Synthesis of Polyurethane Elastomer from Vegetable Oil and Methylene-4, 4'-Diphenyldiisocyanate (Mdi) as Surface Coating for Roller

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Abstract

This research aimed were to synthesize polyurethane from vegetable oil, fatty acid mixture of vegetable oil, hydroxy acid of vegetable oil and fatty acid with methylene-4,4'-diphenyldiisocyanate (MDI) and to study the thermal and mechanical properties, and also to decide the crosslink of the polyurethanes. The subject of this research was the synthesized polyurethane from vegetable oil, fatty acid of vegetable oil and methylene-4,4'-diphenyldiisosyanate, while the object of this research was the thermal and mechanical properties, and the crosslink of the polyurethane product. The separation of fatty acid from ester glycerol was done by extraction with base solution. The obtained fatty acid which was modificated through hydroxylation by oxidation and hydration, then it was characterized including function groups using FTIR spectrophotometry, fatty acid composition with GC-MS, determination of iodine number and hydroxyl number. Polymerization reaction was undertaken by one shot process. Polyurethane characterization included identification of function group using FTIR spectrophotometry, thermal properties by Differential Thermal Analysis (DTA), the mechanical properties were characterized using Shore A Durometer, and the test of crosslink through swelling degree measurement. The results of this research that the modificated fatty acid by hydroxylation has more hydroxyl functional group than fatty acid. Polyurethane from hydrated fatty acid has a higher T_g than polyurethane from oxidated fatty acid. The synthesized polyurethane from hydrated fatty acid has higher crosslink and hardness than polyurethane from oxidized fatty acid. The swelling degree tests show that polyurethane has crosslink structure.

Keywords : *crosslink, fatty acid, hardness, hydration, hydroxyl, polyurethane*

I. Introduction

Polyurethanes are all around us, playing a vital role in many industries from shipbuilding to footwear, construction to cars. They appear in an astonishing variety of forms, a variety that is continuously increasing.1) Polyurethanes are by far the most versatile group of polymers, because products ranging from soft linear thermoplastic elastomers to hard thermoset rigid foams are readily produced from liquid monomers. 1)-3)

Types of polyurethane elastomers commercially available include thermoplastic elastomers in a form suitable for conventional thermoplastic processing, cast elastomers can be made by mixing and casting reactive liquid components, elastomeric fibres and various one- and two-component systems for making elastomeric coatings on textiles and other flexible substrates.

All polyurethanes are based on the exothermic reaction of polyisocyanates with polyol molecules, containing hydroxyl groups. Vegetable oil are materials which are highly adaptable to their circumstances. They are also materials having appropriate reactivity because of functional groups such as hydroxyl groups. Accordingly, vegetable oil having more than two hydroxyl groups per molecule can be used as polyols for polyurethane (PU) synthesis. There are also double bonds in structure of vegetable oil which can be modificated by hydroxylation. Hydroxylation can be done by hydration and oxidation.4) Than fatty acid of vegetable oil can be separated from glycerol by extraction with base solution. The obtained fatty acid was modificated through hydroxylation by oxidation and hydration using potassium permanganate and sulfuric acid solution respectively.

Almost all of polyurethane elastomers are based upon segmented block copolymers of the general molecular structure, $(AB)_n$, having alternating soft and hard segments 5),6). Polyurethane elastomers may be made in a wide range of hardnesses from about 10 Shore A to over 60 Shore D 1)-3). Polyurethanes have hardness about 88 Shore A is used as roll cover in sizing applications on a paper making process 6). There is a strong tendency for polyurethane to swell and then degrade by means of hydrolysis. Degradation will start with water that are trapped within the polyurethane structure.

In these studies, PUs were prepared using hydroxylated monomer (polyols) from vegetable oil such as castor oil (CO), crude palm oil (CPO), soybean oil (SBO) and fatty acid of vegetable oil.

II. Experimental

Materials

Castor oil was commercially obtained from market place. Crude palm oil was obtained from CPO refinery industry. Soybean oil was obtained from soybean through maceration with n-hexane. Methylene-4,4'-diphenyldiisocyanate (MDI), sodium hydroxide, sodium sulphate anhidric, sulfuric acid, and potassium permanganate were commercially obtained from E-Merck.

Isolation of Fatty Acid from Vegetable Oil

To separate fatty acid from ester glycerol in vegetable oil is used base solution through extraction. First, NaOH 10% is added to 100 mL of vegetable oil, and than the mixture is extracted with chloroform and is shaked. After between organic and water phase is separated, H_2SO_4 is added to water phase and is extracted with chloroform, shaked, then separated. Na_2SO_4 anhidric is added to organic phase and filter, then filtrate is vapored by using rotary evaporator and produce fatty acid to be characterized. 4),8)

Hydroxylation of Vegetable Oil and Fatty Acid from Vegetable Oil

Hydroxylation is done by hydration and oxidation. Hydration is done by using sulfuric acid solution. H_2SO_4 is added to sample (vegetable oil, fatty acid), then is shaked about 90 minutes and is kept at room temperature about 24 hours, is extracted to separate water phase. Na_2SO_4 anhidric is added to filtrate and is vapored by using rotary evaporator. And then product is characterized. 4)

Oxidation is done by using potassium permanganate solution. $KMnO_4$ with base and cold condition is added to sample (vegetable oil, fatty acid), then is shaked about 90 minutes and is kept at room temperature about 24 hours, is extracted with chloroform to separate water phase. Na_2SO_4 anhidric is added to organic phase (oxidated fatty acid) and is vapored by using rotary evaporator. Then product is characterized. 8)

Preparation PUs

Polymerization was carried out at difference temperature to CO, CPO, and SBO respectively and mass ratio of vegetable oil to all reactant was 40%. Monomer such as hydroxylated vegetable oil (CO, CPO, SBO), fatty acid, and hydroxylated fatty acid is added to reactor which was filled MDI. Then the mixture were mixed and procured PUs were prepared. Precured PUs is poured at glass mould (Petri dish) and is let harden or following curing process in oven at fixed temperature. 8)

Characterization

Vegetable oil, fatty acid, and hydroxylated vegetable oil, and also hydroxylated fatty acid were characterized, that was functional groups, composition fatty acid, physical-chemistry properties i.e. melting and boiling point, hydroxyl and iodine number. 8)

The PUs were characterized i.e. functional groups, thermal and mechanical properties, and then crosslink structure.

The functional groups were measured using FTIR spectrophotometer, Shimadzu. The thermal properties were measured using Differential Thermal Analyzer, Shimadzu. The DTA thermogram were obtained at the scanning rate of 20^oC/min. The DTA was operated at range temperature -10 – 500^oC. The mechanical properties i.e. hardness were measured using Shore A Durometer. Crosslink was measured by swelling during 48 hours in tapioca solution at 70^oC. 8)

III. Results and Discussion

The Physical-Chemistry Properties of Vegetable Oil and Fatty Acid

Table 1 and 2 show the physical-chemistry of vegetable oil, hydroxylated vegetable oil, fatty acid and hydroxylated fatty acid. Hydroxylation can increase hydroxyl number of vegetable oil and fatty acid. Thus, hydroxylation can increase reactive hydroxyl content in structure of vegetable oil monomer. In addition to the physical-chemistry data can support success of hydroxylation. The melting and boiling point can increase with increasing hydrogen bonding, molecular mass, and polarity. The FTIR spectra of vegetable oil and fatty acid after hydroxylation (Fig. 2 and 3) show that hydroxyl group increases.

These results indicate that vegetable oil, fatty acid, and hydroxylated vegetable oil and fatty acid can be used as polyols in synthesis PUs. Each polyol can react with MDI because it has reactive hydroxyl. Although vegetable oil can used as polyol in synthesis, but modificated vegetable oil has higher hydroxyl content than vegetable oil. Thermal properties of PU increases with increasing hydroxyl number of polyol 8).

Table 1. The Physical-Chemistry Properties of Vegetable Oil

Sample	Melting Point (°C)	Boiling Point (°C)	Hydroxyl Number (mg/g)	Iodine Number (g/g)
CO	5.3	131.3	175.688	*
Hydrated CO	10.0	150.0	216.6020	*
Oxydated CO	10.0	280.0	394.6900	*
SBO	117.7	-1.3 – 1.3	19.8830	125.6900
Oxydated SBO	120.0	1.0 – 4.0	107.6890	51.0960
CPO	16.6 – 21.3	104.0	12.4031	46.9019
Hydrated CPO	4.0 – 7.6	141.0	21.0302	49.7302
Oxydated CPO	31.3 – 33.0	160.0	442.9267	49.4557

*is not determined

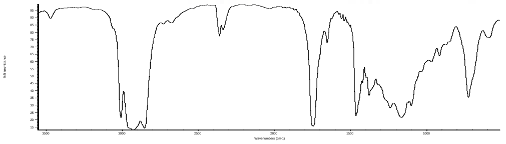
Table 2. The Physical-Chemistry Properties of Fatty Acid from Vegetable Oil

Sample	Hydroxyl Number (mg/g)	Iodine Number (g/g)
Fatty Acid of CO (FACO)	27.5470	*
Hydrated FACO	51.4660	*
Oxydated FACO	80.4870	*
Fatty Acid of SBO (FASBO)	8.2490	103.5580
Hydrated FASBO	62.1100	52.9300
Oxydated FASBO	53.3950	70.6490
Fatty Acid of CPO (FACPO)	42.9330	48.6289
Hydrated FACPO	62.9690	47.9774
Oxydated FACPO	91.5910	43.8705

*is not determined

Functional Groups of PUs

All of synthesized PUs are hard and brittle. FTIR spectra of prepared PUs from each series monomer are identical. The core structure of prepared PUs consists urethane group (~1720cm^{-1}) and end group –NCO (~2280 cm^{-1}). Polymerization has be done successfully and the yield of polymers was high. Figure 3 shows FTIR spectrum of PU based Oxydated SBO and MDI.



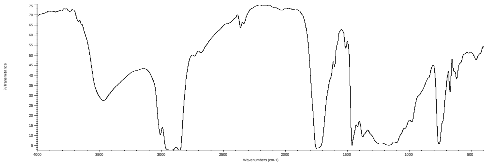


Fig 1. The FTIR Spectra of Soybean Oil Before (Upper) and After Oxidation (Lower)

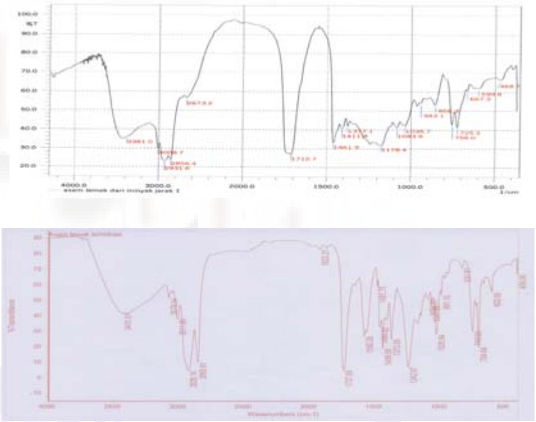


Fig 2. The FTIR Spectra of Fatty Acid from Castor Oil Before (Upper) and After Hydration (Lower)

However, other than primary reactions 3),5), which resulted from the formation of urethane groups, secondary reactions such as allophanate, isosianuric, and carboimide trimer formation (Fig.3) can also be detected by FTIR techniques. PU derived from oxydated CO has uretidine crosslink 8).

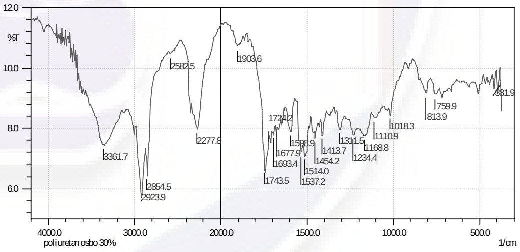


Fig 3. The FTIR Spectrum of PU Based Oxydated SBO - MDI

Thermal Properties of PUs

Table 3 shows glass transition temperature, melting point, and degradation temperature of PUs.

All the polymers derived from Castor Oil show glass transitions in the temperature very low and the values increase from PU based on Oxydated CO to Oxydated FACO and hydrated CO. Then all the PUs derived from CPO and SBO show T_g very high in the temperature range 89.28 – 186.15°C. PUs derived from hydrated vegetable oil have higher T_g than PUs derived from oxydated vegetable oil. Hydration can increase T_g of polymers. This trend is in accord with the amorphous of the polymer; the increase of T_g with increasing amorphous has already been reported 5).

Table 3. The Thermal Properties of PUs

Polyurethane	T_g (^{0}C)	T_m (^{0}C)	T_d (^{0}C)
Oxydated CO-MDI	-18	122	290.00
Hydrated CO-MDI	-6	*	434.20
Oxydated FACO-MDI	-7	90.81	430.49
Oxydated CPO-MDI	146.67	*	403.21
Hydrated FACPO-MDI	186.15	*	442.05
Oxydated FACPO-MDI	89.28	*	450.00
Oxydated SBO-MDI	102.26	*	418.94

*not detectable

The Mechanical Properties of PUs

The hardness of PU is measured using Shore A Durometer is showed in Table 4.

Table 4. The Hardness of PUs

Polyurethane	Hardness (*Shore A*)
Oxydated CO-MDI	78.60
Hydrated CO-MDI	85.00
Hydrated FACO-MDI	87.66
Oxydated FACO-MDI	85.66
Oxydated SBO-MDI	81.40
Hydrated CPO-MDI	25.60
Oxydated FACPO-MDI	87.80
Hydrated Oleic Acid-MDI	86.80
Oxydated Oleic Acid-MDI	67.40

All the polymers derived from CO, CPO, and SBO show hardness in the hardness range 67.40 – 87.80 Shore A, but PU derived from Hydrated CPO has lower hardness than other. The hardness can be caused by crosslink in the structure of PU. The hardness is increase with increasing crosslink of polymers 5). The crosslink structure of PUs is showed by FTIR spectra and swelling degree. PUs derived from hydrated FACO – MDI and derived from oxydated FACPO – MDI can be used as roll cover.

The Crosslink Degree of PUs

Table 5 shows swelling degree of polyurethanes from vegetable oil and fatty acid.

Table 5. Swelling Degree of PUs

Polyurethane	Swelling Degree (%)
Oxydated CO-MDI	10.000
Hydrated CO-MDI	6.140
Hydrated FACO-MDI	17.210
Oxydated FACO-MDI	128.090
SBO-MDI	12.392
Oxydated SBO-MDI	1.299
Oxydated CPO-MDI	20.000
Hydrated CPO-MDI	73.330
Oxydated FACPO-MDI	74.080
Hydrated FACPO-MDI	80.000

All the PUs have positive swelling value, thus all the PUs have crosslink structure. PU derived from Oxydated SBO – MDI has the highest crosslink.

IV. Conclusion

Hydroxylation can increase reactive hydroxyl functional group of vegetable oil and fatty acid. Polyurethanes from hydrated vegetable oil and hydrated fatty acid have a higher T_g than polyurethane from oxidated vegetable oil and oxydated fatty acid. The synthesized polyurethane from hydrated fatty acid has higher crosslink and hardness than polyurethane from oxidized fatty acid. The swelling degree tests show that polyurethanes have crosslink structure.

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VI. Referensi

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