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Fourrier Transform Infrared and Gel Permeation Chromatography Evaluation to Prepared Polyurethane Paint from Polyol Palm Oil Based

[1]Teuku Rihayat, [1]Suryani, [2]Pocut Nurul Alam

[1]Department of Chemical Engineering, Politeknik Negeri Lhokseumawe;
[2]Department of Chemical Engineering, Universitas Syiah Kuala;
Corresponding email: teukurihayat@yahoo.com

Abstract. New emulsion type paint was prepared by utilizing polyol for the production of polyurethane by reaction with an isocyanate was obtained by the synthesis of palm oil-based oleic acid with glycerol. Dodecylbenzene sulfonic acid (DBSA) was used as catalyst and emulsifier. The various methods for preparing Polyurethane /clay Nano composites, but in this research the author choice by a pre-polymer method and were evaluated by Fourier Transform Infrared (FTIR) spectra to determine micro-domain structures of segmented PU. The molecular weight (MW) of polyol was obtained by using gel permeation chromatography (GPC) and the result was about 950. The micro domain structures of the segmented PU were analysed by FTIR by following the work of Seymour *et al*. to estimate the degree of phase separation in segmented PU. 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. The molecular weight (MW) of PU based on palm oil was about 3.266. The performance characteristics of materials indicate to be comparable with the corresponding industrial standard.

Keywords: polyurethane, paint, GPC, FTIR and palm oil

Introduction

Polyurethane (PUR) constitutes a group of polymers with highly versatile properties and a wide range of commercial applications. The applications of polyurethane can be varied over a very wide range, Polyurethane can be manufactured as foam (PURFs), elastomers (PUREs), plastics, adhesives (PURAds), coating (PURCs), leather-like materials (LMs), finishes, etc. (Wirpsza, 1993). The basic component used in the manufacture of polyurethane are polyisocyanates, polyhydroxyl (polyester or polyether polyols), chain extenders (1.4-butanediol or 1.4-dibutylamine) and sometimes water or halohydrocarbon as blowing agent, flame retardant and surfactant (Wirpsza, 1993). Polyurethane coating (PURCs) is a very important group of products although their consumption is much lower than that of urethane foams. They opened a range of new applications which could not be realized before (Petrovic, 1991).

The major challenge in polymer science is to increase its uses and quality. In order to overcome above features which enhancing particular characteristics such as modulus, strength, fire performance and heat resistance, research Polyurethane/ clay Nano composite with polyol base palm oil is being prepared.

The chemical and physical properties of fats and oils derived from plant and animal sources are largely determined by the fatty acids that contain and their position within the triglycerides molecule. Fats and oils are commonly referred to as triglycerides because glycerine molecule has three hydroxyl groups where fatty acids can be attached. Structurally, a triglyceride is the reaction product of one molecule of glycerol with three molecules of a triglyceride. In the present communication, the authors wish to discuss the preparation and characterization of paints from Polyurethane/ clay nan composite with polyol base palm oil.

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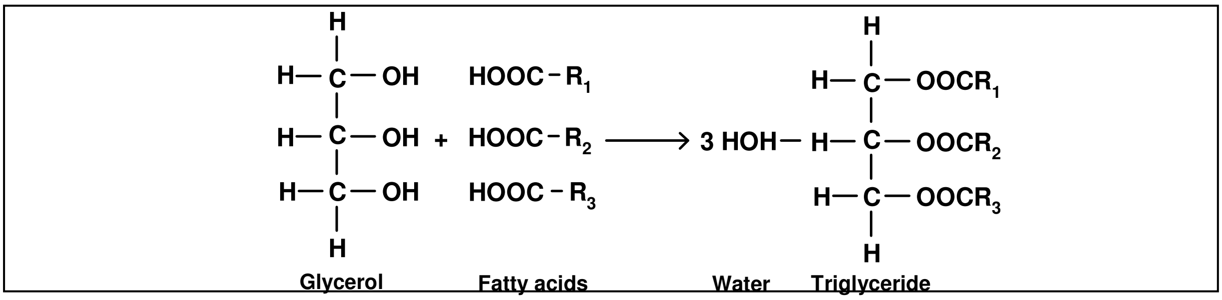

Figure 1 Schematic reaction of triglyceride (modified from Formo, 1979).

Materials and Methods

Experimental

This field details the preparation and characterization of polyol based on palm oil, synthesis of polyurethane based on palm oil, preparation and characterization of organophilic clay and lastly synthesis and characterization of Polyurethane/clay Nano composites based on palm oil polyol. The properties of polyol were determined using Fourier Transform Infrared spectra (FTIR) and gel permeation chromatography apparatus (GPC).

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, systerm ; 4-dodecylbenzenesulfonic acid, fluka ; extruded 3A molecular sieve, Aldrich), 1.4-butanediol (1,4-BD, Fluka), cetyltrimethyl ammonium bromide (CTAB, Fluka), octadodecylamine (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.

Synthesis of polyol base on palm oil

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Synthesis of polyol base on palm oil

Polyol 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 favour 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 catalyst. In the presence of DBSA, all esters of glycerol are formed. Although the conversion of oleic acid was elevated, little glycerol monooleate was formed [Eychenne and Mouloungui, 1999).

Preparation of Thermoplastic Polyurethane Resin (TPR)

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°C, MDI 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, 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-BG), which was preheated at 100°C, was added to the prepolymer under vigorous mixing. The TPR films were formed by casting the solution in a mold and remove the solvent under pressure at 70°C.

Preparation of paints

The polyurethane test paints were prepared in porcelain ball mills using butylated MF and epoxy modified polyurethane resins as respective binders in the grinding stage. At first, the pigment titanium dioxide, extenders, respective resins and around 20% of solvent were charged in the ball mill. The grinding of the pigments and extenders was done for around 18 h to attain the grinding particle sizes of 10_m, as measured by Hegman Gauge. After attaining the required grinding size, the materials were dropped into some containers and mixed with polyurethane ester resin and finally adjusted with remaining solvents and other additives to achieve application viscosity of paint (i.e., 80–100 s in FC4 at 30°C). Finally the mixture was kept for 24 h for better wetting before panel preparation for further study (Dutta *et al*., 2009).

Result and Discussion

This result and discussion of the synthesis of polyurethane based on palm oil polyol, preparation of untreated clay to be clay Nano composites with difference surfactants i.e. Cetyl trimethyl ammonium Bromide (CTAB) and Octadecylamines (ODA), synthesis of polyurethane based on palm oil polyol as metric with clay nanocomposites as reinforcement, and determine the efficiency of thermal resistance of polyurethane/ clay nanocomposites with using thermogravimetric analysis (TGA). The result of investigation to determine the micro-domain structures of segmented PU and PU/clay Nano composites were evaluated by Fourier Transform Infrared spectra (FTIR). The mechanical properties in term of their tensile properties, including the dynamic mechanical properties of pure polyurethane (PU) and PU/clay Nano composites, were measured. Wide angle x-ray diffraction techniques were utilized to explore the extent of dispersion of clay in filled systems. Furthermore, the molecular weights of materials were determined by Gel Permeation Chromatography apparatus but in this communication we just introduce one or two result of our objectives.

Synthesis of polyurethane based on palm oil polyol

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

The preparation of polyol from palm oil based oleic acid and glycerol was monitored by FTIR spectroscopy. The graph in fig. 2 shows a stretching vibration of C=C at 1653 cm^{-1} and C-H unsaturation at 3009 cm^{-1}. The molecular weight (MW) of polyol was obtained by using gel permeation chromatography (GPC) and the result was about 950 [fig. 3]. The MW value that is vital in the synthesis of PU, i.e., the isocyanation process between polyol, MDI and 1,4-BDO.

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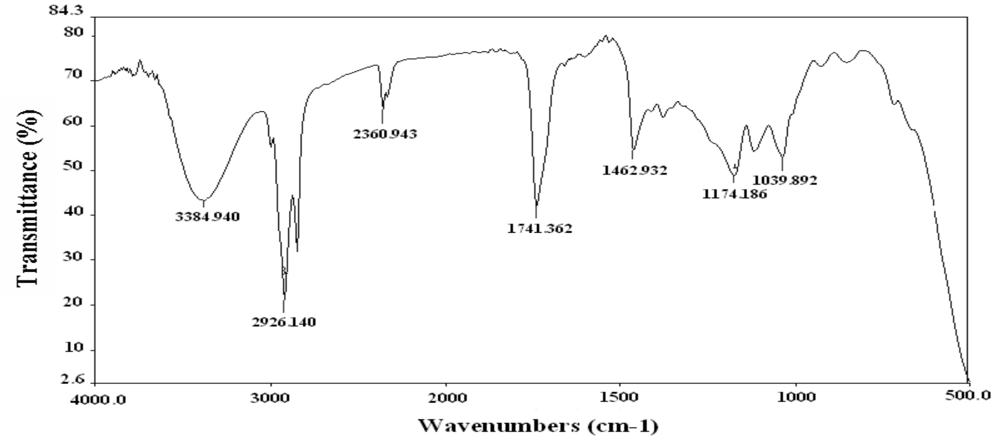

Figure 2. The FTIR spectra of the synthesized polyol based on palm oil.

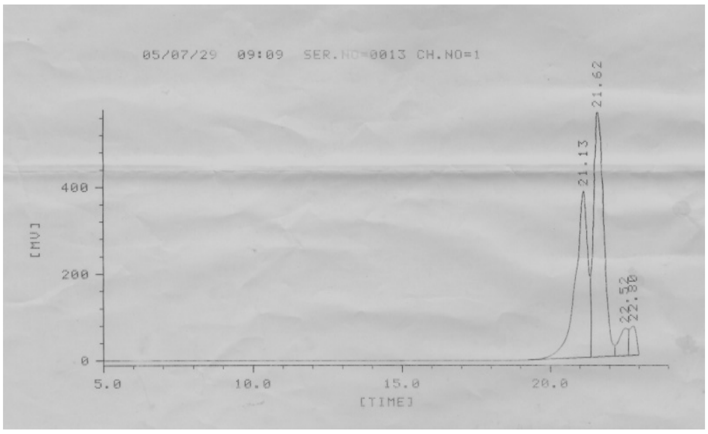

Figure 3. The GPC profiles of the polyol based on palm oil.

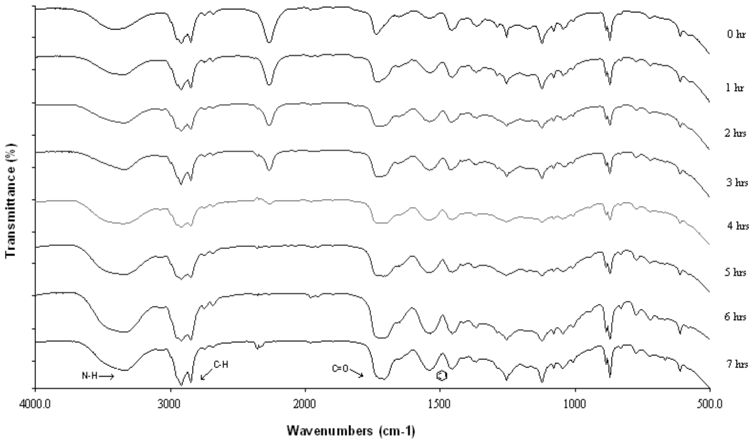

Figure 4. The FTIR spectra of the synthesis polyurethane based on palm oil polyol.

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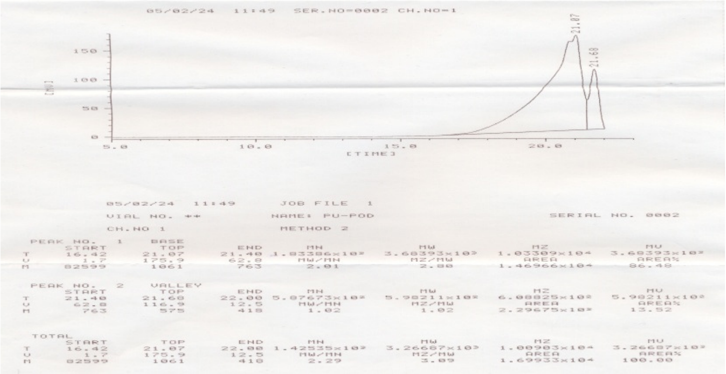

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      VIAL NO. **           NAME: PU-POD                        SERIAL NO. 0002
      CH.NO 1                METHOD 2
PEAK NO.   1    BASE
      START      TOP       END     MN            MW            MZ            MV
T     16.42      21.07     21.40 1.83386x10³  3.68393x10³  1.03309x10⁴  3.68393x10³
V       1.7      175.9      62.8   MW/MN         MZ/MW         AREA          AREA%
M     82599      1061       763    2.01          2.80        1.46966x10⁴    86.48

PEAK NO.   2    VALLEY
      START      TOP       END     MN            MW            MZ            MV
T     21.40      21.68     22.00 5.87673x10²  5.98211x10²  6.08825x10²  5.98211x10²
V      62.8      116.9      12.5   MW/MN         MZ/MW         AREA          AREA%
M       763      575        418    1.02          1.02        2.29675x10³    13.52

TOTAL
      START      TOP       END     MN            MW            MZ            MV
T     16.42      21.07     22.00 1.42535x10³  3.26687x10³  1.00903x10⁴  3.26687x10³
V       1.7      175.9      12.5   MW/MN         MZ/MW         AREA          AREA%
M     82599      1061       418    2.29          3.09        1.69933x10⁴   100.00
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Figure 5. The GPC profiles of the synthesis polyurethane based on palm oil polyol.

The micro domain structures of the segmented PU were analyzed by FTIR as shown in fig. 4. These steps a process synthesis of polyurethane based on palm oil polyol. The collect data start from 0 hrs which the peak of isocyanate still in full and finished of synthesis if the peak of isocyanate were disappearances (7 hrs). Following the work by Seymour *et al*. (1970), the degree of phase separation in segmented PU can be estimated.

The main region interested in the study is –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, T.-K. *et al*.(2000). The molecular weight (MW) of PU based on palm oil was about 3.266 (fig. 5).

Conclusions

Polyols were prepared from the reaction between glycerol and oleic acid based palm oil (purchased from local company). The polyols could also be used as raw materials for the production of polyurethanes by isocyanation with isocyanate compounds. The preparation of polyol from palm oil based oleic acid and glycerol was monitored by FTIR spectroscopy. The molecular weight (MW) of polyol was obtained by using gel permeation chromatography (GPC) and the result was about 950. The micro domain structures of the segmented PU were analysed by FTIR by following the work of Seymour *et al*. to estimate the degree of phase separation in segmented PU. 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. The molecular weight (MW) of PU based on palm oil was about 3.266.

Acknowledgements

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