15]. The batter is stirred using a mixer made of iron, for 10–15 min until it is homogeneous.

Polyester composite is made by mixing matrix and filler:100:; 99:1; 98:2; 97:3; 94:4; 95:5 (wt. %) [8] into (200×200×3) mm^3 iron plate mold which is first smeared with glycerin, so the resin does not stick to the mold. Molding pressure at 8.6 bar for 40 min [10]. Dry composites are removed from the mold and then smoothed unto the surface with a file and sandpaper.

Analyzing of FTIR was carried out at Research Laboratory, Faculty of Pharmacy, University of Sumatera Utara by using instrument IR Prestige-21 Fourier Transform Infrared Spectrophotometer with Serial Number A21004602022 LP, Power 220–240 V 50/60 Hz produced by Shimadzu Corporation.

Transmission Electron Microscopy (TEM) aims to see the shape of particles. TEM analysis was carried out at Medan State University.

XRD analysis is a common technique to find out the crystallinity of a sample. XRD analysis was done in Physic Laboratory, Medan State University by using X-Ray Diffractometer Shimadzu 6100.

Composites of size of (200×200×3) mm^3, made as dumble shaped specimens were tested for their tensile strength and elongation at break properties according to ASTM D 638 using a servo control computer system universal testing machine model AI-7000 M capacity 2000 kg, Power 1F 220 V 50 Hz. A load of this tool is 100 kgf with a speed of 50 mm/min.

Water absorption is tested by soaking in water at room temperature every 12 h until the composite material no longer absorbs water (saturated). Test specimens were made in sizes of (25×25×3) mm^3 according to ASTM D 570. At each time immersion period, samples were taken and cleaned with

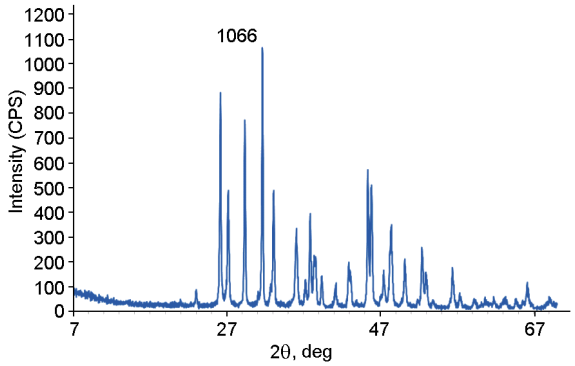

Fig. 1. X-Ray diffraction Clamshell nanoparticles (Anadara granosa).

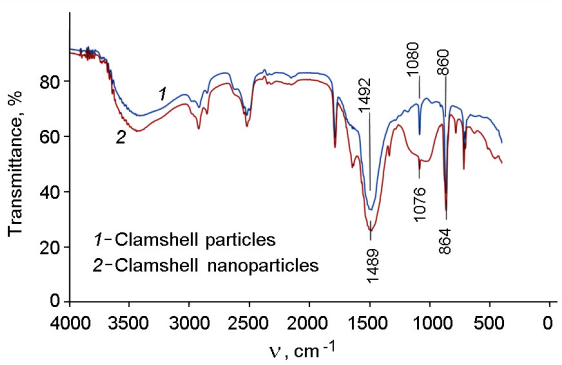

Fig. 2. Fourier transform infrared particles and clamshell nanoparticles (Anadara granosa).

tissue paper to absorb water. The sample is then weighed and calculated using the equation:

$$W_g = \frac{W_e - W_0}{W_0} \cdot 100\%, \quad (1)$$

where W_g is the percentage weight gain of the composite, W_e is the composite weight after immersion, W_o is the weight of composite before immersion.

Specimens were tested on flexibility using the Shimadzu tool based on ASTM D 790-10 standard with specimens of dimensions 3.2 mm×12.7 mm×127 mm and with a test speed of 2 mm minute.

$$UFS = \frac{3PL}{2bd^2}, \quad (2)$$

where UFS is the flexural strength (MPa), P is the load or force given (N), L is the distance between the two dumps (mm), b is the sample width (mm), d is the sample thickness (mm).

3. Results and discussion

3.1 X-Ray diffraction (XRD) of clamshell nanoparticles (Anadara granosa)

The purpose of this characterization is to determine the crystallinity index of the crystals. X-ray diffraction provides information about the structure of the polymer, both the amorphous state and the crystalline polymer.

Calculation of crystallinity index nanoparticles was carried out using the Seagal method, based on the intensity of the absorption peak of the spectra produced, which is $2\theta = 2\theta = 31.64°$ with an intensity of 1066. The crystallinity index of the clamshell (Anadara granosa) is 99.06 %. Analysis of the crystal structure shows that nanoparticles are composed of calcite polymorphic calcium carbonate which is a type of calcium carbonate constituent in addition to aragonite and vaterite. Islam et al. [9] reported the XRD characterization pattern of calcium carbonate nanoparticles from clamshell with the addition of a catalyst in the form of BS-12 surfactant composed of aragonite crystals while clamshell powder was composed of a mixture of calcite and aragonite crystals.

3.2. Fourier transform Infra red (FTIR) particles and clamshell nanoparticles (Anadara granosa).

This purpose to find out the functional groups of clamshell compounds.

Figure 2 indicates the wavenumber 1489 cm^{-1} showing the carbonate group (C–O stretching). The wavenumber 1076 cm^{-1} shows the silicate group (Si–O), and wavenumber 864 cm^{-1} shows the carbonate group (C–O bending). The FTIR results are supported by XRD analysis of nanoparticles composed of calcium carbonate polymorph calcite, Clamshell containing calcium carbonate compounds, $CaCO_3$ (Carbonate group, CO_3) of 94–99 % of the total weight of the shell [4–7], magnesium (Mg) 0.51 %, and silicate (Si–O) 0.078 %.

MgO/Mg wavenumbers were not detected because the Mg metal absorption band was not located at 4000–400 cm^{-1} wavenumbers. Its wavenumbers were below 400 cm^{-1} [16]. Figure 2 shows that the functional group of nanoparticles does not change after a reduction in size, marked by the identification of a typical compound from clamshell (Anadara granosa).

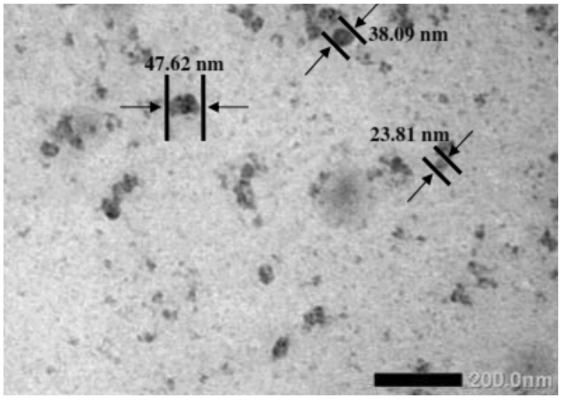

Fig. 3. Transmission electron microscope clamshell nanoparticles (Anadara granosa).

3.3. Transmission Electron Microscope (TEM) clamshell nanoparticles (Anadara granosa).

The purpose of this characterization is to determine the shape and size of the clamshell nanoparticles (Anadara granosa).

Figure 3 showed nanoparticles of clamshell having an average diameter smaller than 50 nm. Making of clamshell nanoparticles has several stages: formation of nanosuspension, making a solution of colloidal shells with stirring to facilitate the ultrasonication stage, chemical treatment (adding surfactant Amphitol 24AB) to reduce the size to nanoparticles and to make the dispersion more stable. The mechanism of the formation of nanoparticles shows that surfactants can control the size and morphology of nanoparticles without changing the chemical structure of the nanoparticles [17]. This is supported by the results of FTIR particles and clamshell nanoparticles without changes in functional groups.

The ultrasonication process occurs under microwaves and shock waves on the surface of the particles, together with collisions between particles resulting in a reduction in particle size. Franco et al. [11] reported the effect of ultrasonic treatment on particle size and specific surface area of kaolinite powder controlled by various variables such as ultrasonic processor power, number of samples and treatment time.

At the stage of separation of clamshell nanoparticles (Anadara granosa) using a dialysis membrane, nanoparticles will diffuse through the membrane from the first medium, nanosuspension and enter the second medium, aquadest, with the aid of stirring using a magnetic stirrer as the driving force [12].

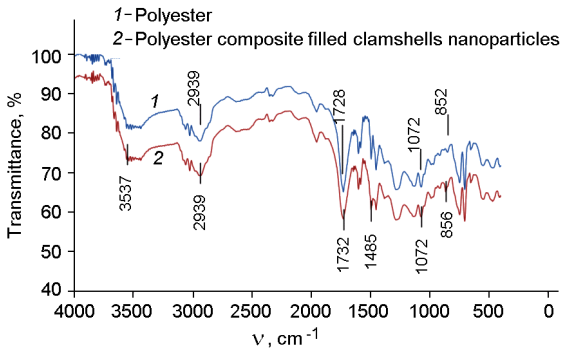

Fig. 4. Fourier Transform Infrared polyester and polyester composite filled Clamshell nanoparticles (Anadara granosa). Description of functional group [18]
— 3537 cm^{-1} : OH group
— 2939 cm^{-1} : alkanes group (C–H)
— 1600 cm^{-1} : alkenes group (C=C)
— 856 cm^{-1} : carbonate group (C–O bending)
— 1485 cm^{-1} : carbonate group (C–O stretching)
— 1072 cm^{-1} : silicate (Si–O)
— 1732 cm^{-1} : carboxylic acid group (–COOH stretching)

3.4. Fourier transform infra-red polyester and composite polyester composite filled clamshell nanoparticles (Anadara granosa)

The purpose of the characterization was to determine the functional groups of unsaturated polyester compounds and polyester composites filled with clamshell nanoparticles (Anadara granosa).

Figure 4 shows the wavenumber 2939 cm^{-1} indicating that the alkane groups in the polyester interacting with nanoparticle fillers increase the hardness of the composite. The wavenumber 1732 cm^{-1} shows the carboxylic group, and wavenumber 3537 cm^{-1} shows OH. The carboxylic group interacts with the O group of CaO clamshells, with the H group from the polyester matrix. The wavenumber 1600 cm^{-1} shows the group (C=C). Wavenumbers 856 and 1485 cm^{-1} indicate the presence of carbonate groups (C–O bending) and carbonate groups (C–O stretching). Wavenumber 1072 cm^{-1} shows the range of the Si–O group. This group is obtained from silica groups derived from clamshell nanoparticles (Anadara granosa).

3.5. Scanning electron microscopy of polyester and composite polyester filled broken clamshell nanoparticles

This characterization is to find out the morphological form of unsaturated polyes-

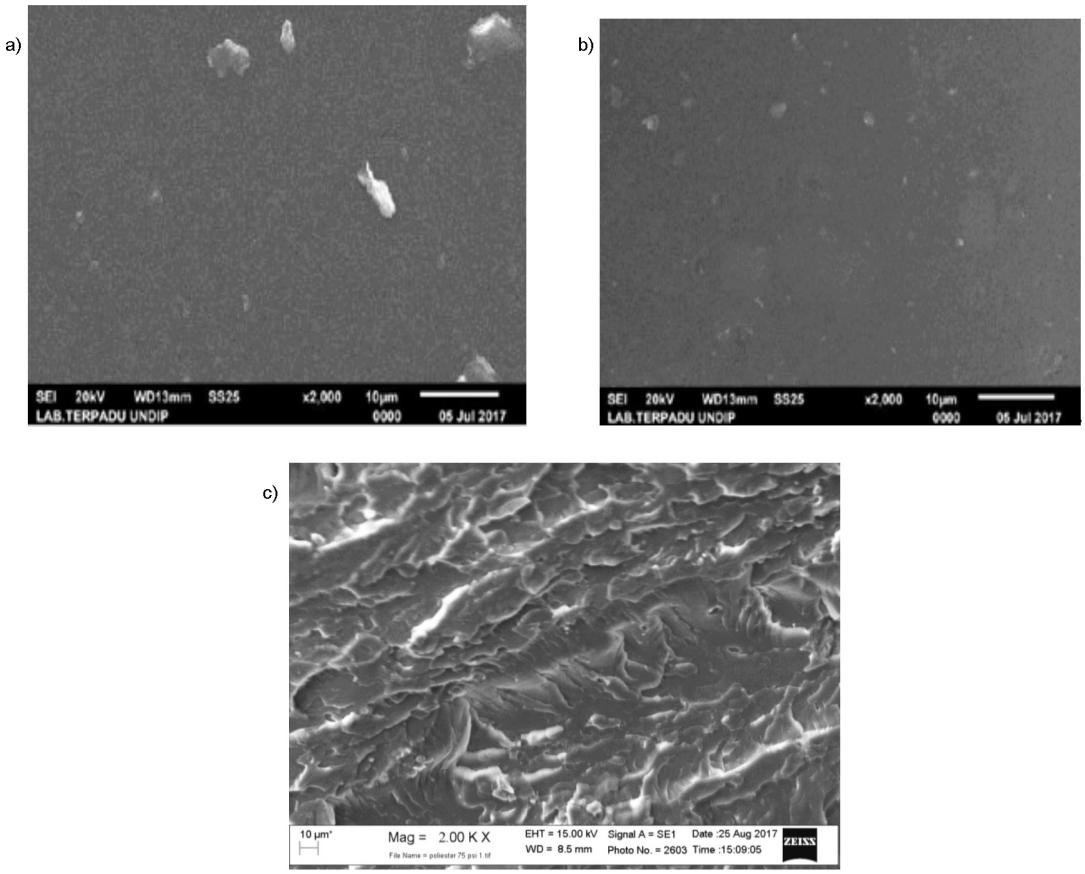

Fig. 5. SEM of break samples (a) polyester (b) polyester composite filled clamshell nanoparticles at composition 97:3 8.6 bar pressure molding and (c) composite polyester composite filled clamshell nanoparticles at composition 97:3 5.17 bar pressure molding at 2000 magnification.

ter and broken polyester composites. Morphology provides information on how the damage occurs at the break. The broken area is the first area of stress that triggers destruction to occur so that we can interpret the cause of the decision.

Figure 5a shows that on the surface of the sample there is an agglomeration of the catalyst due to the mixing of polyester resin and Mekpo. It weakens the interface adhesion thereby reducing the mechanical strength of the polyester.

Figure 5b shows uniformly filled clamshell nanoparticles (Anadara granosa) dispersed on the polyester matrix because the nanoparticles have a relatively small size so that they interact physically between the filler and the matrix. The molding pressure affects the composite — at higher pressure, the density increases, and better interaction between the matrix and the filler is achieved.

Figure 5c shows the surface the sample of break more roughly, indicating high cracking resistance by fillers. There are voids on the surface of the composite. This is due to imperfect wetting due to interactions between nanoparticle fillers and low polyester matrix. Low interaction causes the charger to pull out when stressed. Voids can also be caused by the formation of air bubbles during mixing when the composition of fillers is increased resulting in increased viscosity of the mixture, producing voids that are difficult to remove from the sample.

3.6. Effect of composition of polyester-nanoparticles clamshell (Anadara granosa) and pressure molding on water absorption properties of polyester composites

Water absorption aims to determine how the composite is damaged when immersed in water. Water will diffuse into the composite, thereby damaging the composite structure and reducing the mechanical properties of the composite.

Figure 6 shows the addition of nanoparticle fillers causing increased water absorption. Water absorption at 100:0 is 0.409 %. The highest absorption at the ratio of 95:5 was 1.433 %. The larger the content of the

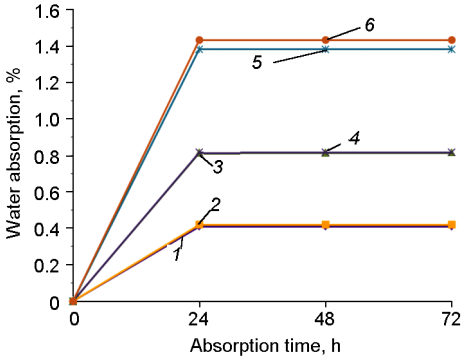

Fig. 6. Effect of immersion time on water water absorption on polyester composites at 8.6 bar. polyester-nanoparticles: *1* – 100:0; *2* – 99:1; *3* – 98:2; *4* – 97:3; *5* – 96:4; *6* – 95:5.

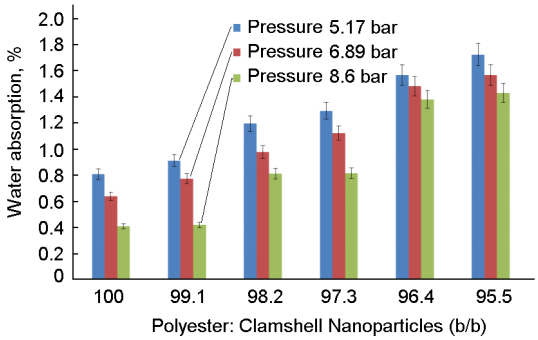

Fig. 7. Effect composition polyester-clamshell nanoparticles (Anadara granosa) and pressure molding on water absorption polyester composite.

filler, the smaller the particle size, which causes the agglomerating nanoparticles to increase the water absorption. The largest compound content of the filler is calcium carbonate (98.99 %) tends agglomeration.

Agglomeration weakens the interface adhesion between the filler-matrix causing the formation of a gap in the interface area so that water molecules are trapped in the gap. This result is supported by Azis and Rahmah research (2016). The higher the composition of the filler ($CaCO_3$ 30 %), the percentage of water absorption and flexural strength is increasing in hybrid compositions of kenaf/rice husk fiber. The effect of the polyester-nanoparticle composition of the clamshell (Anadara granosa) and the pressure of molding on the water absorption properties of polyester composites is shown in Fig. 6 [19].

Figure 7 shows the composite water absorption is greater than the addition of filler and pressure molding. Increasing the pressure molding causes a decrease in the percentage of water absorption of the polyester composite at 100:0;5.17 bar: 0.811 %; 8.6 bar: 0.409 %. Increasing the molding pressure, voids can be reduced in the composite, increasing the interface bond between the matrix and the filler, so the composite density increases. The percentage of composite water absorption decreases in proportion to the increase in the molding pressure [20].

3.7. Effect of polyester-nanoparticles composition clamshell (Anadara granosa) and pressure molding on tensile strength polyester composites

The purpose of this analysis to determine of force needed to pull the material until it breaks.

Figure 8 shows the addition of clamshell nanoparticle fillers (Anadara granosa) causing the tensile strength to increase. The greatest tensile strength in the composition 97:3 and at a pressure of 8.6 bar, which is 30.947 MPa, is due to the filler of clamshell nanoparticles (Anadara granosa) having high calcium carbonate content, its strong brittle nature causes an increase in the stiffness and hardness of the composite [21]. The particle size affects the mechanical properties of composites. The smaller the particle size, the greater the surface area, and stronger the interaction between matrix and filler power, so the better are the mechanical properties of the composite. This is supported by the results of the scanning electron microscopy in Fig. 5b — one can see that the filler is evenly dispersed inside the polyester matrix so that a good interface interaction occurs.

The tensile strength of properties of 96:4 compositions was decreased due to the agglomeration of nanoparticles forming larger and unevenly distributed particles. Veena et al. (2011) stated that an increase in filler content (wt. %) that has exceeded the limit can reduce mechanical strength, decreased interaction of the filler with the matrix due to the agglomeration effect of the filler particles which causes the initial damage/failure [22].

Figure 8 shows that the tensile strength of composites increases with increasing pressure molding increase the density of the composite, reduces voids, and increases the interface bond between the filler-matrix so that the composite becomes more rigid. This statement is supported by the research by Younesi and Bahrololoom [20]. Increasing the pressure molding to 10 bar can increase

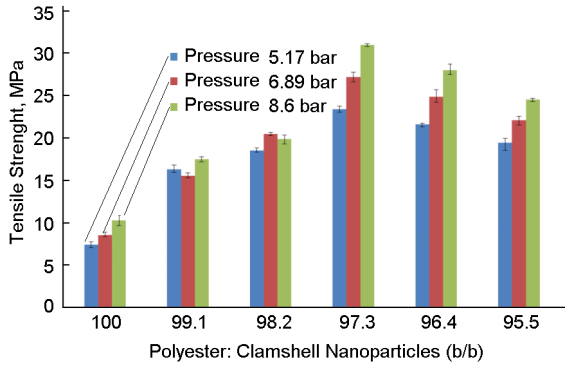

Fig. 8. Effect composition polyester-clamshell nanoparticles (Anadara granosa) and pressure molding on tensile strength of polyester composite.

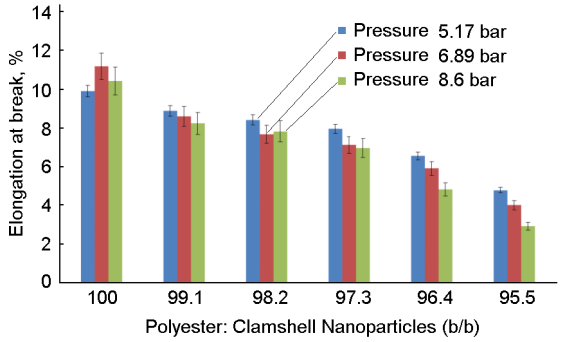

Fig. 9. Effect composition polyester-clamshell nanoparticles (Anadara granosa) and pressure molding on elongation at break polyester composite.

the density, crystallinity, MFI (melt flow index), Ultimate tensile strength and the Young modulus on polypropylene-hydroxyapatite biocomposites [22].

3.8. Effect of composition of polyester-clamshell nanoparticles (Anadara granosa) and pressure molding on elongation at break polyester composites

The purpose of this test to find out which material has deformation or elongation when given load.

Figure 9 showed the elongation at break the highest at the composition of 100:0; 6.89 bar:, 11.169 % and decreased at 95:5; 6.89 bar pressure molding of 3.992 %. The greater the filler content, the elongation at the time of breaking decreases. Fillers give a rigidizing effect on the matrix, non-organic fillers tend to be more rigid resulting in a decrease in the strain on the matrix thereby reducing the value of elongation at break on composites [23].

Figure 9 shows the higher pressure applied causing the elongation at break value to decrease. This is due to the effect of

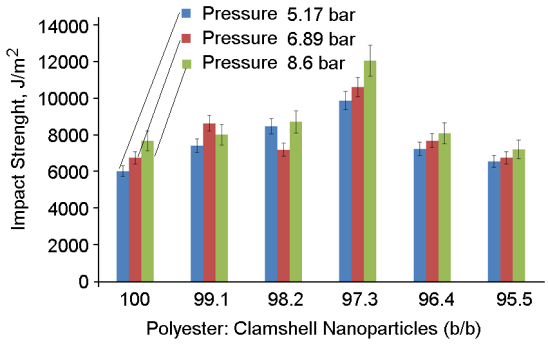

Fig. 10. Effect of polyester-clamshell nanoparticles composition (Anadara granosa) and molding pressure on impact strength of polyester composite.

pressure closing the distance of the interface bond between the matrix and the filler and urging the existence of the pore. This compaction affects the reduction in thickness and increased density of the composite, the resulting composite becoming more rigid, causing a decrease in the percentage of elongation at the break of the the composite.

3.9. Effect of polyester-nanoparticles composition of clamshell (Anadara granosa) and pressure molding on impact strength of polyester composites

This test aims to determine the amount of energy needed to break the material through an impact on the surface.

Figure 10 showed the impact strength of polyester composites increased by 12050 J/m^2 at a composition of 97:3, pressure molding 8.6 bar, but decreased in the composition of 96:4 to 95:5 with pressure molding of 8.6 bar for 7199 J/m^2. The addition of clamshell nanoparticle fillers (Anadara granosa) increases the value of impact strength due to clamshell nanoparticles fillers (Anadara granosa) is a natural mineral having a high calcium carbonate content, has strong and brittle properties causing stiffness and hardness [20]. The impact strength increases due to good interphase network flexibility between matrix-fillers. The presence of fillers causes the composite to absorb the higher impact energy [24].

The decrease in impact strength in the 96:4 composition is due to the fact that when more fillers are added to the matrix, they cannot be properly distributed to cover the entire surface of the filler. Composition of clamshell nanoparticles (Anadara granosa) which exceeds the optimum limit will result in agglomeration in a certain area thereby reducing the mechanical strength of

the composite upon addition of too much filler [25]. Kang and Chan (2004) reported that certain particle sizes with the addition of fillers were easily agglomerated. with the distance between particles becoming larger to result in decreased mechanical strength [26].

Figure 10 shows the strength of the composite impact strength increasing with increasing pressure. Increasing the pressure will be more easily absorbed by the composite energy. Increased impact strength is a compaction effect which results in decreased porosity and forms a strong interface bond. Decreased porosity minimizes crack initiation due to loading. A strong interface bond indicates that the distribution of loading between the matrix and the reinforcing material can work well. Therefore composites can sustain larger loading before experiencing initial cracks and fractures.

4. Conclusions

The results obtained show that clamshell skin nanoparticles of the average diameter smaller than 50 nanometers have the largest content of calcium carbonate compounds, with the crystallinity index of nanoparticles of 99.06 %. The greatest tensile strength properties at composition 97:3 MPa; 8.6 bar pressure molding 30.947 MPa, elongation at break composition 100:0; 6.89 bar pressure molding 11.169 %. The impact strength at 97:3 composition was 8.6 bar at pressure molding of 12050 J/m^2.

Acknowledgments. The authors gratefully acknowledge that the present research is supported by the Ministry of Research and Technology and the Higher Education Republic of Indonesia. This research grant under of PDUPT Implementation of the year 2018 Contract Number: 58/UN5.2.3.1.R/ PPM/2018 date 05 February 2018.

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