Physico-mechanical properties of silanized-montmorillonite reinforced chitosan-co-poly(maleic anhydride) composites

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Abstract. To solve the problems of dependence on petroleum as starting material in the manufacturing of plastics in Indonesia, green plastic from biopolymer like chitosan to be one of promising options and alternative to replace the conventional plastics. However, to overcome the mechanical and physical properties of chitosan, the addition of reinforcement agent was introduced. In this study, silanized-montmorillonite (sMMt) has been prepared as a reinforcement agent in the chitosan-co-poly(maleic anhydride) (referred as Cs-MAH) matrix. Silanizing of montmorillonite is one of strategy to improve the interaction between montmorillonite and chitosan, consequently, the mechanical properties, tensile strength of composites contained 6 phr of sMMt improved 56.5% to chitosan. Moreover, the presence both MAH and sMMt on the composites also reduced swelling degree and swelling area by 20.6% and 26.7%.

1. Introduction

World plastics production growth is increased every year [1]. Plastics to be one of the important materials in daily life. Many application such as automotive, packaging, aerospace, household tools, electrical devices and many other were replaced by plastics [2-4]. However, the availability of petroleum as a source of raw materials in plastic manufacturing will be depleting [5]. Moreover, almost all petroleum based plastics was difficult to degrade thus, the waste plastic to be environmental pollution. To overcome this problem, some conventional strategy was introduced, such as recycling, energy recovery and landfill disposal [6]. However, to provide an environmental friendly plastics for different types of applications in a sustainable manner, an alternative is needed. Therefore, in this study will be introduced bio-based plastic and it’s modification as a candidate to replace conventional petroleum-based plastics.

Chitosan is a polysaccharide derived from deacetylated of chitin or known as poly(N-acetyl-D-glucopyranose). It composed mainly of β-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units. Chitosan and chitin, next to cellulose, are the second most abundant biopolymers [7]. Chitosan has
been extensively investigated for recent decades for food packaging, molecular separation, artificial skin, bone substitutes, water engineering and other, due to its good biocompatibility, biodegradability, multiple functional groups as well as its aqueous solubility [8]. However, its properties, such as water sensitivity, mechanical strength, thermal stability, rigidity and gas barrier properties are frequently not good enough for wide ranges of applications [9]. Recently, there has been a growing study in chemical modification of chitosan to improve its properties and widen its applications via graft copolymerization with maleic anhydride (MAH) which it is widely used as a grafting agent in various material [10, 11]. Incorporation of grafting material MAH in chitosan matrix increased the mechanical properties of the polymer, since the anhydride group could react with hydroxyls of chitosan [12, 13]. Various layered silicates from clay like montmorillonite (MMT) as a reinforcing material for polymers has received considerable research attention because of their potentially high aspect ratio and its unique characteristics [14]. It is clay type 2:1, which consists of the stacking a hydrated alumina-silicate layered clay made up of two silica tetrahedral sheets fused to an edge-shared octahedral sheet of aluminum hydroxide [15]. These superior properties could improve tensile strength and modulus as well as enhance thermal stability [9,16], reduce gas permeability and boost the flammability of matrix polymer [14].

Under natural condition, among layered of the MMT is likely to stack via the Van der Waals forces. Besides, clay are hydrophilic leading to incompatible with most hydrophobic polymeric materials. Thus, chemical modification on the clay or matrix polymer or both have been reached to enhance the interaction between the clay and the polymer [14]. The surface of the MMT is commonly modified via cation exchange technique or adding a compatibilizer materials to compatibilize the layered silicate with most hydrophobic polymer matrix. Recently, modification of the hydrophilic clay surface have been extended using silane coupling agent [16]. Wang et al. (2010) [17] developed GPTMS-modified zeolite for reinforcement of chitosan membranes, their study indicated that by using (3-glycidoxypropyl) trimethoxysilane (GPTMS) was able to achieve denser and stronger surface morphology. GPTMS is a crosslinking agent that has two functional groups, one is an organic functional group bonding with organic materials, and the other one is an epoxy group interacting with inorganic materials [18,19]. From some of these facts, so in this study examined the effect of modification of clay with a silane compound as a filler in the matrix of chitosan-co-poly (Maleic anhydrides) on mechanical and thermal properties. Moreover, the morphology, swelling degree and swelling area were evaluated.
2. Experimental

2.1. Materials
All material in this research was used without further purification. Chitosan (Cs) was purchased from PT. Biotech Surindo, Indonesia. Montmorillonite (MMt) and glycidiloxypropyl trimethoxysilane (GPTMS) were obtained from Sigma Aldrich, Singapore. Toluene, acetic acid (Act), maleic anhydride (MAH), benzoyl peroxide (BPO) and sodium hydroxide (NaOH) were purchased from Merck.

2.2. Preparation and Characterization of Silanized-Montmorillonite (sMMt)
About 10 g of montmorillonite was thermally treated by calcination method in the temperature of 400 °C for 12 h, namely treated-montmorillonite (t-MMt). The t-MMt (5 g) and GPTMS (16 mL) were sonically treated in 100 mL of toluene for 30 min. Then, the mixture was reflux and kept at boiling state for 24 h. The product was filtered and washed several times using dry toluene. The final product, referred as silanized-montmorillonite (sMMt) was dried overnight at room temperature and continuously dried again in oven at 80 °C for 24 h.

The characterization of the sMMt was then characterized using several instruments. Functional group analysis was conducted using FTIR (Fourier Transform Infra-Red) model Prestige21-Shimadzhu. The samples was prepared in fine powder by introducing KBr to form a pellet disc. The applied number of scan was 40 times with resolution 4 cm⁻¹. Crystallinity behaviour of samples was measured using XRD (X-Ray Diffraction) model Shimadzhu Lab-X 6000 by applied Cu Kα as light sources. The samples was prepared in fine powder before analysis. Morphology of sMMt was visualized using SEM (Scanning electron microscopy)-EDAX model Phenom FEI.

2.3. Preparation of the Composites
The chitosan/clay composites were prepared via solution casting method. About 2 g of chitosan was dissolved in acetic acid solution (80 mL, 1.5%) at room temperature. Afterward, 10% wt of MAH was added into chitosan solution and stirred slowly. After 1 h reaction, amount of sMMt (0, 6, 9 and 12 phr) was added into the mixture solution. Mixing process was performed for 1 h at 70 °C. The mixture solution was poured into glass template and dried for 12 h at 50 °C. The film plastic was then washed using 0.05 M sodium hydroxide solution and washed again with distilled water for several times. Finally, the bioplastic sMMt reinforced chitosan-co-poly(maleic anhydride), referred as Cs-MAH/sMMt was dried at room temperature for two days.
2.4. Mechanical Testing
Mechanical testing was conducted using Mechanical Testing Machine Ray-Run M500-50CT. The sample was prepared according to ASTM D638-02a method. The cross speed test was adjusted to 5 mm/min.

2.5. Swelling Testing
Swelling testing was used to determine the water adsorbed ability of composites which correlated with degree of humidity resistance. The composites was prepared into small pieces with 1 x 1 cm² area, approximately. The initial weight of samples is weighted. The samples were soaked into water up to 24 h and afterward, the final weight of samples were recorded.

3. Results and Discussion
3.1. Characterization of sMMt
In order to prove the surface modification of MMt with organo-silane compound, the characterization like FTIR and XRD has been conducted. Fourier transform infra-red is one of the most worthwhile instruments, which is used for chemically investigation. Figure 1 shows the FTIR spectrum of MMt and sMMt. Based on Figure 1, generally MMt has characteristic absorbance band at around 1060 cm⁻¹ and 802 cm⁻¹ corresponding to Si-O stretching vibration (indicated in Figure 1) and –OH deformation vibration from Al-OH group, respectively. After modification with GPTMS compound, the spectrum of sMMt is slightly different from their raw material. It was clearly see that at sMMt infra-red spectrum was found the –CH stretching vibration band at around 2937 cm⁻¹ and 2877 cm⁻¹. The appearance of the bands are consequently of surface modification by organo-silane group which contained hydrocarbon backbone. Moreover, it is also observed a characteristic peak of –C-O-C-stretching vibration around 1211 cm⁻¹ which slightly shift from the GPTMS spectrum. The presence of absorbance band at 905 cm⁻¹ which is characteristic vibration of oxirene ring, is confirming allegation that MMt is successfully modified with GPTMS compound.

Chemically analysis, to prove the surface modification was conducted using XRD technique. Figure 2 showed that the XRD pattern of MMt and sMMt. The MMt have specific 20 peak at 8.66° with d₀₀₁ basal spacing 10.2 Å. After modification, the 20 is 8.74 (d₀₀₁ = 10.1 Å). The decreasing of basal spacing of MMt after modification is due to the presence of siloxane network in MMt layer’s surface, thus shorten the layer space. The surface modification of MMt by GPTMS compound is not change the MMt crystal structure. However, the crystallinity of MMt decreased after modification due to the formation of amorphous siloxane network in the MMt surface.
Figure 1. FTIR spectrum of MMt, GPTMS and sMMt.

Figure 2. XRD pattern of MMt and sMMt.

The SEM image of both MMt and sMMt are presented in Figure 3 and 4, respectively. The MMt physical structure based on the SEM image is like bulk structure with fine surface. However, after surface modification, the MMt surface is more rough and it is connected with solid line as seen in Figure 4. The solid line which is pointed with yellow arrow, is probably the formation of siloxane network. Moreover, the presence of solid line is made the physical structure of sMMt to be porous in their surface.
Figure 3. SEM image of MMt.

Figure 4. SEM image of sMMt.

Figure 5 showed the SEM-EDAX data of sMMt. This analysis is conducted to prove the surface modification of MMt by silane compound. Based on the data, it can be seen that the main elements of sMMt on the surface are C, O, Al, Si atoms, where the O, Al and Si atomic percentages are 36.84, 2.46 and 16.95%, respectively. Additionally, the C atomic percentage is 43.74%. The presence of the Carbon atom in the sMMt surface indicated the modification is successfully achieved due to the C atom is generated from silane compound. Moreover, the ratio of Al:Si is very high, which is 1:6.9. The improvement of Si atom is due to the effect of GPTMS addition, where each molecule of GPTMS contained 1 Si atom.

3.2. Mechanical Properties

Mechanical testing was conducted to determine the mechanical properties of composites. This testing was also used to determine the optimum sMMt addition on composites preparation. The mechanical properties are including tensile strength, elongation percentages and young’s modulus. Tensile strength
and elongation percentages of Cs-MAH/sMMt composites are presented in Figure 6. The tensile strength of chitosan-co-poly(maleic anhydrides) is 25 MPa. The addition of 3 phr of sMMt was able to improved the tensile strength of composites by 20% compared to chitosan-co-poly(maleic anhydrides). The increasing of the composites tensile strength was achieved until 6 phr addition of sMMt, which improved by 56.5% compared to chitosan. Afterward, the tensile strength of composites are decreased by 9.7 and 14.7% of Cs-MAH/sMMt composites contained 9 and 12 phr of sMMt respectively, compared to the composites contained 6 phr of sMMt. Based on this data, it can be concluded that the best condition regarding on tensile strength value is given at 6 phr addition of sMMt in chitosan matrix. The improvement of composites tensile strength by addition of clay is due to the clay minerals which contained alumina and silica layers can be distributed by intercalated or exfoliated [20]. Homogenous distribution of clay particles generated high mechanical properties of composites [21]. In this study, the presence of silane compound in MMT surface is able to act as compatibilizer agent [22]. GPTMS compounds which contained silane group and oxirene group are chemically interaction with both MMT surface to form siloxane network and amino group of chitosan [23]. Moreover, the MMT was known as reinforcement agent, thus it improved the mechanical strength and stiffness of materials [24]. Consequently, the elasticity of composites decreased by addition of reinforcement [25]. Elongation percentages of chitosan is 13.7% and it decreased by addition of sMMt. At optimum composition (6 phr of sMMt), the elongation percentages is 5.7% or decreased to 57.8% compared to chitosan. The more addition of sMMt into chitosan matrix was decreased the elasticity of composites.

![Figure 6](image_url)

**Figure 6.** Elongation and tensile strength of Cs-MAH/sMMt.

Figure 7. is the young’s modulus graph of chitosan/sMMt composites. This data explained the degree of composites brittleness, where the higher of young’s modulus value showed the composites tend to be brittle. The chitosan-co-poly(maleic anhydrides) has 182.4 MPa of young’s modulus value.
However, the addition of high content of sMMt, which is 12 phr increased the young’s modulus by 314%. At optimum condition, the young’s modulus of composites improved to 271.9%.

![Young’s modulus of Cs-MAH/sMMt](image)

**Figure 7.** Young’s modulus of Cs-MAH/sMMt.

3.3. **Morphological Study**

Morphology analysis using scanning electron microscopy was used to observe the fracture surface of sample after applied tensile testing. Figure 8 and 9 are the fracture surface morphology of optimum Cs-MAH/sMMt composites at different magnification. As seen in Figure 9, the fracture surface of composites after tensile testing showed strong interfacial bonding between chitosan and sMMt. It was indicated by the presence of cracking in the sample as result of high force distribution between matrix and reinforcing material [26]. However, at another spot is also found a flat fracture surface. This is due to the properties of clay particles tend to be brittle or the distribution of clay particles in chitosan matrix are unevenly well distributed.

![SEM image of Cs-MAH/sMMt cross section](image)

**Figure 8.** SEM image of Cs-MAH/sMMt cross section

![SEM image of Cs-MAH/sMMt cross section](image)

**Figure 9.** SEM image of Cs-MAH/sMMt cross section

3.4. **Swelling Degree and Area of the Composites**

Swelling properties is one of important testing to analyzed the humidity resistance of composites by soaking the sample in water. The plastic which is applied as packaging plastic should have high
humidity resistance for long period application. To improved the humidity resistance of materials, one of strategy can be conducted by modification the materials surface using hydrophobic materials, such as silane compound [27]. Silane compound was able to form siloxane network, which have ability to limiting the contact of water and materials surface. It can be seen at Figure 10 that the addition of sMMt until 3 phr, decreased both swelling degree and area of composites by 20.6 and 26.7%, respectively. However, the higher of sMMt content on chitosan is turn both swelling degree and area to high value. It is due to the nature of clay mineral which swelled in water [28].

![Swelling degree and area of Cs-MAH/sMMt composites.](image)

**Figure 10. Swelling degree and area of Cs-MAH/sMMt composites.**

4. Conclusion
Surface modification of montmorillonite clay using silane compound has been successfully achieved which proved by functional group and surface element analysis by FTIR and SEM EDAX, respectively. The presence of sMMt in chitosan was able to improve mechanical properties up to 56.5% at 6 phr sMMt addition. However, the elongation of the composites decreased by the addition of sMMt. By the mechanical testing, the composites contained 6 phr of sMMt to be the optimum condition in composites preparation. Based on swelling testing, the humidity resistance of composites contained 3 and 6 phr of sMMt are higher than chitosan. Thus, regarding to mechanical and physical properties, the chitosan/sMMt optimum composites can be used as green bio-based plastic to replaced the conventional plastic.

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