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EFFECT OF SONIFICATION TIME ON THE PREPARATION OF CLAMSHELL NANOPARTICLES USING COCAMIDOPROPYL BETAINE (AMPHITOL 24AB) SOLUTION AS SURFACTANT AS FILLER IN COMPOSITE MATERIALS

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ABSTRACT

This study aimed to determine the effect of sonification time on the size of clamshell nanoparticles as filler in composite materials. This method of providing clamshell nanoparticles uses a top-down approach. This method makes nano-sized particles directly by reducing large materials through the stages of suspension and separation of nanoparticles. The results showed that the sonification time affected the size of the clamshell nanoparticles. The size of the nanoparticles produced in a volume of 8 ml of surfactant solution with a sonification time of 3 hours was 223.93 nm. The morphology of the spherical nanoparticles, with a crystallinity index of 86.40%, did not show any significant changes in the functional groups during the synthesis process of reducing the size of the shell particles.

Keywords: nanoparticle, clam shell, amphitol 24AB, composite, surfactant.

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INTRODUCTION

Clamshells derived from seafood are not consumed or thrown away. So far, they are used as handicrafts or decorative arts, so their use is not optimal. Clamshells contain calcium carbonate ($CaCO_3$) compounds of 94-99% (of the total weight of the complete shell), Carbonate groups (CO_3), 0.51% Magnesium (Mg), and 0.078% Silicate (Si-O) [1]-[4]. From the composition of the clamshell compound, it can be categorized as a natural mineral material.

The filler in composite materials is usually reinforcement. The size of the filler particles in the composite greatly determines the mechanical properties produced. The smaller the particle size, the greater the density of the resulting composite because the distribution of filler in the composite matrix is getting better, so it is necessary to study the provision of clamshell nanoparticles as filler.

The method used in the provision of Clamshell nanoparticles uses a top-down method. This method is easy and simple, namely making nano-sized particles directly by reducing large materials. This method has stages, namely the stirring process, chemical treatment (addition of surfactant Amphitol 24AB), Sonification, and separation using a dialysis membrane using a magnetic stirrer aims to form a colloidal solution of clamshells (*Anadara granosa*) to facilitate the formation of nanosuspension at the sonification stage [5]. At the chemical treatment stage, the addition of surfactant Amphitol 24AB is used to reduce the size of nanoparticles, and the nanoparticle dispersion is more stable. The mechanism of nanoparticle formation shows that surfactants can control the size and morphology of nanoparticles without changing the chemical structure of the nanoparticles [6].

At the stage of separating clamshell nanoparticles (*Anadara granosa*) using a dialysis membrane with the basic principle of the dialysis method, the nanoparticles will diffuse through the membrane from the first medium, namely nanosuspension, and enter the second medium, namely distilled water with the help of stirring using a magnetic stirrer as a driving force [7].

The provision of nanoparticles using the top-down method is influenced by several factors, namely power, sonification processor time, and surfactant concentration [8]. Sonification processor power affects the collision force between particles which can cause particle size reduction; low processor power can minimize collisions between particles so that the particle size reduction process is not optimal. Increasing the surfactant concentration to the point of neutrality will increase the repulsive forces between the particles and thus reduce the size of the particles. This study aimed to determine the effect of sonification process time on the provision of clamshell nanoparticles as filler in composite materials.

MATERIALS AND METHODS

In this research, the clamshells obtained from seafood restaurants around Percut Medan were selected randomly, while the chemical: Cocamidopropyl Betaine/Amphitol 24AB as a surfactant was purchased from CV. Gudang Jaya. The method of providing clamshell nanoparticles uses a top-down process, namely making nano-sized particles directly by reducing large materials. The shells were made of microparticle size 170 -200 mesh [9]. The microsize particles underwent several stages, namely making a suspension of clamshell nanoparticles by adding a solution of Cocamidopropyl Betaine/Amphitol 24A B as a surfactant. Then, the process of separating the nanoparticle suspension formed using a dialysis membrane.

Clamshell Nanoparticle Suspension

Clamshells were washed with water, dried, and dried in the sun for 24 hours. The clam shells were ground using a ball mill and sieved with a particle-size (170 mesh) sieve[9]. The clamshells measuring 170 mesh were made into a suspension: 50 ml aqua dest and clam shells were mixed into an Erlenmeyer and stirred using a hot plate magnetic stirrer for 1-3 hours at room temperature with a stirring speed of 1200 rpm. Next, the clamshell suspension was added with 8 ml of Cocamidopropyl Betaine/Amphitol 24AB, stirred with a hot plate magnetic stirrer for 2 hours at room temperature with a stirring speed of 1000 rpm. Finally, the clamshell suspension was sonicated using an ultrasonic bath for 60 minutes to produce nanosuspension[10].

Separation of Clamshell Nanoparticle from Suspension

The nanosuspension solution was put into a dialysis membrane soaked in 100 ml of distilled water and allowed to stand for 3 to 4 days while stirring. Aquadest was evaporated at 100 °C to get nanoparticles.

Nanoparticle Characterization

Particle size analysis (PSA)

PSA analysis aims to see the shape of the particle size. PSA analysis was carried out at the research laboratory, Faculty of Pharmacy, the University of North Sumatra using the instrument Ultrason solvent properties: water, Refractive index: 1.33, viscosity: 0.91 cp, Laser power: 23.90%, Temperature: 24.00 °C, DTC position: UP, Wavelength: 657 nm, Average count rate: 2 804 kcps.

Fourier Transform Infra-Red (FTIR)

Analysis of FTIR was observed at Research Laboratory and Integrated Testing Universitas Gadjah Mada, Yogyakarta.

Transmission Electron Microscope (TEM)

Transmission Electron Microscope (TEM) analysis aims to see the shape of the particles. TEM analysis was carried out at the Integrated Laboratory, Diponegoro University, Semarang.

X-Ray Diffraction (XRD)

The purpose of X-Ray Diffraction (XRD) characterization is to analyze the crystallinity index and diameter of the crystals. XRD analysis was carried out at the Integrated Laboratory, University of Diponegoro, Semarang.

RESULTS AND DISCUSSIONS

Particle Size

The variation in the time of the sonification process on the size of the clamshell nanoparticles is presented in Figure-1.

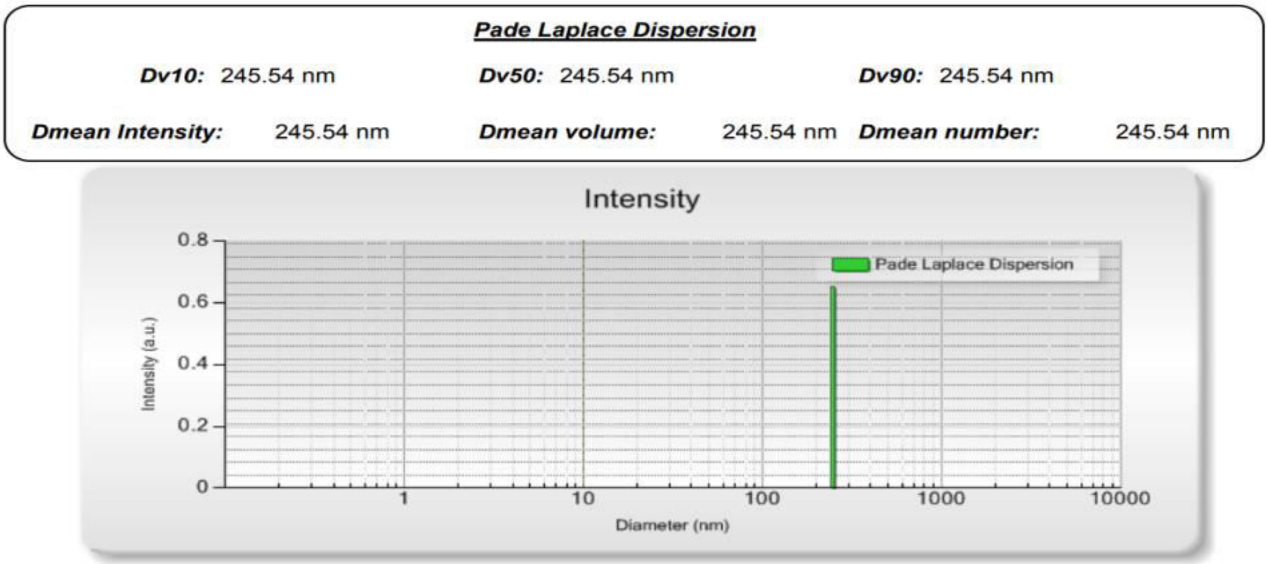

Figure-1a. Sonification process time is one hour.

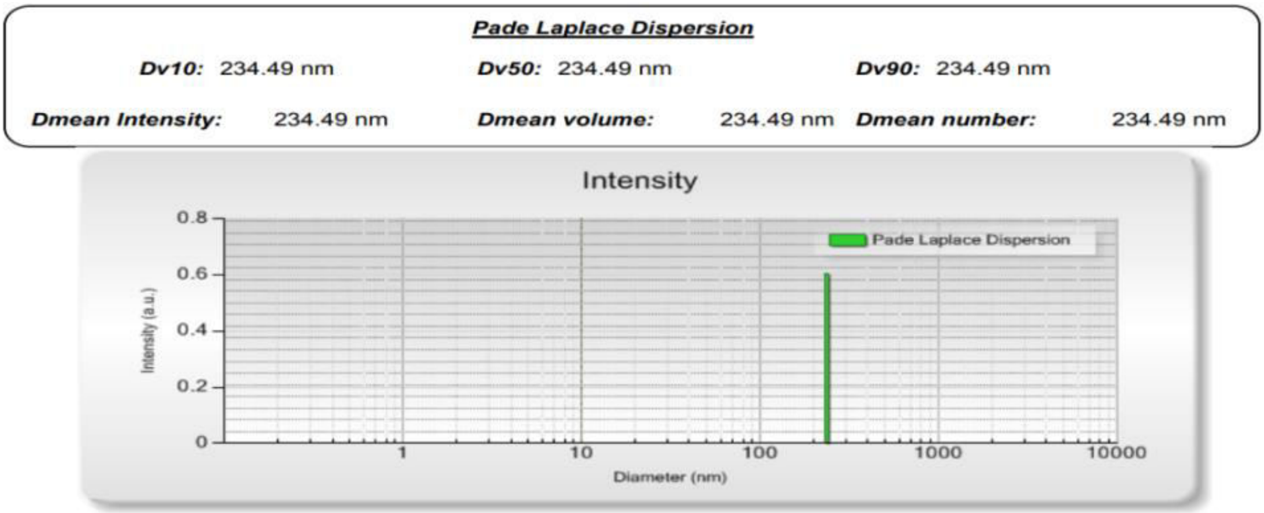

Figure-1b. Sonification process time is one hour.

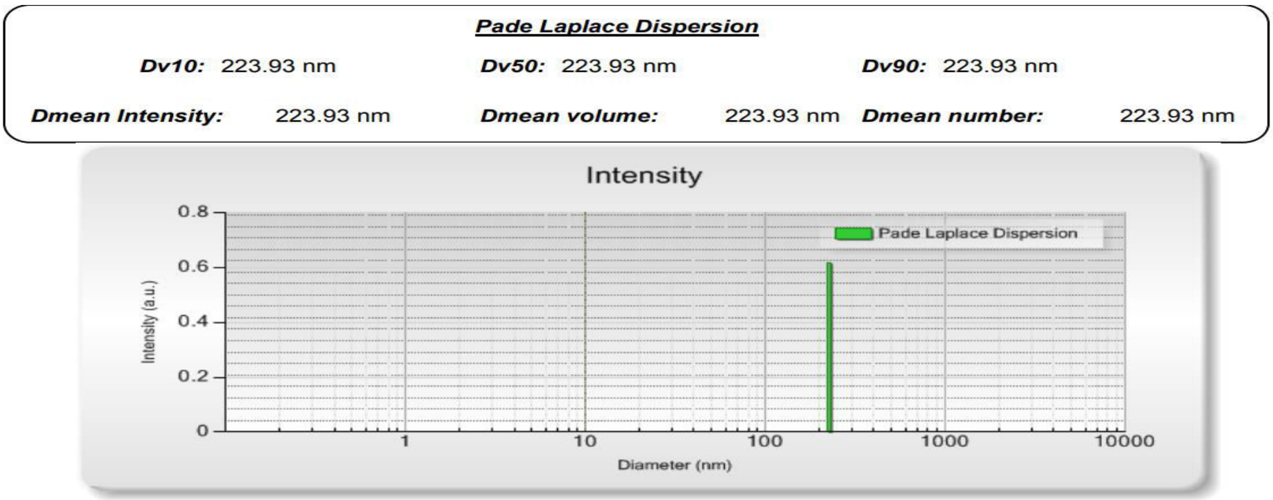

Figure-1c. Sonification process time is three hours.

Figure-1 shows that the longer the sonification process, the smaller the size of the nanoparticles produced. The smallest nanoparticle size during the 3-hour sonification process was 223.93 nm. During the sonification process in the synthesis of nanoparticles, microwaves and shock waves occur on the surface of the particles, along with collisions between particles which can result in a reduction in particle size. Particle size reduction is supported by research by Franco *et al*. (2004), who reported the effect of sonification treatment on particle size and specific surface area of kaolinite powder. The process of adding surfactants with stirring is carried out to form a colloidal solution and facilitate the formation of nanosuspensions, reduce the size and disperse nanoparticles to be more stable [8]. Surfactants can control the size and morphology of nanoparticles without changing the chemical structure of the nanoparticles [6].

Fourier Transform Infra-Red (FTIR)

FTIR analysis of clamshell nanoparticles aims to determine the functional groups of the materials or compounds used. The results of the FTIR variation of the sonification time of clamshell nanoparticles (1, 2, and 3 hours) are presented in Figure-2.

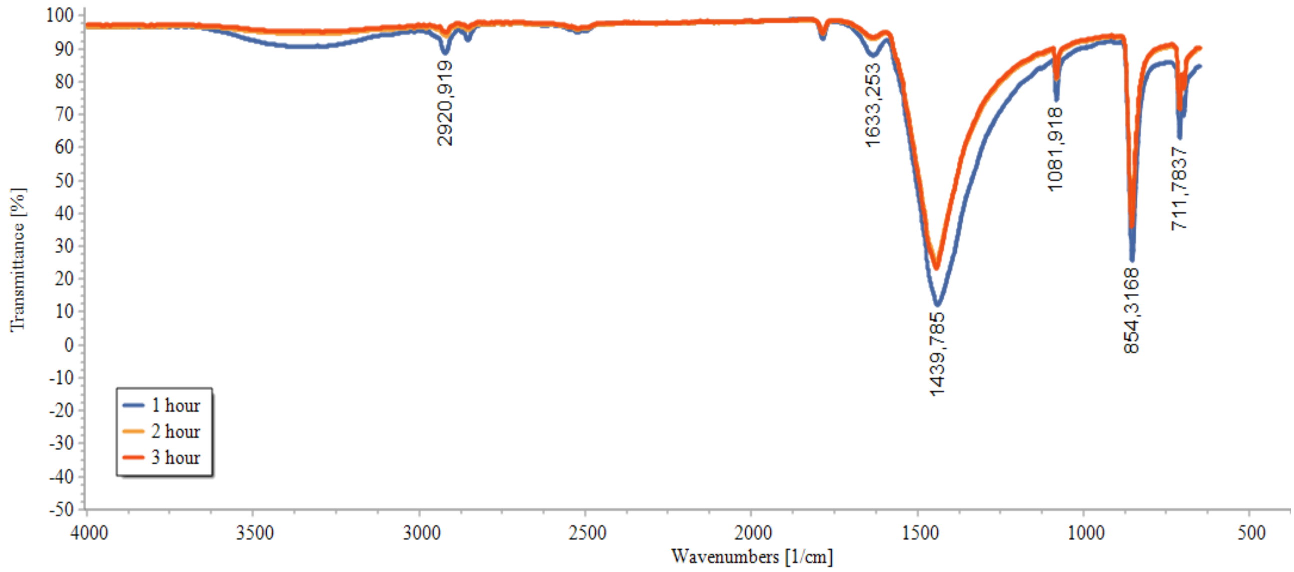

Figure-2. Fourier transform infra-red variation of the sonication process of clamshell nanoparticles.

Figure-2 shows that the variation of the sonication process (1, 2, and 3 hours) on the clamshell wave number did not change significantly. The wave number only varies the transmittance value. Generally, it can be said that there is no change in the peak wave number when the shell particle size is reduced. Wavenumber 2920 cm^{-1} indicates an alkanes group (C-H stretching) with a wave number range of 3000-8500 cm^{-1} [11]. Wave number 1439 cm^{-1} shows a carbonate group (C-O stretching) with a wave number range of 1400-1600 cm^{-1}. The wave number of 854 cm^{-1} indicates a carbonate group (C-O bending). These results are supported by research by Bharatham (2014) [12]. Mineral and physiochemical evaluation of clamshells, Clamshells contain carbonate groups (C-O stretching) and carbonate groups (C-O bending) wave numbers 1453 and 855 cm^{-1}. Wave number 1082 cm^{-1} indicates a silicate group (Si-O). These results are supported by research by Mohamed (2012), clamshells (*Anadara granosa*) containing 98.99% calcium carbonate (carbonate group, CO_3), 0.51% magnesium (Mg), and 0.078% silicate (Si-O) [13]. FTIR cannot detect MgO because the absorption band of Mg metal is not located in the FT-IR analysis range (4000–400 cm^{-1}). The MgO bond lies in the range below 400 cm^{-1}.

Transmission Electron Microscope (TEM) and Scanning Electron Microscope-EDX (SEM-EDX)

The purpose of the Transmission Electron Microscope (TEM) clamshell nanoparticles (*Anadara granosa*) is to determine the shape and size of the nanoparticles, while the purpose of SEM-EDX analysis is to determine the morphology and chemical composition of the materials or compounds used. The results of SEM and TEM analysis with ultrasonication time variations of clamshell nanoparticles (*Anadara granosa*) for three hours are presented in Figure-3.

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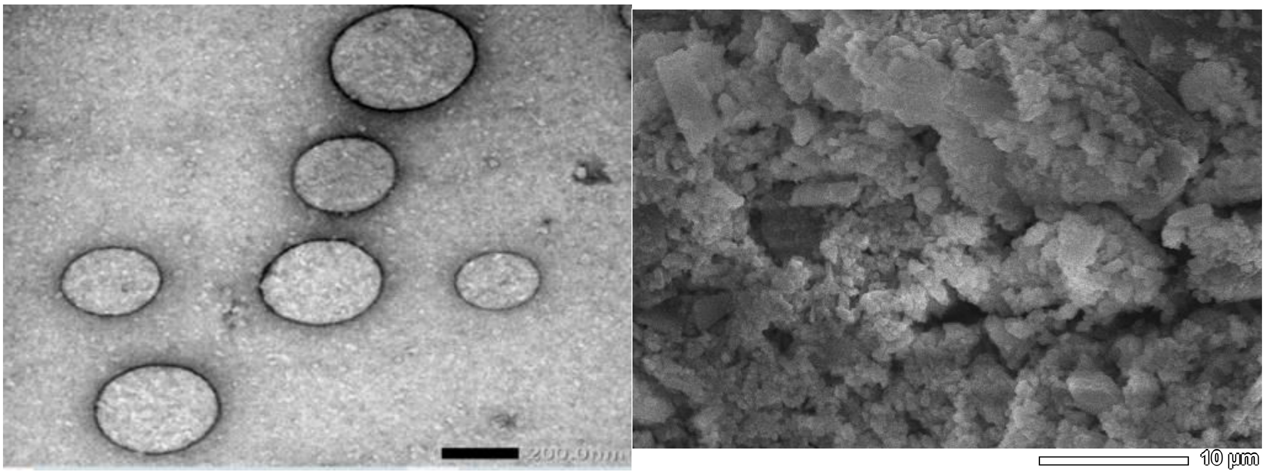
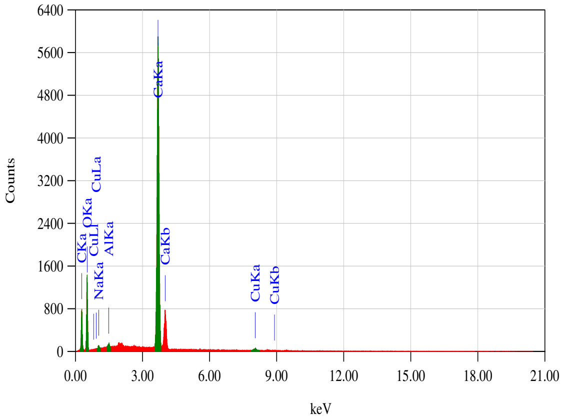


(a)



ZAF Method Standardless Quantitative Analysis(Oxide)
Fitting Coefficient: 0.0235
Total Oxide: 24.0

Element	(keV)	Mass%	Sigma	Mol%	Compound	Mass%	Cation	K
C K	0.277	27.78	0.04	64.58	C	27.78	0.00	20.0631
O		20.51						
Na K	1.041	0.55	0.05	0.33	Na2O	0.74	0.45	0.4666
Al K	1.486	0.36	0.05	0.19	Al2O3	0.68	0.25	0.3533

(b)

Figure-3. (a) Transmission electron microscope and (b) SEM-EDX clamshell nanoparticles with a sonification time of three hours.

Figure-3a shows that the resulting clamshell (*Anadara granosa*) nanoparticles are spherical (Spherical Shapes). This is supported by the results of PSA analysis with various particle diameter sizes. The diameter size at three hours was obtained at 223.93 nm so that the filler material for clamshell nanoparticles (*Anadara granosa*) can be classified as a nanometer-sized filler. Figure-3b shows that the largest composition of cockleshell nanoparticles contains 27.78% C and 48.92% Ca in CaO compounds, so these nanoparticles are classified as mineral compounds. Figure 4b also shows a spherical agglomerate morphology, and this is by Cahyadi research (2022) that the resulting nanoparticles are also globular in shape [9].

The process of stirring a mixture of clamshell particles (*Anadara granosa*) which has been sieved with 170 mesh sieves, with aqua dest and the surfactant Amphitol 24AB using a magnetic stirrer aims to form a colloidal solution of clamshells (*Anadara granosa*) to facilitate the formation of nanosuspension at the sonification stage. In the chemical treatment stage, the addition of surfactant Amphitol 24AB is used to reduce the size of nanoparticles, and the nanoparticle dispersion is more stable. The mechanism of nanoparticle formation shows that surfactants can control the size and morphology of nanoparticles without changing the chemical structure of nanoparticles [6]. These results are supported by the effects of FTIR particles and clamshell nanoparticles, indicating no change in the chemical structure of the nanoparticles during the synthesis process. In the sonification stage, microwaves and shock waves occur on the surface of the particles, along with collisions between particles which can reduce particle size. At the stage of separating clamshell (*Anadara granosa*) nanoparticles using a dialysis membrane with the basic principle of the dialysis method, namely the nanoparticles will diffuse through the membrane from the first medium, namely nanosuspension, and enter the second medium, namely distilled water with the help of stirring using a magnetic stirrer as a driving force [5].

X-Ray Diffraction (XRD)

The purpose of X-Ray Diffraction (XRD) is to analyze the crystallinity index. In addition, x-ray diffraction provides information about the structure of the polymer, both the amorphous and crystalline states of the polymer. The results of the XRD analysis of variations in the sonication process (1, 2, and 3 hours) of clamshell (*Anadara granosa*) nanoparticles are presented in Figure-4.

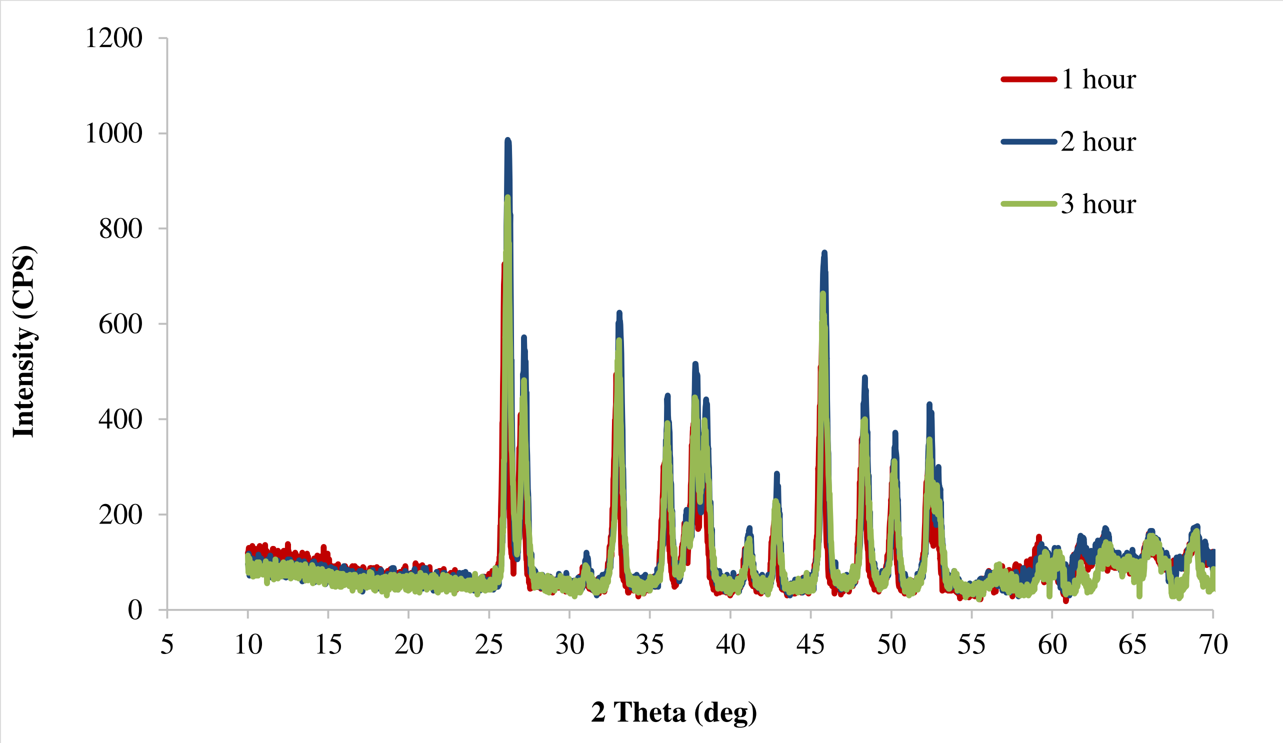


Figure-4. X-ray diffraction (XRD) variation of sonication processing time (1, 2, and 3 hours) clamshell nanoparticles (*Anadara granosa*).

Polymer materials are composed of crystalline and amorphous solids. X-ray diffractograms of crystalline polymers produce sharp peaks, whereas amorphous polymers tend to make broad peaks. X-ray scattering patterns can also provide information about chain configurations in crystals, approximate crystal sizes, and the comparison of crystalline regions with amorphous regions (degrees of crystallinity) in polymer samples. Crystallinity index calculations using the Seagal method. Based on the intensity data on the sharp peak of the spectra produced by the sample of directional conch clamshell nanoparticles, which is integrate from 10 to 90: area = 8031. Figure-4 shows the crystallinity index of the clamshell (*Anadara granosa*) nanoparticles of 86.40%.

CONCLUSIONS

The time of the sonification process affects the particle size of the provision of clamshell nanoparticle filler. The size of the nanoparticles produced in 3 hours is 223.93 nm. The analysis showed that the morphological shape of the nanoparticles was spherical, the crystallinity index of the clamshell (*Anadara granosa*) nanoparticles was 86.40%, and there was no visible change in the functional group/chemical structure of the nanoparticles during the synthesis process.

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