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# NOVELTY DESIGNED HYBRID ORGANIC-INORGANIC NANOCOMPOSITES FROM FUNCTIONAL PALM OIL

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## ABSTRACT

Polyurethanes (PUs) are very versatile polymeric materials with a wide range of physical and chemical properties. PUs also have desirable properties such as high abrasion resistance, tear strength, shock absorption, flexibility and elasticity. Although they have poor thermal stability that however can be improved by using treated clay. The objective of the present work is to study the thermal stability of polyurethane, polyurethane/montmorillonite (PU CTAB-mont 3% wt) and polyurethane/montmorillonite that contain moca nanocomposites are based on palm oil polyol. The interest of investigating the synthesis of polyurethane/clay nanocomposites based on palm oil polyol is to explore the use of palm oil polyol to replace petrochemical based polyol partially. Polyurethane/clay nanocomposites were prepared by a pre-polymer method and were evaluated by fourier transform infrared spectra (FTIR) to determine micro-domain structures of segmented PU, PU CTAB-mont 3% wt, and PU Moca CTAB-mont 3% wt. The morphology of the nanocomposites were characterized by X-ray diffraction (X-RD) and flame retardant was investigated with thermogravimetric analysis (TGA). The result showed that adding clay and moca demonstrated better thermal stability in comparison with the virgin polyurethane.

Keywords: Nanocomposite, polyurethane, synthesis, palm oil polyol

## INTRODUCTION

Recently, more attention is being paid to polymer nanocomposites, especially polymer nanocomposites with organophilic clays used as fillers. Nanocomposite technology has been described as the new frontier in polymer science, because by adding minimum amount (<10 wt.%) of montmorillonite (MMT), it enhances mechanical and thermal properties of the composites significantly [1].

MMT is a naturally occurring 2:1 phyllosilicate with dimensions of approximately 100 nm in diameters and 1 nm in thickness. Its crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesia is fused to two external silica tetrahedrons by the tip so that the oxygen ions of the octahedral sheet do also belong to the tetrahedral sheets [2]. In pure shapes, MMT is hydrophilic and is incompatible with hydrophobic polymer. Therefore, it is very necessary to modify clay mineral with an alkylammonium salt by means of cation exchange.

Polyurethane elastomer is one of the most versatile materials with a wide range of industrial applications because of its desirable properties such as high abrasion resistance, good tear strength and excellent shock absorption, and therefore it is very compatibles for starting materials variety [3].

Despite the versatility of polyurethane elastomer, it also has some limitations notably having lower thermal stability compared to other polymers. In order to solve this problem, research on thermal analysis of polyurethane/clay nanocomposite using polyol based on palm oil is carried out. Currently, majority of the polyols used for polyurethane are derived from petrochemical refining of crude oil and coal. However, in the event of oil crisis, bio based materials can be used as substitutes.

Since initial studies conducted by Usuki et al. [4] in 1993, a lot of research works on polymer/ clay nanocomposites have been carried out such as poly (□-caprolactone) [5-6], polystyrene [7], epoxy [8], and polyimide [9-10]. In addition, PU/clay nanocomposites have also been investigated by numerous research groups [3, 11-14]. However, there is no work has been reported on the investigation of PU elastomer/clay nanocomposites based on palm oil polyol.

Polyurethane properties can be adjusted by two approaches, the first is to change the molecular structure of polyurethane by modify its basic building blocks, polyether or polyester, diisocyanate, and chain extender. The second is to introduce inorganic fillers into the polyurethane matrix, for example, calcium carbonate, aluminum hydroxide, kaolin, titanium, zinc oxide and silica [15].

In this investigation, both approaches are adopted, such as using polyol based on palm oil instead of petroleum and addition of inorganic fillers with layered silicate (clay).

## EXPERIMENTAL METHOD

### 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), 1.4-butanediol (1,4-BG, Fluka), methylene-bis-ortho-chloroaniline (moca), 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.

### Preparation of Organophilic Clays

An amount of 0.05 mol of cetyl trimetyl ammonium bromide (CTAB) and 250 mL of distilled water were placed in a 500 ml beaker. These solutions were heated at 80oC 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 [16]. The treated Kunipia-F was repeatedly washed by distilled water. The filtrate was titrated with 0.1 NAgNO3 until there is no chloride or bromide present. The filter cake was then placed for drying in an oven at 60oC. The organophilic Kunipia-F was ground and particles of size less than 100 µm were collected for preparation of nanocomposite. The product was termed CTAB-mont.

### Synthesis of PU/Clay Nanocomposite: Preparation of Thermoplastic Polyurethane Elastomers (TPU)

The NCO-terminated prepolymer (or quasi-prepolymer) was prepared by reacting MDI and polyol at a specified NCO/OH equivalent ratio by using the following procedure. Polyol 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 70oC, MDI was added in several portions to the reactor under constant mixing. The reaction temperature was maintained at 70oC to 80oC and periodic samples were withdrawn to determine the isocyanate content. After the theoretical NCO% value was reached, 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 90-100oC and a specified amount of the prepolymer was weighed into a 250 ml plastic cup. The chain extender (1,4-BG), which was preheated at 100oC, was added to the prepolymer under vigorous mixing [17]. The TPU films were formed by casting the solution in a mold and remove the solvent under pressure at 70oC.

### Synthesis of PU/Clay Nanocomposite: Preparation of Polyurethane/Clay Nanocomposites

Film composite compound of CTAB-Mont (3%), MOCA and TPU was prepared by melt mixing using a Haake internal mixer, W50E. The compound was compression moulded to produce sample sheets [18].

### Synthesis of PU/Clay Nanocomposite: Characterization

Wide-angle X-ray diffraction (WAXD) analysis of PU/clay nanocomposites were performed at room temperature by using a Shimadzu XRD 600 X-ray diffractometer (30 kV, 30 mA) with nickel filtered CuK□ radiation to measure the d-spacing of organoclay. The scanning rate data were obtained from 1o/min from range of 2□ = 2-10o . DATR-FTIR spectra were obtained using the Perkin - Elmer Spectrum One FTIR spectrometer with golden gate ATR that was attached with diamond crystal. The absorbance measurements were carried out in the range of 500 cm-1- 4000 cm-1. Thermogravimetric analysis was perfomed with a Perkin Elmer instrument under nitrogen atmosphere using 5 mg samples. The measurement was carried out with heating rate at 10 oC/min from room temperature to 800 oC.

## RESULTS AND DISCUSSION

The X-ray diffraction (X-RD) analysis is an effective method for examining the crystal structure of pristine clay and polymer-clay nanocomposites. The organoclay (Kunipia-F) is modified with cetyl trimetyl ammonium bromide (CTAB).

The X-RD patterns of CTAB-mont and Kunipia-F are shown in Figure 1 (a). In this figure, the d-spacing in CTAB-mont and 1.9 nm and Kunipia-F are 1.9nm and 1.2nm respectively. This means that the interlayer distance of pristine clay (Kunipia-F) was expanded from 1.2 nm to about 1.9 nm for CTAB-mont. The amount of alkyl ammonium that intercalated in the galleries increased with the increasing alkylammonium chain length [18].

The XRD patterns of PU Moca CTAB-mont 3%wt and PU CTAB-mont 3%wt are shown in Figure 1(b). The gallery spacing of layered clay in the composite increases to 3.7 nm for the PU CTAB-mont 3% wt and 3.9 nm for the PU moca CTAB-mont 3%wt. This indicate that the PU chains were intercalated between the layered clays. The gallery spacing for PU moca CTAB-mont 3%wt is bigger than PU CTAB-mont 3%wt, which indicates that moca as a chain extender is mainly dependent on the chain length of the modifier in interlayer and similar results were reported by Xiong et al. [14].

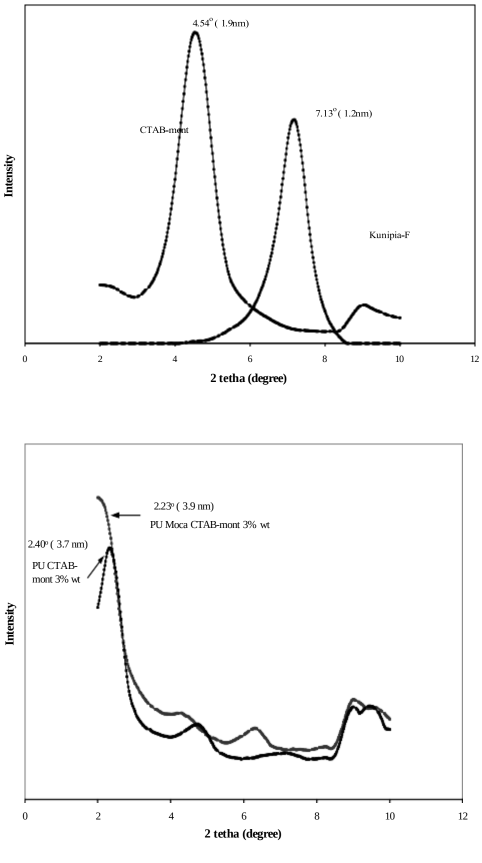
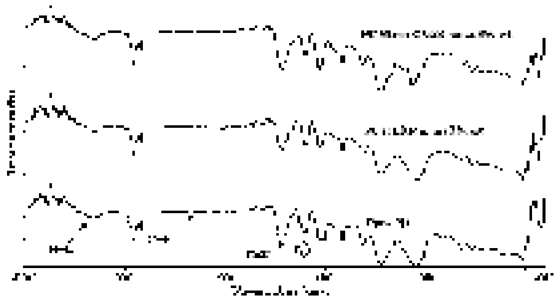


Figure 1: The X-ray diffraction pattern of (a) organoclay (b) PU CTAB-mont 3% and PU moca CTAB-mont 3%

The micro-domain structures of the segmented pure PU, PU CTAB-mont 3% wt and PU moca CTAB-mont 3% wt were analyzed by FTIR and the results are shown in Figure 2. It was found that the positions of peaks for distinctive functional groups in the IR spectra of the pure PU, PU CTAB-mont 3% wt and PU moca CTAB-mont 3% wt are identical, which means that the chemical structures of polyurethane had not been affected by the presence of organoclay.



The thermal properties were determined using thermogravimetric analysis (TGA). The TGA analysis of pure PU, PU CTAB-mont 3% wt and PU moca CTAB-mont 3% wt are shown in Figure 3. The results show that thermal resistance are enhanced in the presence of clay and moca 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 200oC, and is lower than of the PU CTAB-mont 3% wt and PU Moca CTAB-mont 3% wt takes place at about 318oC and 330oC. It means the thermal resistance of nanocomposites improved above 62% compared pure polymer.

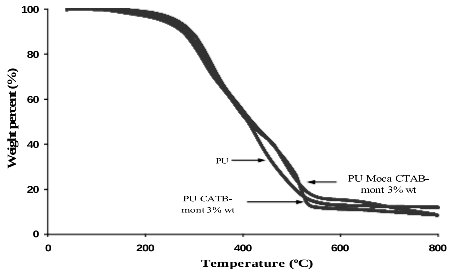


Figure 3: The TGA curves of pure PU and PU 3% wt clay

## CONCLUSIONS

Novelty PU/ clay nanocomposites that based on palm oil polyol have been synthesized. First, the PU and pristine clay were prepared and PU was dispersed and intercalated into the gallery of layered silicate. The d-spacing of organoclay was found to be 1.9 nm compared to 1.2 nm for pristine clay (Kunipia-F). The polyurethane/clay nanocomposites formed intercalated structure with d-spacing of 3.9 nm. The FTIR results confirm that the chemical structure of polyurethane were not altered by the presence of moca and silicate layers. The flame retardant of PU containing moca and clay is better compared to the flame retardant of pure PU and PU containing clay.

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