# The Physical and Mechanical Properties of Polyurethanes from Oleic Acid Polyols

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**ABSTRACT:** Three different polyester polyols, with various oleic acid content, were used in the preparation of polyurethane (PUR) coatings. The polyols were designated as Alk28, Alk40, and Alk65, in which 28, 40, and 65 represent the percentage of oleic acid of the polyol formulations. These polyester polyols were reacted with aromatic diisocyanate [toluene diisocyanate (TDI)] to form PUR coatings. The acid value, hydroxyl value, molecular weight, and viscosity of the polyols have been determined. The reaction between the polyols and TDI was studied by Fourier Transform Infrared spectroscopy and X-ray diffraction (XRD). The effects of varying NCO/OH ratio and oleic acid content of polyols on physical and mechanical properties of PUR films were studied. XRD results indicate that the samples are amorphous. PURs, made with Alk28, have the best mechanical properties followed by Alk40 and Alk65. The mechanical properties of the samples have increased as the NCO/OH ratio was increased from 1.2 to 1.6. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3554–3559, 2009

**Key words:** polyurethane; oleic acid; polyester; polyol; mechanical properties

## INTRODUCTION

As the oil crisis and global warming deepen, many researchers have refocused their attention on renewable resources as substitutes for petrochemical derivatives.[1,2] Vegetable oils are important sources for green polyols and have a number of excellent properties which could be utilized in producing valuable polymeric materials such as epoxy, polyesteramide, alkyd, and polyurethane (PUR) in addition to its many applications in other areas. Literature studies reveal synthesis of different kinds of polymeric resin made from seeds of plants such as nahar,[3] linseed,[4] soybean,[5–7] amaranth,[8] castor,[9–11] sunflower kernels,[12] cashew nut,[13] and karanja.[14]

Casting resins and PUR foams synthesized from vegetable oils have been in existence for some time.[15–20] Technologies to produce polyols from palm oil and palm kernel oil that are economically competitive to petroleum-based polyols have been developed in Malaysia.[21–28] These polyols are then reacted with polyisocyanate to produce PUR.

For many years, researchers have been trying to develop PUR coatings[29] and interpenetrating networks[30] as well as many different types of PURs have been made from synthetic chemicals.[31,32] In the present work, an attempt has been made to develop PUR coatings synthesize from polyols derived from oleic acid, glycerol, and phthalic anhydride. The chemical composition of polyols plays an important role in the properties of the PURs and therefore polyols having different oleic acid content were prepared to study the effect of different amount of side chains. The NCO/OH ratios of PUR were also varied to evaluate the influence on mechanical properties.

## EXPERIMENTAL DETAILS

### Materials

Oleic acid (purity 99.5%) and glycerol (purity 99.5%) were obtained from Cognis Oleochemical (M) Sdn. Bhd. (Banting, Selangor) Phthalic anhydride (PA; P.T. Petrowidada, Gresik, East Java, Indonesia) and toluene diisocyanate (TDI; Aldrich (St. Louis, MO); 80 : 20; 2,4-toluene diisocyanate : 2,6-toluene diisocyanate) mixture of the two isomers were used as received. Toluene (JT Baker, Phillipsburg, NJ, USA) was used as solvent; it was dried over activated molecular sieve overnight before use. Silicone surfactant used was L6900 (Air Products) [Allentown, PA] and defoamer BYK-088 was from BYK Chemie, Wesel, Germany.

### Synthesis of polyester polyol

Preweighed PA, glycerol, and oleic acid were charged into a 2 L four-neck round bottom reactor flask. The mixture was stirred and heated up to a

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TABLE I
Composition of PA, Glycerol, and Oleic Acid Used in the Preparation of Polyols

|  | Alk28 | Alk40 | Alk65 |
|---|---|---|---|
| Glycerol (g) | 456 | 256 | 145 |
| Phtalic anhydride (g) | 700 | 338 | 103 |
| Oleic acid (g) | 452 | 400 | 460 |
| Projected OH value (mg KOH per gram resin) | 142 | 142 | 143 |

temperature of 120 to 130°C whereas a slow stream of nitrogen gas was bubbled through the mixture for 30 min. The temperature was then increased to 180–200°C when the reaction could proceed readily with the evolution of water, which was collected at the decanter arm. Sample was taken periodically to check the acid number until it fell below 50 mg KOH per gram. The reaction was considered complete after the water of reaction collected was as predicted in the formulation. Three different formulations of polyols were synthesized by varying the content of oleic acid to 28%, 40%, and 65%. The samples were named as Alk28, Alk40, and Alk65, respectively, in accordance to the percentage of oleic acid in the samples. The compositions and characteristic of polyols are summarized in Tables I and II. The formulations were based on the method as described in reference,[33] and the targeted alkyds would have similar hydroxyl value and acid numbers.

## Synthesis of polyurethanes

The polyol and additives were dried under reduced pressure at 80°C for 2 h before being poured into a three-neck flat-bottom flask equipped with thermometer, dropping funnel, and magnetic stirrer. Polyol was allowed to react with a calculated amount of TDI in the presence of solvent, toluene, and surfactant, and defoamer. TDI was added dropwise into the reaction mixture at 80°C over 3 h with constant

TABLE II
Properties of Oleic Acid Polyols

| Properties | Alk28 | Alk40 | Alk65 |
|---|---|---|---|
| Color | Dark brownish | Brownish | Light brownish |
| Viscosity | 12,800 cps | 8000 cps | 2800 cps |
| Stability | >6 months | >6 months | >6 months |
| Acid value (mg KOH) | 48.2 | 40.4 | 33.5 |
| OH value (mg KOH) | 132 | 134 | 135 |
| $M_n$ | 953 | 999 | 859 |
| $M_w$ | 2322 | 2251 | 1441 |
| $M_P$ | 1171 | 1070 | 1092 |
| Poly dispersity | 2.44 | 2.25 | 1.68 |

stirring. The partially reacted sample formed a viscous solution, which was then poured into a rectangular mold of 12 cm × 12 cm to cure under ambient temperature overnight to form film of 0.5 mm thickness and left in the oven at 60°C for 2 days to evaporate off all the solvent. The composition and designation codes of the PUR systems are shown in Table III.

## FTIR and DSC characterization

The polyols were characterized by Fourier Transform Infrared (FTIR) spectroscopy (Perkin–Elmer FTIR spectrum RX-1 spectrometer), acid number and hydroxyl value of polyols were also determined by standard methods which are ASTM D1639-90 and ASTM D1957-90, respectively. The molecular weights of the polyols were determined by gel permeation chromatography (GPC, waters, polystyrene standards) in THF (elution rate: 1 mL/min) at 35°C. The viscosity of the polyols were measured using a Brookfield model RVT plate and cone viscometer (serial no 206505) at room temperature. The final PURs were analyzed using X-ray diffraction (XRD; Siemens D5000) and FTIR spectroscopy. Tensile measurements were carried out with Zwick Z050

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TABLE III
Compositions of Polyols and TDI Used in the Preparation of Polyurethanes

| Type of polyol | Designation of PU composition code | NCO/OH ratio | Amount of polyol (g) | Amount of isocyanates adduct (g) | Available NCO in prepolymer (%) |
|---|---|---|---|---|---|
| Alk28 | PUalk28(1.2) | 1.2 | 397.89 | 104.40 | 10.17 |
|  | PUalk28(1.4) | 1.4 | 397.89 | 121.8 | 19.67 |
|  | PUalk28(1.6) | 1.6 | 397.89 | 139.20 | 28.54 |
| Alk40 | PUalk40(1.2) | 1.2 | 399.59 | 104.40 | 10.14 |
|  | PUalk40(1.4) | 1.4 | 399.59 | 121.8 | 19.60 |
|  | PUalk40(1.6) | 1.6 | 399.59 | 139.20 | 28.45 |
| Alk65 | PUalk65(1.2) | 1.2 | 400.46 | 104.40 | 10.12 |
|  | PUalk65(1.4) | 1.4 | 400.46 | 121.8 | 19.57 |
|  | PUalk65(1.6) | 1.6 | 400.46 | 139.20 | 28.41 |

Concentration of surfactant and defoamer: 0.02 wt %; Solids by weight: 42%.

tensile tester at strain rate of 5 mm/min according to ASTM D638.

## RESULTS AND DISCUSSION

### Characteristic of polyols and PUR

i. Polyols

In the preparation of polyols, the reaction of phthalic anhydride involves two distinct steps. The first step is the reaction between anhydride and glycerol to form a half ester and a free carboxylic group. This ring opening of phthalic anhydride does not evolve any water and could occur quite readily at moderate temperature around 120 to 130°C. In this series of polyols, there is a great excess of glycerol over the phthalic anhydride at the initial stage which lead to the formation of a mixture of oligomers with terminal carboxylic and excess hydroxyl groups. At this stage, there was no noticeable reaction between free —COOH and —OH as no water was evolved. At the second stage, the temperature was raised to 180–200°C. Both the carboxylic acid of the half ester and oleic acid would compete to react with hydroxyl group to form ester linkages with liberation of water. The oleic acid is incorporated as flexible side chains. The resulting low molecular weight polyols are viscous liquids. From the results, it can

be noted that viscosity and molecular weight of the resin decreases as the oleic acid content increases.

These steps and the predicted polyols structure are represented in Scheme 1.

ii. PURs

Formation of the PUR occurs by simultaneous solvent evaporation (physical process) and chemical reactions of —NCO group with —OH group[34,35] as represented in Scheme 2.

In this study, good film formation, which was nonsticky to touch, after 48 h curing requires the use of excess equivalent amount of isocyanate. Presumably, the excess of diisocyanate (for NCO/OH ratio of 1.2–1.6) could introduce allophanate and polyisocyanurate structures, which were effectively bonding between polymer chains giving rise to crosslinking.

### Infrared spectroscopy

The FTIR spectra of Alk28, Alk40, and Alk65 were as shown in Figure 1. The OH stretching band at 3460–3480 cm$^{-1}$ indicates the presence of free hydroxyl groups. There relative intensities were quite similar as they were formulated with similar hydroxyl value. The band observed at 2925 cm$^{-1}$ due to the —CH stretching. Typical ester C=O peak was observed at wavelength around 1730 cm$^{-1}$. The
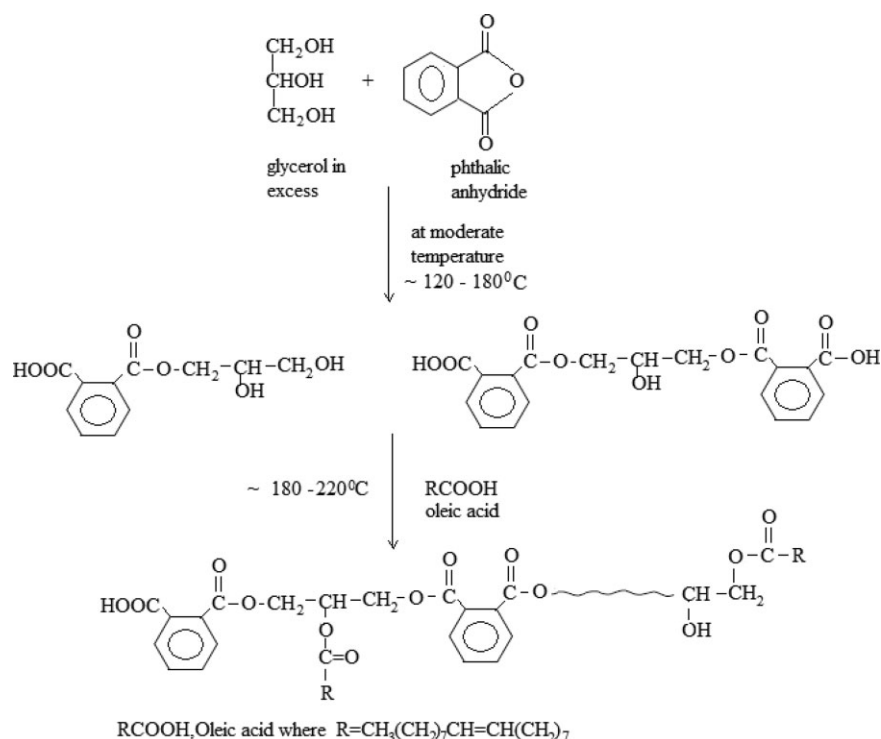


**Scheme 1** Reaction of phthalic anhydride, glycerol and oleic acid to form polyols.
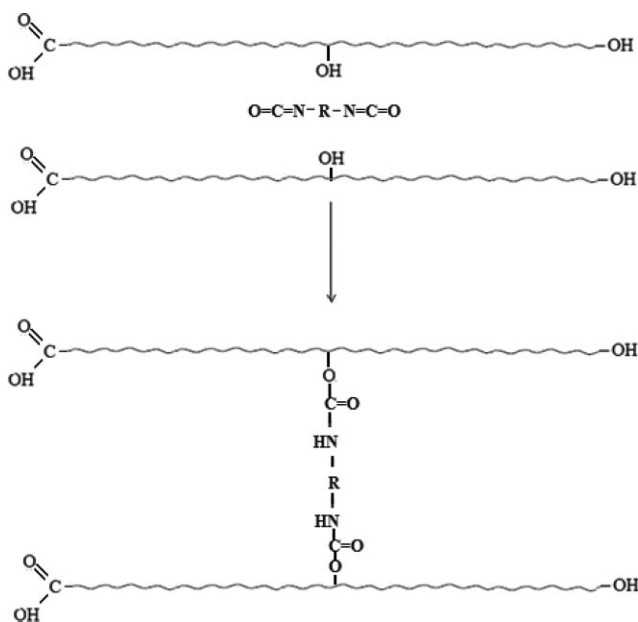
**Scheme 2** Reaction of polyols with isocyanates to form polyurethanes.

twin peak at 1580 and 1599 cm$^{-1}$ shows conjugation of C=O with an aryl group which is the phenyl ring from PA.

Structures of the PURs were studied by spectral analysis in Figure 2. IR spectra of PUalk28, PUalk40, and PUalk65 in the range of 3500–3150 cm$^{-1}$ show broader peak than the IR spectra of polyols Alk28, Alk40, and Alk65, and this phenomenon occurs presumably due to the overlapping of OH and NH groups. The absorption peaks resulting from NH stretching and bending vibrations were observed at 3350–3380 cm$^{-1}$ and 1540–1550 cm$^{-1}$, respectively. In the spectra, the characteristic of carbonyl stretching of C=O ester urethane linkage was observed at 1734–1745 cm$^{-1}$. The band observed at 2930–2940 cm$^{-1}$ was due to the —CH stretching. Benzene ring
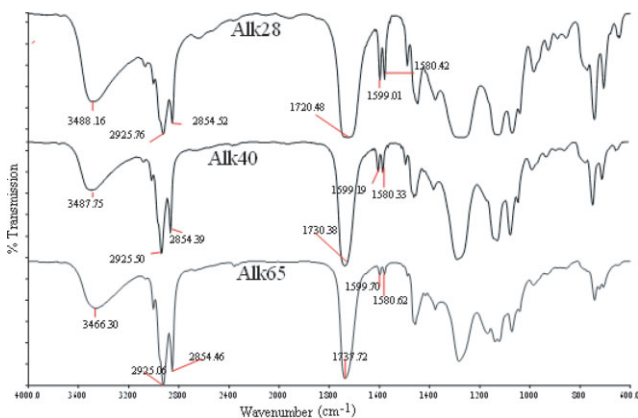


**Figure 1** IR spectra of oleic acid polyester polyols. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
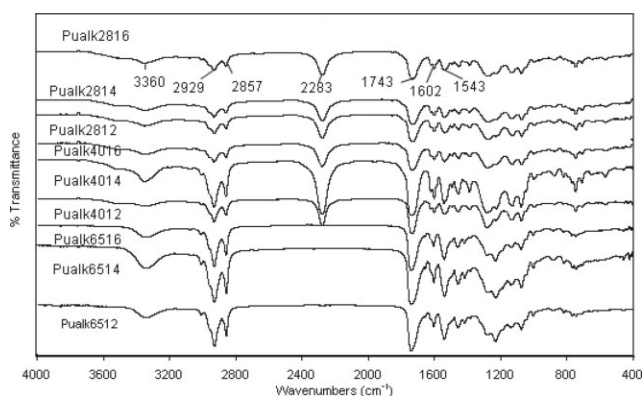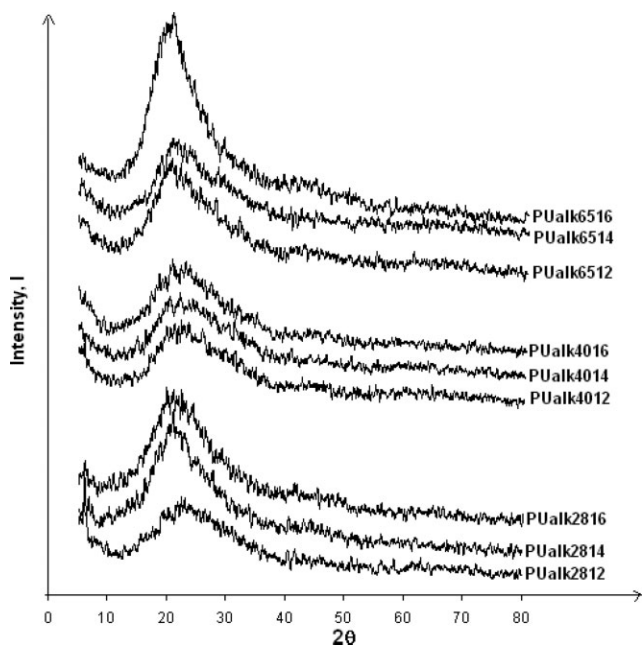


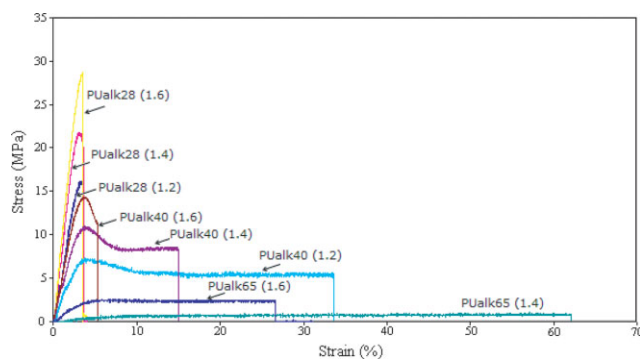**Figure 2** IR spectra of polyurethanes with various NCO/OH ratios.

and NH bending were indicated by their peaks at 1602, 1540, and 1550 cm$^{-1}$, respectively. The formation of PUR is clearly indicated due to the disappearance of —OH absorbance band of polyol and the appearance of a —NH band of PUR. The presence of isocyanurates (2283 cm$^{-1}$) from trimerization of isocyanates was observed for the sample at high NCO/OH ratio.

## XRD

XRD patterns for the nine PUR films are shown in Figure 3. The broad scattering halos between 5° and 80° of 2θ are observed. The diffraction patterns exhibit broad peaks at approximately 2θ = 23° for all samples which indicates that the samples are predominantly amorphous in nature at room temperature. However,



**Figure 3** X-ray diffraction profiles of polyurethanes with various NCO/OH ratios.

**Figure 4** Stress–strain curve of polyurethanes with various NCO/OH ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

it is expected that there might be some amount of crystalline phase due to the presence of hard segments. This small amount of crystallinity is overshadowed by the presence of long hydrocarbon chain of polyols and the hydrogen bonding between ─OCONH─ groups of PUR. Hence, the PUR exhibit overall amorphous character.[36]

## Mechanical properties

Stress–strain (%) curves obtained from tensile tests are displayed in Figure 4. The Alk28-based PUR (PUalk2812, PUalk2814, and PUalk2816) samples exhibited brittle fracture and very low elongation at break compared with the other PUR, but the tensile strength and modulus value are high. PUalk4012, PUalk4014, and PUalk4016 initially undergo elastic deformation followed by yielding and region of plastic deformation. PUalk65 follows the trend of an elastomer with high elongation but low modulus and tensile strength.

Mechanical properties such as tensile strength, rupture strength, elongation at break, and Young modulus ($E_{mod}$) of the PUR are given in Table IV. PUR made from Alk65 polyols shows poorer mechanical properties than those made from Alk40 and Alk28. The mechanical properties of PUR were gen-

erally accredited to the result of pseudocrosslinking effect due to the hard segment aggregation distributed in the soft matrix.[37] PURs are heterophase system composed of alternating aromatic urethane and polyols as macroglycol segments.[38] Incompatibility between the chemically dissimilar blocks prevents formation of homogeneous mixture, the urethane and macroglycol segments cluster into separate domains forming two phase system. Hard segments act as filler particles and crosslinks to restrain the motion of soft segment chains. This mechanism enhances the mechanical properties of PUR. Hard segments give high mechanical strength whereas soft segments give high extensibility and resiliency.

i. The effect of NCO/OH ratio

Results indicate that tensile strength, $E$ modulus, and rupture strength increases progressively with NCO/OH ratios although elongation decreased. The higher tensile strength is due to the higher rigidity imparted by the higher crosslink density and intermolecular interaction of the hard domain through hydrogen bonding.[39–41] As the NCO/OH ratio is increased from 1.2 to 1.6, more three-dimensional allophanate and isocyanurates crosslinks[42] will be formed. The increase of chemical crosslinking leads to a change in morphology[43] and affects the mechanical properties.[44] The increase of intermolecular attraction between hard segments, due to the increase of NCO/OH ratio, increases the stress property and decrease the strain property as shown in Figure 4. At higher degree of crosslinking, the polymer molecules are completely immobilized and become rigid thermoset plastic. Increased hydrogen bonding of the carbonyl group increases the phase mixing of soft and hard segment and in return increases the stress property and decreases the strain property.

ii. The effect of oleic acid content in polyols

The oleic acid is an unsaturated fatty acid and the functionality of the polyols is expected to be higher than two, due to the presence of

## TABLE IV
## Mechanical Properties of Polyurethanes

| Samples | Young modulus, $E_{mod}$ (MPa) | Tensile strength (MPa) | Rupture strength (MPa) | Elongation at break (%) |
|---|---|---|---|---|
| PUalk2812 | 683 ± 3 | 17 ± 2 | 16 ± 2 | 3.2 ± 0.3 |
| PUalk2814 | 805 ± 2 | 22 ± 1 | 22 ± 1 | 3.6 ± 0.3 |
| PUalk2816 | 1033 ± 4 | 30 ± 4 | 29 ± 4 | 3.5 ± 0.5 |
| PUalk4012 | 221 ± 5 | 7 ± 4 | 5 ± 3 | 34 ± 8 |
| PUalk4014 | 343 ± 1 | 11.2 ± 0.3 | 8.4 ± 0.2 | 15 ± 1 |
| PUalk4016 | 473 ± 4 | 14 ± 1 | 11 ± 0.8 | 5.4 ± 0.6 |
| PUalk6514 | 30 ± 1 | 1.1 ± 0.1 | 0.81 ± 0.03 | 60 ± 3 |
| PUalk6516 | 71 ± 2 | 2.61 ± 0.02 | 2.46 ± 0.07 | 26 ± 1 |

glycerol in the formulation of polyols. As the oleic acid content increases, there are more dangling side chains in the bulk of PUR polymers. These dangling chains may function as plasticizers and, therefore, decrease the modulus and tensile strength of the material. This may explain why the Alk65-based PUR have lower tensile properties and higher elongation compared with Alk28-based PUR. As expected Alk40-based PUR displays medium tensile properties, which were in between those of Alk28 and Alk60.

## CONCLUSIONS

In this study, three polyols from different oleic acid content were made. Nine different PUR samples were prepared from the polyols with NCO/OH ratios 1.2, 1.4, and 1.6. XRD results indicate that the samples are predominantly amorphous. Study on mechanical properties of the samples show that PURs made with polyols with the lowest oleic acid content, Alk28, have the best mechanical properties followed by Alk40 and Alk65. Furthermore, the mechanical properties of the samples increased as the NCO/OH ratio of the samples increased from 1.2 to 1.6 for all the samples.

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