Mechanical Properties, Morphology and Thermal Degradation of PCL (Poly ε - Caprolactone) Biodegradable Polymer Blended Nanocomposites with Aceh Bentonite as Filler

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Abstract. Polycaprolactone (PCL) is an important polymer due to its mechanical properties, miscibility with a large range of other polymers and biodegradability. Polycaprolactone (PCL) was chosen as the matrix because of its biodegradability characteristics. This paper reports on an investigation of the influence of the presence of bentonite. It was found that of bentonite significantly influenced the mass loss behavior of the nanocomposite because of physical interactions between the clay and the polymer chains and degradation volatiles. Melt drawing of the composite, however, had little influence on the degradation behavior of the investigated samples. Based on mechanical properties results, addition of bentonite significantly enhances the flexibility of PCL blends. TGA showed that the presence of bentonite improves thermal stability of blends.

1. 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 [7]. Nanocomposites that use layered silicates produce intercalation by dispersing silicate (filler) into the polymer matrix and bio nanocomposite specifically using polymers derived from renewable and biodegradable resources. There is an increase in high interest in both of these fields based on the tendency to avoid the use of materials derived from fossil materials with environmentally friendly materials. 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. Biodegradable polymers, such as polylactide (PLA) and poly(e-caprolactone) (PCL), have generated a great deal of interest as ones of the most innovative materials being developed for a wide range of applications because of their thermoplastic, biodegradable, and biocompatible properties. Blending of two or more polymer components is a novel method for producing balanced properties for specific end uses. However, most polymers are thermodynamically immiscible and their blends produce immiscible phase domains with sharp interfaces, because of their unfavorable interactions and high molecular masses. The final properties of blends are strongly influenced by the interface and the size scales of the minor phase, which are determined by the processing conditions and morphological development.

PCL \((C_6H_{10}O_2)\) is a known as a commercial biodegradable polymer with a rather low melting point of around 60 °C. This is a type of biodegradable, hydrophobic and partly crystalline polymer with good mechanical properties [2]. 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 [3]. The composite material is a mixture of two or more different phases, to produce properties and superior specific features that cannot 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 [4].

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 [5].

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 [6].

PCL is also useful for biomedical materials due to its physical properties and biological properties. 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 [4]. PCL is biodegradable polyesters, and these include polymers such as poly glycolic acid (PGA), poly-L-lactide (PLLA) and their copolymers. It is a semi crystalline 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 [8]. To improve the physical and mechanical properties of polycaprolactones such as strength, stiffness and fire retardant, polycapronlactone is often added with fillers such as clay. One type of filler is montmorillonite. This clay is obtained from the purification of bentonite. Nevertheless, so far, no researchers have tried to modify clay with antibacterial compounds to add anti-bacterial properties to PCL. One compound that has anti-bacterial properties is chitosan. Chitosan has the ability to deactivate bacteria and fungi in a broad spectrum and do not cause effects on mammalian cells, so it has been widely used in the medical field [9].

2. Research Method

The materials used in this study were Polycaprolactone (PCL), bentonite from the local area (North Aceh), chitosan, Lactobacillus bacteria, zinc oxide catalyst, Staphylococcus aureus (Gram Positive), Pseudomonas aeruginosa (Gram negative). chitosan, Cetyltrimethyl ammonium bromonitride (CTAB),
AgNO3 0.1 N, Phosphate-buffer saline (PBS), Thiophosphates (TPP), glutaraldehyde solution (GA, 25% in H2O), acetic acid, sodium cacodylatetrihydrate, Staphylococcus aureus bacteria and Pseudomonas aeruginosa, as well as other ingredients to revive bacteria, Nutrient Agar (Nutrient Broth). The raw bentonite was collected from North Aceh – Indonesia, Quantitative analyze for the mineral composition of the bentonite, confirming the interlayer cation is Ca2+. Its chemical composition was found to be as follows: 49.95 % SiO2, 30.701 % Al2O3, 9.813 % Fe2O3, 0.369 % MnO, and 0.173 % MgO from Analysis Xrf Oxford Instruments.

2.1. Preparation of Bentonite Nanoparticles
A total of 0.05 moles (18.2 grams) of cetyltrimethyl ammonium bromtontide (CTAB) and 250 mL of distilled water were placed in 500 mL of glass beaker. This solution is then heated at 80°C for 1 hour. Then 20 grams of bentonite and 500 mL of distilled water were stirred separately in a 1000 ml glass beaker. Then the dispersion of bentonite solution was added to CTAB and stirred for 1 hour. Then bentonite continued to be washed with water distillate. Next the filtrate was titrated with 0.1 N AgNO3 until there was no more chloride or bromide. Then bentonite is placed for drying in an oven at a temperature of 60°C. Bentonite is then filtered using a 100 µm sieve tray to produce bentonite nanoparticles. Furthermore, bentonite was analyzed using X-RD to determine the crystal structure of bentonite.

2.2. Preparation of Chitosan Nanoparticles
A number of thiophosphates solutions are added to the solution of chitosan. Distirer with speed 1200 rpm to obtain chitosan emulsion. Acetic acid added to make chitosan pH 3.5 emulsion with the result will be a chitosan suspension. Furthermore, bentonite was analyzed using X-RD to determine the crystal structure of chitosan.

2.3. Preparation of Bentonite-Chitosan PCL Nanocomposite
Purified bentonite is dispersed into PCL using melt blending equipment. For its treatment, a number of bentonites are mixed in PCL according to the range of research levels in weight percent (wt%). Material mixture (PCL / nanocomposite bentonite) was compressed with HSINCHU into molding under certain conditions.

2.4. Characterization

2.4.1. Tensile Strength
The tensile test using the Universal Tensile Machine (UTM) device is a method used to test the strength of a material by providing an axial force load at a rate of 5 mm / min. Standardized test specimens, carried uniaxial loading so that the test specimen stretches and increases in length until it is finally broken. The specimens used were standard ASTM D 638 type IV rod-shaped (bone) with a length of 150 mm and a thickness of 2 mm.

2.4.2. Scanning Electron Microscopy (SEM)
Scanning electron microscope was used to evaluate the dispersion of PCL/Bentonite/Chitosan nanocomposites in the fractured surfaces of the composites. Before SEM observation, the composites were fractured in liquid nitrogen and then the fractured surfaces were sputtered with platinum.

2.4.3. Thermal Stabilization Test
In principle, this method measures the reduction in material mass when heated from room temperature to high temperatures which are usually up to 1000 ° C. The Thermogravimetric Analyzer (TGA) apparatus is equipped with a micro scale in it so that automatically the weight reduction of samples at any time during heating can be recorded and presented in the graphical display.
3. Results and Discussion

3.1. Purification results and interlayer opening of bentonite

In the initial treatment process before mixing, 230 mesh mashed bentonite filler was purified using Sodium Hexamethaphosphate (NaPO\textsubscript{3})\textsubscript{6} which acts as a dispersant to clean bentonite from impurities so that pure montmorillonite can be produced. The particle size affects the contact with the dispersant, the smaller the particle size is the toned particle, the more effective the dispersant works. When dispersing for 6 hours and the quantity of dispersant as much as 1% by weight of processed bentonite is the best value for bentonite purification based on research conducted by Gong, [10].

3.2. Mechanical properties

The mechanical properties such as tensile strength PCL blends with different filler contents were evaluated as compared with neat PCL as a control. 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 1. In this figure, it showed that the processed PCL has higher tensile strength than neat PCL. It also is observed that the tensile strength increased, with increasing proportion of filler.

![Figure 1. Graph of Tensile Test Results](image)

Based on the test results, it can be seen that the addition of polymer filler material shows the results of an increase in composite properties. The new material produced shows a better quality of strength properties compared to pure PCL polymer without mixing. Samples of PCL-Bentonite nanocomposite in each variation of type and number of bentonite fillers used showed differences. The tensile strength value is directly proportional to the amount of filler used. The more amount of bentonite mixed into the PCL matrix, the greater the tensile test value produced. That is, the amount of bentonite content causes polymers to have higher stretching resistance to the top. Based on the data in Figure 1, the results of nanocomposite tensile test with bentonite filler from the Sawang region of North Aceh showed higher tensile strength and stress at break values so as to improve the mechanical properties of PCL material.

3.3. Effects of a – bentonite on Morphology of PCL composite

Figure 2 gives SEM micrographs of fractured surfaces for PCL blends with various compositions. Figure 2 shows the SEM micrographs of the neat PCL blend nanocomposites with 5wt% bentonite and
chitosan. In order to achieve good material properties, the reinforcement or filler should be well dispersed and should have good interaction with the matrix. In this system, no chemical interaction was expected, so only physical interactions were studied. The small particulate objects the circle in are bentonite and chitosan nanoparticles in the blend; they seem to be well dispersed and embedded in the polymer matrices.

![SEM micrographs of neat PCL at (a) 2000x and (b) 200x of PCL blend with 5wt% Bentonite/Chitosan](image)

(a) (b)

**Figure 2 SEM micrographs of neat PCL at (a) 2000x and (b) 200x of PCL blend with 5wt% Bentonite/Chitosan**

### 3.4. Thermal Stability Test of PCL /Bentonite/Chitosan Nanocomposite

Thermal degradation test using TGA (Thermal Gravimetric Analysis) tool is aimed to know qualitatively the thermal stability of PCL/ Bentonite/Chitosan Nanocomposite. Tests are based on changes in sample weight due to heating from room temperature to high temperatures typically hundreds of degrees Celsius so that samples of ± 10 mg in the alumina cup will experience a reduction in mass (degraded) as it burns at a certain temperature. The process of losing mass occurs due to the decomposition process that is the breaking of chemical bonds. Here is a table of TGA test results on nanocomposite 3 samples as well as pure PCL without mixing as a comparison.

![TGA curve showing thermal test results of PCL/Bentonite/Chitosan](image)

**Figure 3. PCL/Bentonite/Chitosan Thermal Test Results**

Bio composite with the maximum degradation temperature was shown by PCL with the addition of 5% bentonite-chitosan which was degraded at a temperature of 364.39°C. However, the surface of PCL composite 1% bentonite-chitosan is less good than the surface of PCL composite 3% bentonite-chitosan. This indicates that the composition of bentonite-chitosan filler which can be used as the best filler for increasing thermal stability by perfect mixing of PCL polymers is 5wt bentonite-chitosan. This also proves that bentonite can be combined with chitosan as the latest double filler innovation in the world of bio composites to improve the thermal properties of PCL materials.
4. Conclusion
Characteristics of PCL / BENT + CHIT tensile strength test 5% composite material produced optimum tensile strength compared to pure PCL and PCL / BENT + CHIT 1% and 3%. The mechanical properties of polymer materials increase with increasing filler in the PCL matrix. The composite morphology structure in the 5% mixture shows a better bonding interface between matrices (PCL) with fillers (Bentonite and Chitosan).

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