Synthesis and Properties of Biobased Polyurethane/Montmorillonite Nanocomposites

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Abstract—Polyurethanes (PURs) are very versatile polymeric materials with a wide range of physical and chemical properties. PURs have desirable properties such as high abrasion resistance, tear strength, shock absorption, flexibility and elasticity. Although they have relatively poor thermal stability, this can be improved by using treated clay. Polyurethane/clay nanocomposites have been synthesized from renewable sources. A polyol for the production of polyurethane by reaction with an isocyanate was obtained by the synthesis of palm oil-based oleic acid with glycerol. Dodecylbenzenesulfonic acid (DBSA) was used as catalyst and emulsifier. The unmodified clay (kunipia-F) was treated with cetyltrimethyl ammonium bromide (CTAB-mont) and octadodecylamine (ODA-mont). The δ-spacing in CTAB-mont and ODA-mont were 1.571 nm and 1.798 nm respectively and larger than that of the pure-mont (1.142 nm). The organoclay was completely intercalated in the polyurethane, as confirmed by a wide angle x-ray diffraction (WAXD) pattern.

The results showed that adding clay demonstrated better thermal stability in comparison with the virgin polyurethane. Onset degradation of pure PU is at 200°C, and is lower than that of the CTAB-mont PU and ODA-mont PU which takes place at about 318°C and 330°C, respectively. The mechanical properties (including the dynamic mechanical properties) of pure polyurethane (PU) and polyurethane/clay nanocomposites, were measured. The modified organoclay had a remarkably beneficial effect on the strength and elongation at break of the nanocomposites, which both increased with increasing clay content with the increase of the tensile strength of more than 214% and 267% by the addition of only 5 wt% of the montmorillonite CTAB-mont PU and ODA-mont PU, respectively.

Keywords—Polyurethane, Clay nanocomposites, Biobase

I. INTRODUCTION

Many years ago, price of mineral oil are as low as compared to the bio-based materials. That is why research on the use of renewable resources is not of the public interests. But in the event of oil crisis and unpredictable price, we must pay more attention on finding an alternative from fossil which is finite to renewable bio-based resources [1-5]. At the Division Polymer Department of Chemical Engineering, Politeknik Negeri Lhokseumawe, we have been intensely involved in the observation of the developed polyurethanes derived from palm oil based on polyol.

Beside the isocyanates, compounds with the several hydroxyl functions in the molecule are the important components for the formation of polyurethane elastomers (PU).

The polyols mostly used in the formation of segmented PU are based on hydroxyl terminated polyesters or polyethers, and palm oil and its derivatives [6].

Unlike conventional rubbers which are crosslinked by primary valence bonding vulcanization processes, PUREs are crosslinked by secondary valence bonding, such as van der Walls interaction, dipole interactions or hydrogen bonding [7]. Those cause PUREs known as one of the most versatile materials because in principle, no damage to the materials result from the break-down and restoration of crosslinking and show rubber elasticity at service temperatures also compare than that materials crosslinked by primary valence [8].

The major challenge in polymer science is to increase its uses and quality. Because new material’s of polymer come to the market with better product every day. In order to overcome this situation which enhancing particular characteristics such as modulus, strength, fire performance and heat resistance, research Polyurethane/ clay nanocomposites with polyol base palm oil is being prepared.

In this paper we are adopted the novelty investigation: using polyol based on palm oil instead of petroleum and addition of inorganic fillers with layered silicate (clay). Manufacturers fill polymers with particles in order to improve the stiffness and the toughness of the materials, to enhance their barrier properties, to enhance their resistance to fire and ignition or simply to reduce cost [9].

II. EXPERIMENTAL

2.1 Materials

Materials used in this study were: Kunipia F (supplied by Kunimine Ind. Co. - it is a Na+ type montmorillonite, with a cation exchange capacity of 119 meq/100 g), 4,4-diphenylmethane diisocyanate (MDI, Merck), polyol based on palm oil (patent application no. PI20043190, used materials i.e. : palm oil based oleic acid ; glycerol, system ; 4-dodecylbenzenesulfonic acid, fluka ; extruded 3A molecular sieve, Aldrich), 1,4-butanediol (1,4-BDO, Fluka), cetyltrimethyl ammonium bromide (CTAB, Fluka), octadecylamine (ODA, Merck) and dimethylformamide (DMF, 99%, Fisher) as a solvent. Other inorganic and organic materials that were used in this study were obtained from commercially available source, such as : Natrium Chlorid (NaCl, Merck), Ethyl Alcohol (C2H5OH, 95%, System) and Dioxane (Mallinckrodt).

2.2 Synthesis of polyol base on palm oil

The experiments were carried out in a 250 ml three-necked flask fitted with a mechanical stirrer and a cooling system. The
operation conditions were as follows: oleic acid, glycerol, docdeylbenzene sulfonic acid (DBSA), and an extruded 3A molecular sieve. After filtration to remove the molecular sieves, the reaction mixture was washed with a solution of NaCl to remove excess glycerol.

Polyl based on palm oil was prepared by the reaction of oleic acid and glycerol. Since the two reactants are not miscible, need to added additives to favor contact between them. Surfactant such as CTAB or DBSA will be producing a homogeneous reaction. In this case, DBSA choose as emulsifier in this system. Because DBSA can work in dual action, as emulsifier and as catalyst. In the presence of DBSA, all esters of glycerol are formed. Although the conversion of oleic acid was elevated, little glycerol monoooleate was formed [10].

2.3. Preparation of Thermoplastic Polyurethane

The polyurethane-terminated prepolymer was prepared by reacting MDI and polyl at a specified NCO/ OH equivalent ratio by using the following procedure. Polyl (12 grams) in DMF was placed in a 0.5L glass reaction kettle, which was equipped with a mechanical stirrer, thermometer, heating mantle and a gas inlet and outlet for continuous flow of nitrogen. When the temperature of the isocyanate reached 70°C, MDI (6 grams) was added in several portions to the reactor under constant mixing. The reaction temperature was maintained at 70°C to 80°C and periodic samples were withdrawn to determine the isocyanate content. After the theoretical NCO% value was reached (using FTIR graph), the reaction was stopped by cooling and the prepolymer stored in a sealed glass bottle under nitrogen. In the second step, the prepolymer was heated at 90-100°C and a specified amount of the prepolymer was weighed into a 250 ml plastic cup. The chain extender (1,4-BDO) (1.08 grams), which was preheated to the prepolymer was weighed into a 250 ml plastic cup. The PU films were formed by casting the solution in a mold and remove the solvent under pressure at 70°C.

2.4 Preparation of Organophilic Clays

An amount of 0.05 mol (18.2 grams) of cetyl trimethyl ammonium bromide (CTAB) and 250 mL of distilled water were placed in a 500 ml beaker. These solutions were heated at 80°C for 1 h. Twenty (20) grams of Kunipia-F and 500 ml of distilled water were dispersed in a 1000 ml beaker. The dispersion of Kunipia-F was added to the solution of ammonium salt of CTAB, and this mixture was stirred vigorously for 1 h [Yano et al., 1993]. For the preparation of octadecylamine (ODA-mont), a similar procedure as for the preparation of CTAB-mont was adopted.

2.5 Preparation of Polyurethane/Clay Nanocomposites

Polyurethane/clay nanocomposites were prepared by melt blending. In this study, the amounts of organoclay used in the PU/clay nanocomposites were 1, 3, 5 wt% of polyurethane, respectively. The total volume in each blending was 40 gr. Mixings were carried out using a laboratory internal mixer (Haake Polydrive) at temperature setting of 80°C and a rotor speed of 50 rpm. The compounds were then compressed using HSINCHU moulded into 1 mm thickness sheets under a pressure of 98 x 10^5 Pa at 100°C to produce sample sheets. Similar procedures were done for ODA-mont.

2.6 Characterization

The preparation of polyl from oleic acid and glycerol was monitored by Fourier Transform Infrared Spectra (FTIR) and to determined molecular weight of polyl for synthesis with isocyanated for producing polyurethane was obtained by using Gel Permeation Chromatography (GPC). Wide-angle x-ray diffraction (WAXD or XRD) was used to examine the extent of dispersion of clay in filled samples. The dynamic mechanical technique of applying a sinusoidal oscillating stress to a material and the analysis of the resultant strain is now widely practiced. The applications of dynamic mechanical analysis (DMTA) are a wide range of materials ranging from solid composites through to polymer melts. The tensile strength tests were carried out with Instron 4468 machine according to the specifications of ASTM D 638 type V, where samples were cut to 120 x 15 x 2 mm³ in size and used the 50 mm/min crosshead speed. The thermal stability properties were determined using thermogravimetric analysis. Thermogravimetric analysis (TGA) is defined as the study of the change in mass as a function of temperature, time, and/or atmosphere. Scanning Electron Microscopy (SEM) was performed using a FEI Quanta 400 scanning electron microscope operated at 20 to 30 kV and finally Transmission Electron Microscopy (TEM) micrograph of a thin layer of the nanocomposite sample was recorded using LEO 912AB energy filter transmission electron microscope with an acceleration voltage of 120 kV. The thin layer of sample was prepared using a Reichert Jung Ultracut E microtome equipped with cryosectioning unit. The samples were sliced into thin layers of about 90 nm by a diamond knife cooled at -120°C.

III. RESULT AND DISCUSSION

The synthesis of polyurethane based on palm oil polyl, preparation of untreated clay to be clay nanocomposites with difference surfactants i.e. cetyl trimethyl ammonium bromide (CTAB) and Octadecylamines (ODA), synthesis of polyurethane based on palm oil polyl as metric with clay nanocomposites as reinforcement, and determine the efficiency of thermal resistance of polyurethane/ clay nanocomposite will be discuss in this chapter.

3.1 Synthesis of polyurethane based on palm oil polyl

Manufacturing polyurethane elastomers (PU) needs at least two groups as reactants: compounds with isocyanate groups and compounds hydroxyl groups (polyls). In this study, we are using palm oil as raw materials for production polyl.

3.2 FTIR Spectroscopy Analysis

Oleic acid and glycerol was synthesized by direct esterification in the absence of solvent. Since the two reactants are not miscible, additives was employed to favor contact between them. The employed additives can produce a homogeneous reaction system also and dodecylbenzene
sulfonic acid (DBSA) selected as it has both emulsifying and catalytic activity [10].

The preparation of polyol from palm oil based oleic acid and glycerol was monitored by FTIR spectroscopy. Some notable features of the IR spectra include 3384.940 (\(\nu\)O-H), 2926.140 (\(\nu\)C-H saturation), 1741.362 (\(\nu\)C=O), 1462.932 (\(\nu\)CH=CH) and 1174.186 and 1039.892 cm\(^{-1}\) (\(\nu\)C-O-C).

The main regions interested in the study are –NH absorption peak at 3320 cm\(^{-1}\) was due to hydrogen bonded –NH groups of urethane linkages. The hydrogen bonding was constituted as proton donor and the oxygen in carbonyl of the hard segment and in ether linkages as soft segment. The formation of hydrogen bonding by –C=O group can be determined by examining the peak position at 1709 cm\(^{-1}\) for hydrogen bonded –C=O and at 1731 cm\(^{-1}\) for free –C=O similar results were reported by Chen (2000) [11].

3.3 Molecular Weight

The GPC data tabulated possesses the molecular weight averages was about \(M_n = 955\) and \(M_m = 679\). This gives dispersity value of 1.4. From the data also show the result of \(M_w\) was about 1256. The \(M_w\) value that is vital in the synthesis of PU, i.e., the isocyanation process between polyl, MDI and 1,4-BDO.

The molecular weight (\(M_w\)) of PU based on palm oil was about 3266. \(M_n\) of the products has become 1425 and \(M_z\) become 10090. The corresponding dispersity value is 2.29. That is, there is an overall increase in the molecular weight of the sample synthesized. The increase molecular weight value indicating that product is high polymers.

In the case of synthesis of polyurethane elastomers, the structure segmented polyurethane is important parameters for control of physical properties. GPC is most measurements to determinant the segmented of polyurethane by calculated of molecular weight of the hard segment concentration (HSC) and calculated soft segment concentration (SSC).

The flexible (soft) segments in polyurethane elastomers greatly influence the elastic nature of the material and significantly contribute to its low temperature properties and extensibility. Therefore the parameter of soft segment is highly important [Jia et al, 2007].

The hard segments in polyurethanes typically consist of an isocyanate and chain-extender glycol or amine components. Structure of the disiocyanate can have a critical influence on the properties of thermoplastic polyurethanes, such as highest levels of modulus, tear, and tensile. The disiocyanate structure apparently influences the ability of the hard segments to pack more regularly and consequently to have higher intermolecular hydrogen bond interaction and stronger physical network [12].

3.4 Preparation of untreated clay to be clay nanocomposites with difference surfactants i.e. Cetyl trimethyl ammonium Bromide (CTAB) and Octadecylamines (ODA).

The WAXD was used to extent the use of dispersion of clay in the filled samples. It was also used to measure the silicate layers distribution of the modified clays in the polymer matrix. The montmorillonite (Kunipia-F or termed pure-mont) that was modified with cetyltrimethyl ammonium bromide (CTAB) and octadecylamine (ODA) are termed CTAB-mont and ODA-mont. In Figure 4.5, the \(d\)-spacing in CTAB-mont and ODA-mont are 1.571 nm and 1.798 nm, respectively, being larger than that of the pure-mont, 1.142 nm. These indicate that both CTAB and ODA were successfully intercalated into the silicate layer.

![Fig.1. The WAXD pattern of CTAB-mont-PU](image1.png)

Figure 1 and 2 present three series WAXD curves of CTAB-mont-PU and ODA-mont-PU that were corresponded to polyurethane clay nanocomposites based on palm oil. In that graphs the appearance of WAXD peaks (\(2\theta = 2-10^\circ\)) in 1, 3, and 5% CTAB-mont-PU indicated that these organoclay were completely intercalated in polyurethane as matrix. The similar results were obtained for 1, 3, and 5% ODA-mont-PU and as shown in Figure 2, the intercalated could also be obtained.

3.5 Mechanical properties

The mechanical properties of PU and PU/clay nanocomposites are given in Table 1. The modified organoclay had a remarkably beneficial effect on the strength and elongation at break of the nanocomposites, which both increased with increasing clay content, the ODA treated varieties having the highest values.

<table>
<thead>
<tr>
<th>Name</th>
<th>MW</th>
<th>Tensile strength (Mpa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PU</td>
<td>3266.19</td>
<td>14.983</td>
<td>253.4</td>
</tr>
<tr>
<td>1% CTAB-mont PU</td>
<td>3960.33</td>
<td>21.766</td>
<td>270.7</td>
</tr>
<tr>
<td>3% CTAB-mont PU</td>
<td>3809.29</td>
<td>28.342</td>
<td>415.3</td>
</tr>
<tr>
<td>5% CTAB-mont PU</td>
<td>3917.25</td>
<td>32.178</td>
<td>431.1</td>
</tr>
<tr>
<td>1% ODA-mont PU</td>
<td>3745.12</td>
<td>30.491</td>
<td>490.0</td>
</tr>
<tr>
<td>3% ODA-mont PU</td>
<td>3929.45</td>
<td>39.257</td>
<td>677.9</td>
</tr>
<tr>
<td>5% ODA-mont PU</td>
<td>3810.11</td>
<td>40.100</td>
<td>700.5</td>
</tr>
</tbody>
</table>

The fact that the elongation at break of the nanocomposites increased with the organoclay content suggests that elongation was related to the interaction between the pure PU and the treated clays [13].

As shown in Table 1, the ultimate strength was increased dramatically with the increasing of the organoclay content and
has reached maximum values at 5 wt% organoclay content with the increase of the tensile strength of more than 214.76% and 267.63% by the addition of only 5% of the montmorillonite CTAB-mont and ODA-mont respectively.

The dynamic mechanical analysis (DMA) was performed to examine the effect of the clays on the structure, concentration and organization of the hard-segments, and their interaction with the soft segments, have a dominant influence on the physical and mechanical properties of the urethane polymer [14].

The loss factors (tan \( \delta \)) value of pure PU and PU/clay nanocomposites are presented in Figure 3 and 4. Treated clay seems to be more efficient for increasing the glass transition temperature (\( T_g \)). According to Choi et al. (2004)[15] and Agag et al. (2001)[16], it was confirmed that the \( T_g \) increase with the increased of the clay content resulting from the confinement effect of clay to polyurethane molecules and the strong interactions of hydrogen bonding in between the urethane groups of polyurethane molecules and oxygen atoms on the surface of organoclay.

In Figure 3, the \( T_g \) of CTAB-mont-PU were -11.776°C, -8.113°C and -6.764°C for clay content of 1%, 3% and 5%, respectively. Those values are higher than pure PU which was: -12.200°C. But in figure 4 the \( T_g \) of ODA-mont-PU is higher than the \( T_g \) of CTAB-mont-PU with the results (for the ODA-mont-PU sample) are -11.114°C, -6.5°C and -5°C at the similar clay contents respectively.

The results show that thermal resistances are enhanced in the presence of clay compared to pure PU. This indicates an improvement in thermal stability of PU because the organic material can prevent the heat from expanding quickly and limit the further degradation. Onset degradation of pure PU is at 200°C, and is lower than of the CTAB-mont-PU and ODA-mont-PU takes place at about 318°C and 330°C. It means the thermal resistance of nanocomposites improved above 62% compared pure polymer.

The TGA analysis of pure PU, CTAB-mont 1, 3, 5 wt% and ODA-mont-PU 1, 3, 5 wt%, respectively, are shown in Figure 5 and 6. With regard to pure PU, the degradation at 200-400°C is attributed to depolycondensation reaction. Then at higher temperature, the material degrades slowly, and it degrades completely at about 700°C.

3.6 Thermal stability

The TGA analysis of polyurethane, CTAB-mont 1, 3, 5 wt% and ODA-mont-PU 1, 3, 5 wt%, respectively, are shown in Figure 5 and 6. With regard to pure PU, the degradation at 200-400°C is attributed to depolycondensation reaction. Then at higher temperature, the material degrades slowly, and it degrades completely at about 700°C.
In figures 7, morphological observations on the fractured surfaces of the PU and PU/clay nanocomposites samples are shown. The filler employed as reinforcements for polymers and resins are invariably coated with sizing resin whose role to protect them during handling and impregnation. Figure 8 show the transmission electron micrograph of sections of the PU/Clay nanocomposites. The dark lines are intersections of silicates layers, and the other region is PU matrix. It can be seen that silicate layers have reached nanometer scale and effectively intercalated or exfoliated in the PU matrix.

IV. CONCLUSIONS

Segmented PU/clay nanocomposites have been synthesis were succesfully prepared with polyol base on palm oil. The tensile strength and elongation at break increased more than 200% compared the virgin PU. The dynamic mechanical analysis was employed to examine the effect of clay contents on the thermomechanical properties and microstructure of the material and it was found that, the glass transition (Tg) was increased with the increasing of the clay contents. The results also show that thermal resistances are enhanced in the presence of clay compared to pure PU.

REFERENCES


