JurnalReaksi (Journal of Science and Technology)
JurusanTeknik Kimia PoliteknikNegeriLhokseumawe
Vol. 22 No.01, Juni 2024 ISSN1693-248X

STUDY ON FORMULATION OF POLYURETHANE/CLAY NANOCOMPOSITES BASED ON PALM OIL POLYOL

Teuku Rihayat[a], Saari B. Mustapha[a,*], Mohd. Hilmi B. Mahmood[b], Wan MD Zin Wan Yunus[c], Suraya Abdul Rashid[a], Khairul Zaman B. Hj. Mohd. Dahlan[b]

[1]Department of Chemical Engineering, Lhokseumawe State Polytechnic, Lhokseumawe City
[a] Department of Chemical and Environmental Engineering,
University Putra Malaysia, Selangor, Malaysia
[b] Malaysian Institute for Nuclear Technology Research (MINT) Bangi, 43000 Kajang, Malaysia
[c] Department of Science, University Putra Malaysia, Selangor, Malaysia

*Email: teukurihayat.1007@gmail.com

ABSTRACT

A novel segmented polyurethane/clay nanocomposites has been synthesized by polyurethane based on palm oil and Kunipia-F as organoclay with an ammonium salt of cetyltrimetyl ammonium bromide (CTAB). In this investigation, we give much interest to synthesis of polyurethane/clay based on palm oil as raw materials for polyols to open new era for partial replacement of petrochemical based polyol with palm oil based polyols. Surprising, we got the polyurethane elastomer after along time polyurethane based on palm oil only using in coating applications. However, it is the first report in investigation about polyurethane/clay nanocomposites based on palm oil. Polyurethane/clay nanocomposites were prepared by a pre-polymer method and evaluated by fourier transform infrared spectra (FTIR) and X-ray diffraction measurements (X-RD) respectively.

Keywords : Nanocomposite, polyurethane, synthesis, palm oil

1. INTRODUCTION

In recent years, organic-inorganic nanocomposites have attracted great interest of researchers because they offer a great potential in providing superior properties when compared to pure polymers and conventional filled composites [1-5,7-9 and 11-12]

Polyurethanes are very versatile polymeric materials with a wide range of physical and chemical properties as well as desirable properties such as high abrasion resistance, tear strength, excellent shock absorption, flexibility and elasticity. However, they show poor thermal stability and barrier property which can be improved by two approaches: to change the molecule structure and to introduce inorganic fillers into the polymer matrix.[7].

Dispersion inorganic fillers into polymer matrix can cause another problem because it will be a material with worsens in fatigue property and reduces the elongation break. Solved problem can

come from still used inorganic filler, but before dispersion phase doing, we must to modify by organic cations. For the example, organoclay, after treated with organic cation such as alkylammonium, the filler be improve in strength and stiffness.

Another reason to modified pristine organoclay is to improve the compatibility of organoclay with polymer matrix. Moreover, the compatibility between organoclay and polymer can increase the thermal and mechanical properties of polymer-clay nanocomposites [J.xiong].

In this investigation, we want to focused about two approach, firstly to change the molecule structure with using polyol based on palm oil instead of petroleum because if the oil crisis and global warming deepens, bio based material have received particular attention and the second addition of inorganic fillers with modified organoclay. [8].

II. EXPERIMENTAL

Materials

Materials used were ; "Kunipia F" (supplied by Kunimine Ind. Co., 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), and dimethylformamide (DMF, 99%, Fisher) as a solvent. Other inorganic and organic materials were used as received from commercially available source.

Preparation of Organophilic Clays

In a 500 mL beaker were placed 0.05 mol of cetyl trimetyl ammonium bromide (CTAB) and 250 mL of distilled water. This solution was heated at 80^{o}C for 1 h. In the other hand in a 1000 mL beaker were dispersed 20 gr of Kunipia-F and 500 mL distilled water. The dispersion of Kunipia-F was added to the solution of ammonium salt of CTAB, and this mixture was stirred vigorously for 1 h [9]. The treated Kunipia-F was repeatedly washed by distilled water. The filtrate was titrated with 0.1 N $AgNO_3$ until there is no chloride or bromide present. The filter cake was then placed for drying in an oven at 60^{o}C. The organophilic Kunipia-F was ground with amortar and particles of size less than 100 µm were collected for preparation of nanocomposite. The product was termed CTAB-mont. The flow chart of preparation of organophiliclays is depicted in figure 1.

Synthesis of PU/clay Nanocomposite

Preparation of thermoplastic polyurethane elastomers (TPU)

Prepolymer Method. 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 70^{o}C, MDI was added in several portions to the reactor under constant mixing. The reaction temperature was maintained at 70^{o}C to 80^{o}C 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 90-100^{o}C 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 100^{o}C, was added to the prepolymer under vigorous mixing [10]. The TPU films were formed by casting the solution in a mold and then removing the solvent under pressure at 70^{o}C. A flow chart showed in figure 2.

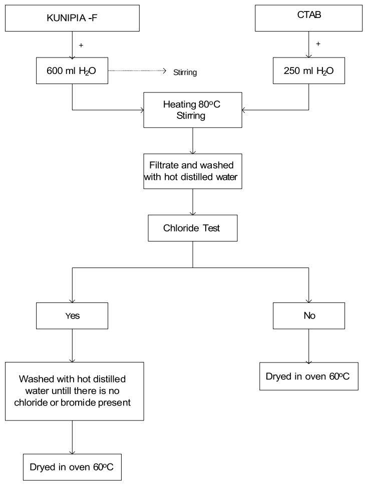

Figure 1. Synthesis of organophilic clays

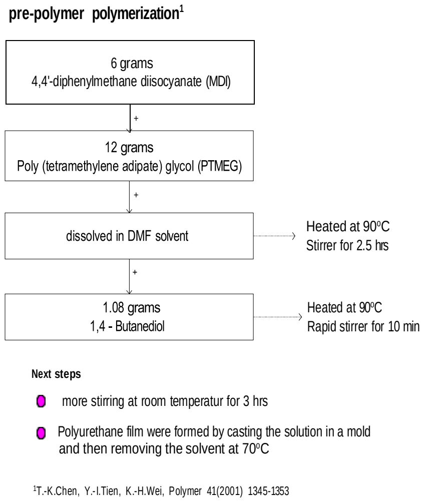

Figure 2. Synthesis of Polyurethane

Preparation of polyurethane/ clay nanocomposites

Film composite compound of CTAB-Mont (3%) and TPU was prepared by melt mixing using a Haake internal mixer, W50E. The compound was compression moulded to produce sample sheets [11].

Characterization

XRD analysis of PU/clay nanocomposites were performed at room temperature by using a Shimmadzu XRD 600 X-ray diffractometer. DATR-FTIR spectra were obtained using the Perkin - Elmer Spectrum One FTIR spectrometer with golden gate ATR attachment with diamond crystal. The absorbance measurements were carried out in the range 500 cm^{-1}- 4000 cm^{-1}.

III. RESULT 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 [1-12]. The organoclay (Kunipia-F) modified with cetyl trimetyl ammonium bromide (CTAB) is 3%wt Clay.

X-RD pattern of 3%wt Clay and Kunipia-F are shown in fig. 3 (a). In fig. 3(a), the d-spacing in 3%wt Clay is 1.9 nm and for Kunipia-F is 1.2 nm . It means that the interlayer distance of pristine clay (Kunipia-F) was expanded from 1.2 nm to about 1.9 nm for 3%wt Clay. The amount of alkyl ammonium intercalated in the galleries increased with increasing alkylammonium chain length [12].

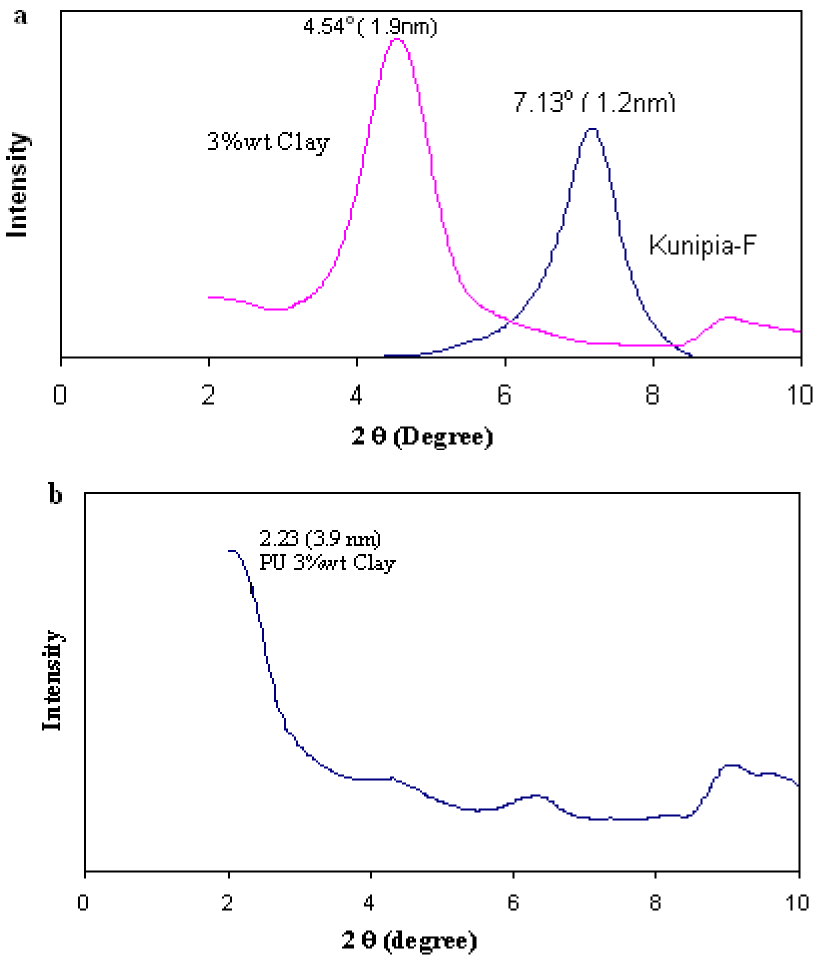

Figure 3. The X-ray diffraction pattern of: (a) organoclay; (b) PU clay and PU 3%wt Clay

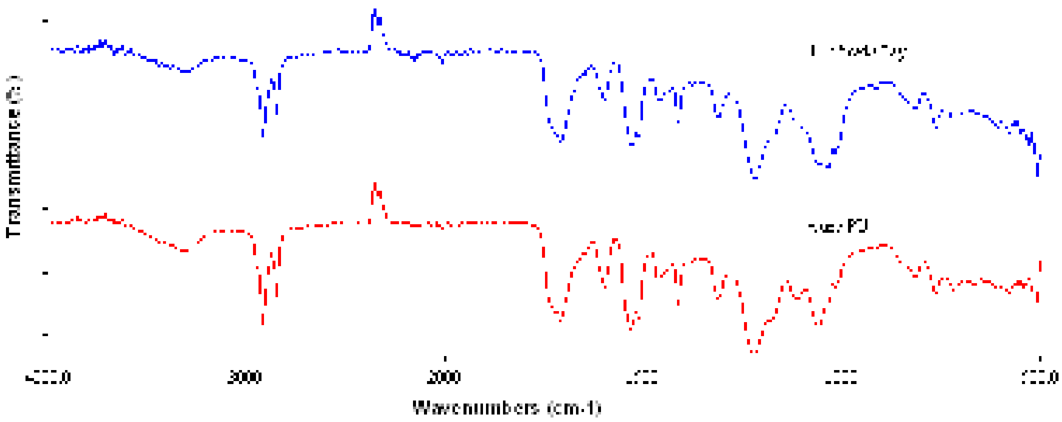

Fig.4 The FTIR spectra of pure PU, PU 3% wt Clay

The XRD patterns of PU 3%wt Clay is shown in fig. 3(b). The gallery spacing of layered clay in the composite increases to 3.9 nm for the PU 3%wt Clay .This indicates that the PU chains were intercalated between the layered clays.

The microdomain structures of the segmented pure PU and PU 3%wt Clay were analyzed by FTIR as shown in fig.4. It was found that the positions of peaks for distinctive functional groups in the IR spectra of the pure polyurethane, polyurethane clay are identical, which means that the chemical structures of polyurethane had not been affected by the presence of organoclay.

IV. CONCLUSION

A novel PU/ clay nanocomposites based on palm oil polyol have been synthesized. Firstly, a kind of PU and pristine clay were prepared; 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 pristine clay (Kunipia-F). The polyurethane/clay nanocomposites formed the intercalated structure with *d*-spacing 3.9 nm. The FTIR confirming that the chemical structures of polyurethane were not altered by the presence of moca and silicate layers.

V. REFERENCE

[1] K.J. Yao, M.Song, D.J.Hourston, D.Z.Luo. Polymer 43(2002) 1017-1020
[2] J. Xiong, Y. Liu, X.Yang, X.Wang. Polym. Degrad. Stab. 86(2004) 549-555
[3] B.K.Kim, J.W.Seo, H.M.Jeong. Eur. Polym. J. 39(2003) 85-91
[4] Y.I.Tien, K.H.Wei. Polymer. 42(2001) 3213-3221
[5] K. Kojio, S. Nakamura, M. Furukawa. Polymer 45(2004) 8147-8155
[6] Z. Wirpsza, " Polyurethanes Chemistry, Technology and Application" (Ellis Horwood Limited Publ., Chichester, British, 1993)
[7] M. Song, H.S. Xia, K.J. Yao, D.J. Hourston. Eur. Polym. J. 41(2005) 259-266
[8] M. Alexandre, P. Dubois. Mater. Sci. Eng.,R. 28 (2000) 1-63
[9] K. Yano, *et al.* J. Polym. Sci., Part A: Polym. Chem. 31 (1993) 2493-2498
[10] http://www.shellchemicals.com/chemicals/pdf/pdo/Utilizationof13Prop.pdf
[11] T.-K.Chen, Y.-I.Tien, K.-H.Wei. Polymer 41 (2000) 1345-1353
[12] J.Sharif, W.M.Z.Wan Yunus, K.Z.H.Mohd. Dahlan, M.H.Ahmad. Polym.Test. 24 (2005) 211-217.