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Processing and Characterization of Bentonite North Aceh Indonesia as PCL (Poly ϵ - caprolactone) nanocomposite filler for Biomedical Material Applications

Ridwan^{1,2*}, Basuki Wirjosentono¹, Tamrin¹, Teuku Rihayat², Nurhanifa²

¹Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Sumatera Utara, 20155, Medan, Indonesia

²Departement of Chemical Engineering, Politeknik Negeri Lhokseumawe, 24301, Aceh Indonesia

Corresponding author: ridwan.kimia@yahoo.com

ABSTRACT

Poly ϵ -caprolactone (PCL) gets a lot of attention, and shows great potential in biomedical applications among synthetic polymers. This is because the thermoplastic polymer possesses some desirable features, including good stability, ease of process and has been used in some medical products, such as drug delivery and network engineering applications. This research, is modifying montmorillonite which is purification result of bentonite clay of North Aceh Indonesia, as nanofiller for PCL matrices. This bentonite clay can be intercalated with chitosan nanoparticle for biomedical material applications. The results showed that the presence of bentonite in PCL nanocomposite improve mechanical properties of the nanocomposite. Biomedical properties of nanocomposite still are being investigated.

Keywords: Poly ϵ -caprolactone, bentonite, montmorillonite, chitosan nanoparticles, biomedical material.

INTRODUCTION

Plastic polymers are one of the most dominant types of polymers that dominate everyday human activities. Each year about 100 million tons of synthetic plastic is manufactured worldwide for use in various industrial sectors [9]. Plastic polymers are the best-selling belle of the material in the community for the reason that they are multifunctional, lightweight and strong and anti-corrosion making it easy to apply in a variety of equipment. Some of the examples of the use of plastic polymers as packaging of various products, kitchen utensils, electronic equipment insulators, to medical fields such as medical equipment to tissue engineering.

Attention to ecology encourages businesses to find natural and composite materials. Biodegradable issues, compatible properties of tissue, hygienic and nontoxic properties are especially important in the medical field. In recent years the development of breakthrough biodegradable materials derived from renewable materials (renewable resources) is quite increased. This can be seen from the number of publications discussing about natural polymer-based composites.

Considering the desire for more qualified polymeric material products, several research groups in different countries have innovated by combining synthetic polymers such as poly caprolactone (PCL) with a polymer composite forming material [2]. The composite material is a mixture of two or more different phases, to produce properties and superior



specific features that can not be achieved by a single element. The formation of composites can be standardized by mixing polymers with similar elements or with certain filling materials such as fibers, bentonite, chitosan and so on which have reported an increase in the properties of pure polymers.

There are varieties of aliphatic polyesters that can be used in the preparation of biodegradable polymer nanocomposites. The most one is Polycaprolactone. Polycaprolactone (PCL) is a polymer synthesized chemically based on caprolactone units. PCL does not occur in nature but it is a very good biodegradable material in the packaging sector [7]. PCL is biodegradable polyesters, and these include polymers such as polyglycolic acid (PGA), polylactide (PLLA) and their copolymers. It is a semicrystalline polymer due to its regular structure, and its melting temperature is above body temperature (59-64°C), but its T_g is -60°C, so in the body the semi crystalline structure of PCL results in high toughness, because the amorphous domains are in the rubbery state [4]. PCL is also useful for biomedical materials due to its physical properties and biological properties [7]. Tissue engineering (TE) is a multi-disciplinary field focused on the development and application of knowledge in chemistry, physics, engineering, life and clinical sciences to the solution of critical medical problems, as tissue loss and organ failure [7]. It involves the fundamental understanding of structure function relationships in normal and pathological tissues and the development of biological substitutes that restore, maintain or improve tissue function [2].

PCL has some drawbacks that are very hydrophobic, the biodegradation process is rather slow, and has a sensitivity to microbial activity. However, the ability of PCL to mix with filling materials such as bentonite and through the modification process is able to overcome these deficiencies [6]. The addition of chitosan can offer an antimicrobial characteristic so it is suitable to be applied to medical equipment.

The performance of the PCL can be improved by the addition of inorganic filler such as nanoclay in nanometer size. By adding small amount nanoclay into the polymer matrix will greatly enhance the mechanical, thermal, barrier and biodegradable properties, flammability, water adsorption as well as creep resistance of the polymer [5]. To produce a high performance polymer/clay nanocomposite several factors need to be considered. The polymer matrix and the nanoclay surface are not compatible. The surface of natural bentonite is hydrophilic while the polymer is hydrophobic in nature. Bentonite is unsuitable for hosting non-polar organic molecules without prior treatment. In order to introduce the bentonite into the polymer material, the surface of bentonite has to be organically modified by organic cation from surfactant in advance. This should be done by increasing the interlayer spacing of the bentonite. By surface modification, the interlayer spacing of the nanoclay galleries can be increased and the miscibility of the bentonite with the polymer can be increased to achieve a good dispersion of layered structure within the polymer matrix.

In an attempt to find superior PCL properties, the PCL study combined into nanocomposites with natural mineral mixtures (bentonite) which are believed to enhance the mechanical properties of the material and the chitosan filler that can offer protection against microbial activity in the material. On the basis of this paper, the aim of this study tries to examine deeper on how to process the appropriate bentonite filler (bentonite and chitosan) so as to provide an enhanced effect on the quality of the PCL polymer. The final product produced by the characterization of XRD, FTIR and Universal Tensile Machine (UTM).



MATERIALS AND METHODS

Material

The PCL polymer (Poly e-Caprolactone) used in this study came from Nature Works Co. (USA). Chitosan obtained from CV. Rudang Jaya (Indonesia). Bentonite is derived from the North Aceh region modified by the use of Aquades, Ethanol, Sodium Hexametaphosphate (NaPO₃)₆, and Cetyl Trimethyl Ammonium Bromide (CTAB) surfactant.

Modifying of Bentonite as Filler

As many as 100 grams of raw bentonite chunks crushed using a crusher then sifted to pass 300 mesh size. The bentonite powder of the sieve was inserted into a beaker glass containing 1200 ml of aquades and added (NaPO₃)₆ by 1 g. The solution was dispersed by stirring for 6 hours on a hot plate using a magnetic stirrer at moderate speed without heating. The dispersion results are then allowed to form bentonite precipitate and separated by water containing impurities. The precipitate was washed with ethanol to remove excess (NaPO₃)₆ excess and filtered using filter paper. Cleaned bentonite was re-introduced into 1,250 ml of aquades and added 1.24 g of CTAB surfactant and then re-dispersed for 2 hours. Furthermore, the process of centrifugation for 2 minutes with a speed of 700 rpm to separate the solids bentonite with liquid. Bentonite is dried in an oven with a temperature of 105 ° C to a moisture content of ± 0% [1].

Furthermore, Bentonite analyzed the determination of its CEC value using BaCl / MgSO₄ method and karaterisasi d-spacing layer using XRD and FTIR tool.

Prepare of PCL-Bentonite-Chitosan Nanocomposites

The PCL is dried in a vacuum oven at ± 40 ° C for 24 hours. Furthermore, using a melting 150 ° C temperature extruder device, various PCL polymers were mixed with filler (Bentonite-Chitosan) ratio of (95%: 5%); (93%: 7%); and (91%: 9%) in which each total mixture meets the weight of 10 grams. After the extraction process, the composite is then fed into a specimen mold of ASTM 638D Type IV Standard covered with aluminum foil, then compressing with hot press at 160 ° C for 20 minutes in atmospheric pressure. The formed nanocomposite is immobilized at room temperature until fully compacted for further testing of mechanical properties. At the same time, a single 100% PCL polymer is prepared as a comparative sample. The sample is then characterized by mechanical properties using UTM tools.

Characterization Technique

Determination of CEC Value

100 MgSO₄ mixed in wet bentonite, apply approximately 2 hours in the beaker glass, add 5 ml of ammonia buffer, add 6 drops indicator EBT. Titration with standard EDTA solution (titer A ml). Then titration again using MgSO₄ solution (titer B ml). The end of the equivalence point is marked by a change in blue to pink (pink).

$$\text{CEC (meq per 100 g of clay)} = 8 (B-A2)$$



X-Ray Diffraction

The nanobentonite interlayer spacing was determined by X-ray Diffraction (XRD) measurements using Cu Ka radiation ($k = 0.1542$ nm), while the generator was set up at 50 kV and 40 mA. The data was collected over a range of scattering angles (2θ) of 1–10.

FT-IR

FT-IR spectrum is measured in the range of wave numbers $500\text{--}4000$ cm^{-1} using a spectrophotometer Fourier Transform Infrared (Shimadzu IR Prestige-21 Serial No. A210048 02 519, Kyoto, Japan). Samples were adjusted to the size of $20 \times 25 \times 0.8$ mm.

Tensile Test

Dog-bone-shaped specimens for nanocomposite of 150 mm in total length, with a gage section of 12 mm wide by 4 mm thick and 80 mm long, type I based on standard ASTM D638, were prepared by compression molding at 150 °C and a pressure of 25 MPa and subsequent cooling down to 5 °C to avoid sample shrinkage. An Universal Tensile Machine was used to measure the tensile strength of pure PCL and PLA/Bentonite-Chitosan nanocomposite, according to standard ASTM D638. All tests were carried out under ambient conditions using a cross-head speed of 5 mm/min.

RESULT AND DISCUSSION

CEC Value Determination

CEC is one of the important variables for quantitatively measuring the quality of bentonite to be applied as filler and adsorbent. Cation Exchange Capacity is needed to see how much bentonite ability to exchanged the cations present with the cation of the surfactant. The greater the cation exchange ability, the more surfactant cations that fill the bentonite interlayer space so that it can expand larger. This will affect the properties of bentonite to bind better with the polymer at the time of mixing.

The determination of the value of CEC (Cation Exchange Capacity) of North Aceh bentonite using $\text{BaCl}_2 / \text{MgSO}_4$ method at various sizes (100,120,150,200 and 250 mesh) as shown in Table 1.

Tabel 1. CEC Value of Bentonite on Particle Size Variation

Particle Size (Mesh)	CEC (meq/100 g)
100	60,7
120	61,48
150	69,11
200	71,08
250	79,00

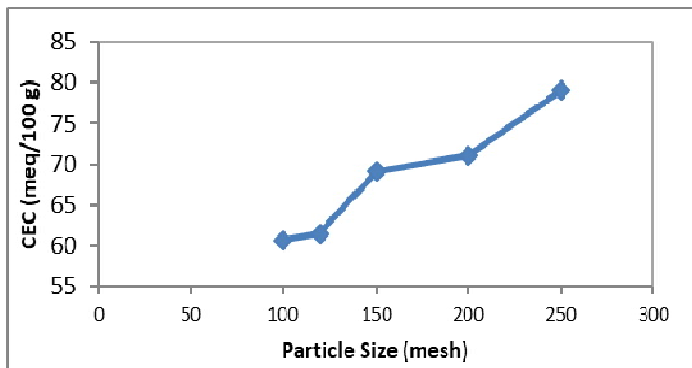


Figure 1. CEC Value of Bentonite on Particle Size Variation

The BaCl₂ / MgSO₄ method is an efficient method used in the analysis of the determination of the bentonite CEC value because the results obtained are more accurate and close to the standard although the process is more complex than other methods such as the pH Balance method or Methylene Blue adsorption method [1]. Based on the measurements, the North Aceh CEC bentonite produces different values on each particle size of the smallest (100,120, 150, 200 and 250 mesh) in a row is 60.7 meq / 100g; 61.48 meq / 100g; 69,11 meq / 100g; 71,08 meq / 100g; and 79.00 meq / 100g. The highest CEC value was obtained at 250 mesh particle size, while the smallest value was in the particle size of 100 mesh. We can see that the smaller the particle size the greater the value of the resulting CEC. This is influenced by the contact surface area of bentonite interacting with the surfactant cation, the small size of the particle makes the contact surface greater so that the cation exchange capacity is more optimal.

X-RD Analysis

XRD analysis is done to find out bentonite d-spacing layer (spacing layer). This analysis is performed on one particle size of the best results of the CEC value determination. Pure bentonite with 250 mesh particle size before modification and after modification with CTAB surfactant were analyzed under X-Ray diffraction rays to determine the success rate of modification ie the presence or absence of increased d-spacing layer after surfactant was added. Figure 4.1 shows a bentonite XRD graph before and after modification with the surfactant. Changes in the diffracted intensity are measured and plotted against the diffraction angle (2θ).

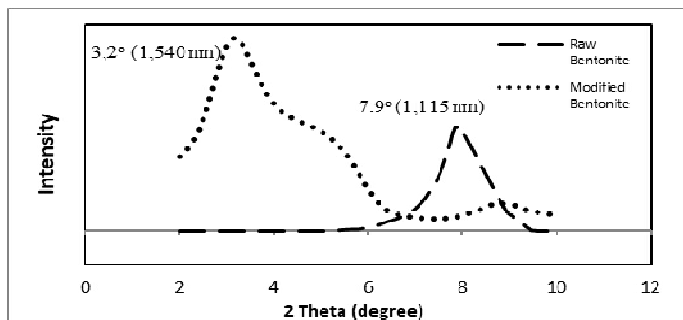


Figure 2. Graph of XRD Result

Based on Figure 2, the bentonite d-spacing layer shows the increasing from before and after the modification process. The X-RD graph plots data between the angle of reflection on the x-axis and the intensity on the y-axis to produce a bentonite d-spacing layer automatically. bentonite from North Aceh prior to modification had a maximum reflection angle peak of 7.9° with a d-spacing value of 1.115 nm, and increased its d-spacing size to 1.540 nm at the maximum reflection angle of 3.2° . If large calculated opening of d-spacing layer bentonite equal to 0,425 nm. With the value achieved, it can be said that North Aceh bentonite has a good swelling power and is suitable for use as a polymer filler. It also proves that the use of Cetyl Trimethyl Ammonium Bromide (CTAB) as a surfactant has succeeded in opening the d-spacing layer in bentonite in the presence of an organic compound exchanging between the two cations (ammonium) of surfactants with ions in bentonite (Na^+). The opening of d-spacing is also due to the use of $(\text{NaPO}_3)_6$ as a cleansing agent, as revealed in the 2016 Zhijin Gong study which suggests that $(\text{NaPO}_3)_6$ has worked effectively to remove impurities which may block the interaction between surfactants and bentonite.

FT-IR Analysis

This analysis was performed to identify the functional groups contained in North Aceh bentonite the best results of the CEC value using the Shimadzu IR Prestige-21 (Fourth Transform Infrared) (FT-IR) Spectrophotometer (Serial No. A210048 02519). This analysis also aims to determine whether the addition of surfactant affects the existing functional groups and observes the possibility of reaction at the processing stage characterized by the emergence of newly undetectable functional groups or vice versa.

Infrared spectroscopy of bentonite obtained in the mid-infrared section ($400\text{-}4000\text{ cm}^{-1}$) at room temperature.

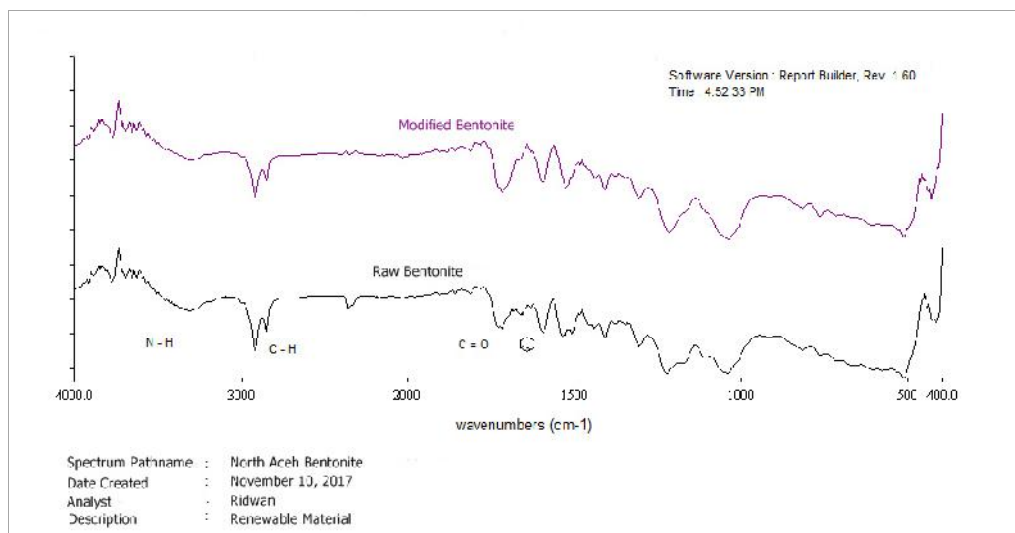


Figure 3. FTIR Graph of Raw Bentonite and Modified Bentonite

FTIR spectral analysis results show that in general, FTIR spectra produced by pre-and bentonite bentonite after modification are similar. Fig. 3 shows the absorption bands around the 3800 cm^{-1} wave number which is the top of the structural OH (hydrogen bond) in the

bentonite silicate frame. The OH band and the HOH bend of the water molecule are shown around the wave numbers 2900 cm⁻¹ and 1700 cm⁻¹. In addition, the Si-O and Al-O vibrations appear on wave numbers 420 cm⁻¹ - 1200 cm⁻¹. From the results of the visible FTIR spectra it can be said that there is no significant effect on the bentonite base group between bentonite before and after domodification with CTAB surfactant. However, there is a typical peak of surfactant at a wave number of about 2940 cm⁻¹ visible an absorption peak showing the symmetric and asymmetric vibrations of C-H in methylene. This peak proves that cationic surfactants having carbon chains have entered into bentonite.

Tensile Test

The tensile strength of a material is defined as the magnitude of the maximum voltage that the specimen can retain when stretched or withdrawn before the material is broken. This test was performed on the application of North Aceh bentonite as a filler (polymer) PCL (Poly-ε-Caprolactone) forming Nanocomposite. In addition to bentonite, chitosan is also added as a mixture of filling materials that are believed to offer an anti-bacterial property material that is one of the benchmarks in medical applications.

PCL-Bentonite-Chitosan Nanocomposites which have been mixed according to the variation of the composition and molded according to ASTM D 638 standard specimen by melting method, tested its tensile strength through the axial force provided by the UTM tool. Here are the results of tensile test of 7 samples of Nanocomposite and 1 sample of pure PCL without mixing with filler as comparison shown in Figure 4.

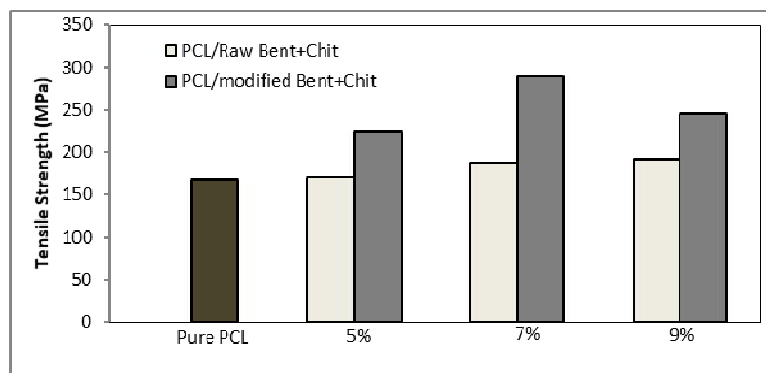


Figure 4. Graph of Tensile Test Results

The graph in Figure 4 plots the value of tensile strength produced by PCL with filler variations in the form of mixture of chitosan and crude bentonite and chitosan with modified bentonite of 5%, 7% and 9%. Based on the graph in FIG. 4, it can be seen that the addition of filler (Bentonit-Chitosan) showed a better tensile strength when compared to pure PCL polymer. The tensile strength values of 3 modified PCL-Chitosan-Bentonite nanocomposite samples were 225 to 290 MPa, while for raw PCL-Chitosan-Bentonite nanocomposites only ranged from 170 to 193 MPa only. The graph illustrates that the modified bentonite modified samples are samples with the best tensile strenght values compared to raw bentonite nanocomposite nanocomposites. That is the reason why it is necessary to do pretreatment to modify bentonite before it is applied to the material because the large bentonite interlayer

chamber will provide an opportunity for the polymer to be intercelled and bonded better [11,12].

PCL Nanocomposite with modified bentonite filler showed a significant effect of tensile strength increase based on the addition of filler composition. In the composition of filler Bentonit-Chitosan 7% is the maximum value of 290 Mpa. The ability of the polymer to bind to the filler has a certain restriction at 8%, this is why if the additive is added too much it will have an effect on its poor connectivity and the sample will become brittle. Therefore, the sample with filler composition as much as 9% decreased tensile strength.

CONCLUSION

The results showed that CEC bentonite North Aceh is suitable for use as a polymer filler. This is evidenced by a good CEC value of 79 meq / 100g, an expanding property characterized by increased d-spacing layer of 0.425 nm based on XRD test. The C-H bond, which is the typical peak of the surfactant in bentonite, is seen through FTIR analysis of a wave number of about 2940 cm⁻¹. Mixing of bentonite and chitosan filler in PCL polymer to form PCL Bentonite-Chitosan Nanocomposite can increase tensile strength of material compared to single polymer. Based on the result of tensile test, the sample with maximum value is in the nanocomposite: filler composition (93%: 7%) where the tensile strength value generated is 290 MPa. The modification of bentonite and the corresponding filler content which in the polymer affects the quality of the nanocomposite material.

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