PREPARATION OF CHITOSAN PCL/PLA NANOCOMPOSITE BLENDED WITH BENTONITE FROM ACEH, INDONESIA

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ABSTRACT

Polycaprolactone (PCL) and PolyLactic Acid (PLA) are categorized as an extensive polymer for its mechanical properties, biodegradability and a large range of miscibility. In this research, Polycaprolactone (PCL) and Poly Acid Lactic were determined as a matrix for its biodegradability properties. In particular, an observation regarding bentonite addition effects is reported. Moreover, bentonite was found to significantly influence the nanocomposite mass-loss properties, as a result of physical interactions among polymer chains and clays. On the other hand, a melt drawing process of composite could lead to a limited effect on the degradation properties of samples. Based on tensile strength analysis results, it was found that bentonite could increase the flexibility of PCL/PLA blends. Moreover, Thermal Gravimetric Analysis (TGA) result indicated that bentonite could enhance thermal stability of blended samples. In conclusion, the addition of bentonite as filler has great contribution to enhance the mechanical properties.

Keywords: Polycaprolactone, Poly Lactic Acid, Bentonite, Nanocomposite, Biodegradability.

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INTRODUCTION

Plastic-based polymers are categorized as the most assertive polymers which are widely prevailed for daily human activities. Particularly, synthetic plastic was produced in a very huge amount globally for every year in diverse industrial activities.¹ Nanocomposites that adopt layered silicates are able to yield intercalation through dispersion process of silicate as filler into polymer matrices. Specifically, bio-nano composite used is polymers that isolated from biodegradable and renewable natural resources. To date, an escalation interest in these fields is resulted due to the willingness to evade the utilization of fossil-based materials and replace them with environmentally friendly materials that can be found naturally.

In addition, Plastic-based polymers are the most commercial material as they are, lightweight, strong, non-corrosive and multifunctional. Therefore, it is easier to apply them for various equipment. For instance, plastic polymers are frequently utilized as various products packaging material, insulators for electronic equipment, kitchen utensils. In addition, these polymers are also developed for medical use in tissue engineering. On the other hand, polymers with considerable biodegradation ability, such as poly(*ε*-caprolactone) (PCL) and polylactide (PLA), are resulting vast interest, since those are categorized as the most innovative and affordable materials which currently are being developed and observed for a wide spectrum of applications.²

Currently, mixing two or more amount of polymer components is determined as a new method for fabricating equitable and optimum natures for a specific application. Most of polymers, however, are considered to be thermodynamically immiscible. Moreover, the mixture produced is having immiscible phase domains with distinct interfaces. It is resulted in their high molecular masses and unfavorable

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interactions. Finally, the resulted blends properties are significantly affected by the interface and the minor phase size scales. These factors are strongly regulated by morphological development and processing conditions.

PCL ($C_6H_{10}O_2$)_n has widely known as an economic biodegradable polymer which is having a low melting point of 60 °C. Moreover, this polymer is also found to be partly crystalline polyester and hydrophobic with considerable mechanical properties.^{3,4} Considering the enthusiasm in seeking better qualified polymer-based materials, plenty amount of researches in various countries have performed in order to combine synthetic polymers with a polymer-based composite forming materials.⁵ In particular, composite material is produced by mixing two or more different phases, so that it will possess superior specific features and optimum properties which cannot be provided by only a single compound. In terms of process, composites formation could be generally conducted by blending polymers with analogous elements or certain fillers, for instance; chitosan, bentonite and fibers which have indicated to be able to enhance the properties of single polymer. Furthermore, it is found that varieties of aliphatic polyesters are favorable for the fabrication of polymer nanocomposites with strong biodegradation ability. One of these is Polycaprolactone. It is a polymer that is chemically produced by employing caprolactone units. Although PCL is hardly found in nature, it is an exceptional biodegradable material for packaging.⁶

On the other hand, PCL possesses several drawbacks, such as highly hydrophobic, slow-rate of biodegradation process, and quite sensitive to activity conducted by microbes. Nonetheless, the PCL ability to blend with filler, such as bentonite, and also via modification process is considered to beat those drawbacks.⁷ Furthermore, the performance of PCL can be enhanced through the administration of inorganic filler, such as clay in nanometre-scale size. Also, by administrating a little amount of nano clay, its thermal, barrier, mechanical and biodegradable properties will greatly improve. Moreover, it could also enhance water adsorption, flammability properties, polymer creep resistance.⁸

PLA is categorized as an aliphatic thermoplastic polyester with linear structure which is a derivation of lactic acid, as a result of fermentation from rice, corn and sugar feedstocks, making it a potential renewable and biodegradable material. In detail, it also could be prepared by chemical conversion process of carbohydrate sources into dextrose. Then, dextrose is fermented, becoming lactic acid and followed by poly-condensation process of lactide (monomers of lactic acid). However, the top prevailing method to fabricate PLA is through the Ring-Opening Polymerization (ROP) of lactide.⁹ In terms of utilization, PLA has majorly studied in biomedical sector, especially for tissue engineering.

Recently, PLA fabrication techniques combined with polymerization routes are now leading to affordable cost for the resulting PLA with high molecular weight. Consequently, PLA is a distinct material for consumer goods and food packaging utilization. With considerable optical and mechanical properties compared to regular plastics used, PLA could potentially be an alternative towards Polystyrene (PS), Polyethylene terephthalate (PET), Low-Density Polyethylene (LDPE) or High-Density Polyethylene (HDPE), for food packaging utilization. Although several factors could limit its performance, various modifications towards polymers have been performed to accustom PLA properties to meet the packaging application requirements.¹⁰

In order to enhance the mechanical and physical properties of poly-caprolactones, it is frequently combined with fillers, for instance, clay. One type of this is montmorillonite. It can result in the purification process of bentonite. Moreover, in order to employ wide range uses, especially for medical use, clay could be modified with antibacterial compounds, such as chitosan. Particularly, chitosan is able to overcome fungi and bacteria issues in broad range, by not causing drawbacks on mammalian cells. Therefore, chitosan is a very critical compound to use in medical field.¹¹ To sum up, PCL and PLA blending could contribute to the reduction of thermal stabilities of both polymers, therefore, by employing bentonite and chitosan nanoparticles, it is expected to elevate the polymer's thermal stabilities, as well as their antimicrobial properties.

EXPERIMENTAL

Materials

Polycaprolactone, Poly Acid Lactic, Cetyl Trimethyl Ammonium Bromtontide (CTAB), Phosphate-buffer saline (PBS), glutaraldehyde solution Tripoliposfat (TPP), AgNO₃, zinc oxide catalyst, sodium cacodylate trihydrate and acetic acid were purchased from Sigma Aldrich. Bentonite was obtained from the local

area, Aceh province, Indonesia with calcium ion as the confirmed interlayer cation. Other materials used were chitosan, Gram-positive *Staphylococcus aureus*), *Lactobacillus* bacteria, Gram-negative *Pseudomonas aeruginosa*, as well as Nutrient Broth.

Bentonite Nanoparticles Production

An amount of 18.2 grams of CTAB was used to produce 0.05 moles of CTAB solution in 250 mL of distilled water. This solution was then treated with the heating process for 1 hour and at a temperature of 80 °C. Then, as much as 20 grams of bentonite and was inserted into 500 mL of aquadest. This solution was stirred separately with the previous CTAB solution. After that, the bentonite dispersion was inserted to CTAB solution and stirred for 1 hour. After that, the filtrate was titrated with silver nitrate in order to wash chloride or bromide away. Bentonite was dried in an oven at 60 °C and filtered using a 100 µm sieve tray. This process was carried out in order to yield bentonite in nanometer scale. Furthermore, the crystal structure of bentonite was investigated using X-ray Diffraction (XRD) analysis.

Chitosan Nanoparticles Production

Chitosan was dispersed in distilled water and added with tripolyphosphate solutions. Then, the mixture was stirred with 1200 rpm rotation speed to yield a chitosan emulsion. After that, chitosan emulsion was set to be acidic by adding acetic acid, and finally yielding a chitosan suspension. Lastly, crystal structure of chitosan was analyzed through XRD analysis.

Bentonite-Chitosan PCL/PLA Nanocomposite Preparation

Purified bentonite from previous treatment was dispersed into PCL/PLA via simple melt blending equipment. In terms of its treatment, bentonites were blended to PCL/PLA due to several ranges of composition in its weight percentage (wt%). Finally, PCL /PLA nanocomposite blended with bentonite was hot-pressed using HSINCHU equipment and molded under certain conditions.

Characterization

The resulting nanocomposite was then investigated with several analyses in order to obtain its properties. Firstly, tensile strength analysis was performed to analyze its mechanical properties. This test was conducted by using Universal Tensile Machine (UTM) device. Secondly, in order to investigate the morphology of resulted nanocomposite, Scanning Electron Microscopy (SEM) analysis was performed. Lastly, thermal stabilization test was carried out through TGA analysis.

RESULTS AND DISCUSSION

Bentonite Purification and Interlayer Opening

Initially, mashed bentonite was decontaminated by using Sodium Hexametaphosphate (NaPO_3)₆, acting as a dispersant to wash bentonite from impurity substances. Therefore, pure montmorillonite was obtained. As it is known that particle size could affect the contact site with the dispersant, so it can be concluded an effective dispersant works could achieve with a smaller particle size. In this research, as previously stated that bentonite used has various range of weight percentage to mix, it was found that after dispersing for 6 hours, bentonite with 1% of weight in mixture was considered as the best composition for bentonite purification.¹²

Mechanical Properties Analysis

The mechanical properties, particularly tensile strength of PCL/PLA mixed with various amount of filler composition were investigated and compared to neat PCL/PLA as a control. The tensile strength of PCL/PLA/bentonite/chitosan nanocomposites which were blended with various composition and molded was investigated through axial force and carried out by using UTM tool. Furthermore, the tensile strength result of samples are displayed in Fig.-1. Based on Fig.-1, it can be seen that treated PCL possesses bigger value of tensile strength compared to pure PCL/PLA. Moreover, it can be seen that the tensile strength was enhanced as well as the increasing proportion of filler used.

In addition, test result indicates that the involvement of polymer filler material contribute to an improvement in composite mechanical properties. Based on the research result, the material produced gives better tensile strength result, compared to neat PCL/PLA polymer which was not blended with bentonite and chitosan. Furthermore, the tensile strength value was found to be proportional to the composition amount of filler used.

Fig.-1: The Graph of Tensile Strength Test Result

In conclusion, the higher composition of bentonite blended within the PCL/PLA matrix, the greater the tensile strength resulted. Therefore, by adding bentonite as filler, it can considerably enhance the PCL/PLA material mechanical properties.

Morphological Analysis of PCL/PLA-Bentonite-Chitosan Nanocomposite

SEM micrograph of surfaces of PCL/PLA blend with different compositions of bentonite is displayed in figure 2. Moreover, the SEM micrograph of the pure PCL/PLA blend nanocomposites with 5 wt% bentonite and chitosan was also displayed in Fig.-2. In order to obtain optimum properties, the reinforcement or filler used should be well dispersed and possess excellent interaction with the matrix. In this research, as there is no chemical interaction was expected, it is only physical interactions which were investigated. Based on Fig.-2, the small particulate circle objects observed are bentonite and chitosan nanoparticles existed in the blend. Also, it can be seen that both bentonite and chitosan are regularly dispersed within the polymer matrices.

Fig.-2: The Morphological Analysis Result of (A) Neat PCL/PLA With 2000x Magnification and (B) PCL/PLA Blend with 5wt% of Bentonite/Chitosan with the Magnification of 1500 X

Thermal Gravimetric Analysis of PCL/PLA /Bentonite/Chitosan Nanocomposite

The thermal stability test was performed via TGA analysis. This test was aimed to qualitatively investigate the thermal stability of PCL/PLA/Bentonite/Chitosan nanocomposite. Particularly, during the

thermal stability analysis, the process of losing mass will occur. This process is occurred due to the decomposition process, as a result of chemical bond breakage. The TGA analysis results on nanocomposite of 3 samples with various amounts of bentonite, as well as raw PCL/PLA as a comparison are displayed in Fig.-3 below.

Fig.-3: The thermal Gravimetric Analysis Result of PCL/PLA/Bentonite/Chitosan

Based on Fig.-3, it can be seen that nanocomposite with optimum degradation temperature is PCL/PLA with 5% bentonite-chitosan addition, at 364.39 °C. Moreover, an interesting trend could be observed further. PCL/PLA composite with the addition of 1% bentonite-chitosan indicates lower thermal stability compared to PCL/PLA added with 3% bentonite-chitosan. Based on this result, it can be seen that the addition of bentonite-chitosan filler contribute to thermal stability of PCL/PLA composite. Moreover, the thermal stability is increasing as the amount of bentonite-chitosan filler increased.

X-Ray Diffraction Analysis

The crystalline structure of PCL / PLA / Bentonite / Chitosan nanocomposite was tested using XRD with an imbalance (2θ) within a distance of 10-100° and speed of 0.25°.sec⁻¹. Tests were carried out at the Chemical Engineering Department of ITB, Indonesia. Based on the results, the crystal structure for PCL/PLA purely from the crystal structure of the XRD test results in a level of crystallinity as high as 42.2% and an amorphous level of 58.2%. The crystal structure of the XRD test results for PCL / PLA / Bentonite / 5% chitosan obtained a crystallinity level of 43% and an amorphous level of 57%.

Fig.-4: X-Ray Diffraction Analysis Result of Pure PCL/PLA

XRD analysis was carried out on a mixture of PCL / PLA / bentonite / chitosan to determine the interaction between the crystalline phase of the matrix and filler. Analyzing Figures 4 and 5, it confirms

the lack of interaction between phases. Pure PCL / PLA main crystalline peaks at $2\theta = 16.33$ and 18.64° were present and did not change in all mixtures, without new peaks observed as PCL / PLA under amorphous conditions. In addition to bentonite and chitosan, two new peaks were identified at 12.59 and 15.06° and this was associated with the structure of the bentonite and chitosan fillers. This reveals that mixing bentonite and chitosan fillers into the PCL / PLA matrix had an effect on PCL / PLA / bentonite / nanocomposite chitosan crystallinity.

The intensity of PCL / PLA / bentonite / chitosan (5%) has a lower value than the intensity of pure PCL / PLA. In the spectrum of measurement results, there are several dominant peaks where the intensity of PCL / PLA / bentonite / chitosan is 1109 and 1564 respectively while pure PCL / PLA (F21) intensity values are 2089 and 2147 respectively. The diffractogram of XRD PCL / PLA / bentonite / chitosan 5 results % shows a widening peak existence when compared to a pure PCL / PLA diffractogram pattern. This is due to the addition of amorphous bentonite and chitosan so that it can reduce some peaks in the diffractogram. It will reduce the degree of nanocomposite crystallinity produced to be more amorphous and easily degraded. This is in accordance with the research conducted by D.L. Zhao in 2010.¹³

Fig.-5: X-Ray Diffraction Analysis Result of PCL/PLA/Bentonite/Chitosan 5

CONCLUSION

The addition of bentonite from Aceh, Indonesia as a filler contributed to the improvement of mechanical properties of nanocomposite produced. The optimum tensile strength was achieved with 5% wt of bentonite used. Furthermore, it is also applied to the thermal stability test which indicates a trend describing that the larger amount of bentonite-chitosan composition used, the higher the thermal stability observed. Lastly, a 5% nanocomposite mixture displays an exceptional bonding interface of matrices (PCL/PLA) within fillers (Bentonite and Chitosan).

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