

Synthesis of Urethane Oils from Palm Oil and Waste PET Bottles

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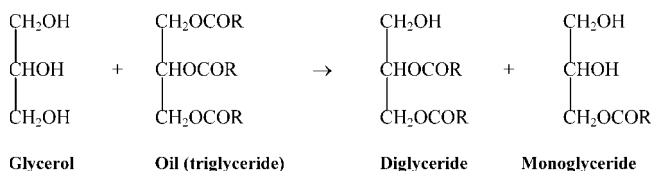
ABSTRACT: Waste PET bottles were depolymerized by propylene glycol at a weight ratio of PET to propylene glycol of 37.5 : 62.5, using zinc acetate as a catalyst. The glycolyzed product, consisting of oligomeric diols with a number-average molecular weight range of 240–1107, was obtained. It was further reacted with palm oil and tolylene diisocyanate to obtain urethane oils at hydroxyl to isocyanate ratios from 1 : 1 to 1 : 0.8, with and without methanol acting as a blocking agent. It was found that all the synthesized urethane oils were yellowish transparent liquids of low molecular weights. A lower isocyanate content or the presence of a blocking

agent resulted in higher viscosity, higher molecular weight, and shorter drying time. The films of all synthesized urethane oils exhibited good hardness, excellent flexibility, and high impact strength. They also showed excellent water resistance, good acid resistance but only fair alkali resistance. Moreover, these prepared urethane oils had better adhesion compared with those of the commercial urethane oil. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1802–1807, 2007

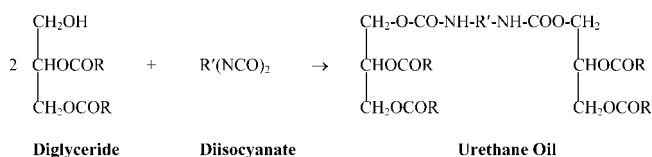
Key words: recycling; waste PET bottles; urethane oil; palm oil

INTRODUCTION

Urethane oil or uralkyd is an oil-modified polyurethane coating. It is prepared from the reaction between diisocyanate and mixture of mono- and diglycerides resulting from alcoholysis of oils, such as linseed oil, sunflower oil, etc.^{1–3} The following reactions shown below are one example of urethane oil synthesis¹:



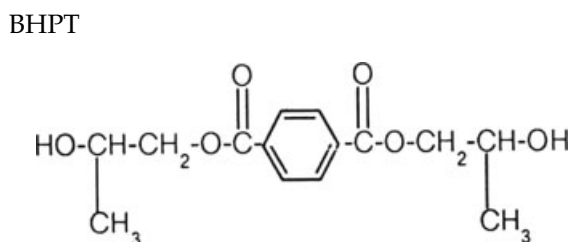
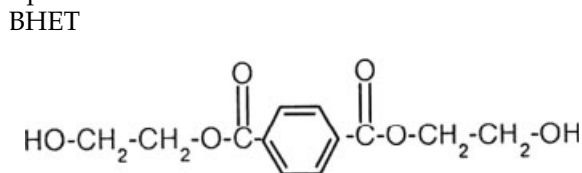
where R represents fatty acid chain (C₉–C₂₂).



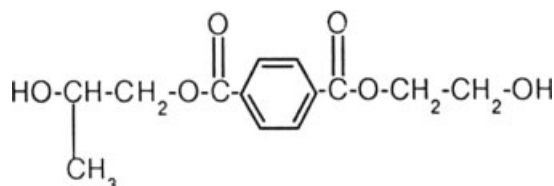
The properties of urethane oil films depend on the types of oil, polyol, and isocyanate used in preparation. For example, by substituting glycerol in the

previous reaction with a glycolyzed product of PET, a urethane oil was obtained.⁴

The glycolyzed product mentioned earlier is obtained from depolymerization of PET by glycolysis^{4–7} in excess propylene glycol. The components of the glycolyzed product are usually the monomers, dimers, trimers, and oligomers of bis(hydroxyethyl) terephthalate (BHET), bis(hydroxypropyl) terephthalate (BHPT), α -(2-hydroxyethyl)- α' -(2-hydroxypropyl) terephthalate whose structures are shown as follows:



α -(2-hydroxyethyl)- α' -(2-hydroxypropyl)terephthalate



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TABLE I
Formulas for Synthesizing Urethane Oils

Formula no. ^a	Glycolized product (g)	Palm oil (g)	TDI (g)	Xylene (g)	CaO (g)	Drier (g)	Methanol (g)
1-1	50	61.98	58.88	161.16	0.0465	0.1859	–
1-1b	50	61.98	58.88	161.16	0.0465	0.1859	1
1-0.9	50	55.78	52.99	145.04	0.0418	0.1673	–
1-0.9b	50	55.78	52.99	145.04	0.0418	0.1673	1
1-0.8	50	49.58	47.11	112.80	0.0372	0.1488	–
1-0.8b	50	49.58	47.11	112.80	0.0372	0.1488	1

^a Formula no. X–Y indicates molar ratio of hydroxyl groups in glycolized product to isocyanate groups in TDI where X = OH and Y = NCO. Formula no. X–Yb indicates the presence of methanol using as a blocking agent.

From previous work,⁴ the glycolized product was further reacted with soybean oil and toluene diisocyanate to obtain urethane oils. All the synthesized urethane oils were of low molecular weights and the properties in both liquid and dry film were comparable with those of a commercial urethane oil.

In this research, palm oil, the highest domestically produced vegetable oil in Thailand was used instead of soybean oil. Since the characteristics of palm oil are different from soybean oil, the properties of the synthesized urethane oils were investigated and compared with those of commercial urethane oil to study the possibility of using palm oil for urethane oil preparation.

EXPERIMENTAL

Materials

Waste PET flakes were obtained from grinding of postconsumer bottles. Analytical-grade propylene glycol (1,2-propane diol, PG) was purchased from Ajax Finechem (Auckland, New Zealand), whereas zinc acetate and calcium oxide (CaO) were purchased from Fluka (Buchs, Switzerland). Analytical-grade ethanol and methanol were purchased from Merck (Darmstadt, Germany) and Lab-Scan (Bangkok, Thailand), respectively. Commercial-grade palm oil and zirconium drier were supplied by Olean (Samut Sakorn, Thailand) and Siam Chemical Industries (Samutprakarn, Thailand), respectively. Toluene diisocyanate (TDI 80/20) consisting of 80% 2,4- and 20% 2,6- isomers was donated by Thai Mitsui Specialty Chemical (Chachoengsao, Thailand). Xylene was purchased from Panreac Quimica SA (Barcelona, Spain). All materials were used as received without further purification.

Methods

Glycolysis of PET

Waste PET flakes, PG (ratio of PET:PG = 37.5 : 62.5 w/w), and zinc acetate, 0.5% w/w of PET were

mixed in a 500-mL 4-necked-round-bottom flask connecting with a stirrer, a thermometer, a reflux condenser, and a nitrogen gas inlet. The mixture was heated to 190°C within 30 min and the reaction mixture was carried out at this temperature under reflux for 6 h in nitrogen atmosphere. After that, the mixture was allowed to cool to room temperature under nitrogen atmosphere and the glycolized product was obtained.

Characterization of glycolized product

The chemical structure of the glycolized product was analyzed using a Nicolet FTIR spectrophotometer (Model Impact 400; Nicolet Analytical Instruments, Madison, WI). Its hydroxyl values were determined based on ASTM D 4274 Method C. The molecular weight and molecular weight distribution were also characterized by GPC (Waters Model 1515; Milford, MA) using THF as solvent standard polystyrene as reference.

Synthesis of urethane oils

The amounts of all materials used in this step are given in Table I. Glycolized product and palm oil were mixed in a 500-mL 4-necked round bottom flask equipped with a stirrer, a thermometer, a reflux condenser, and a N₂ gas inlet. The mixture was stirred and heated to 200°C under nitrogen atmosphere followed by the addition of CaO. The temperature was then raised to 245°C, and the mixture was maintained at this temperature until a sample (1 part) was soluble in ethanol (2 parts). The mixture was cooled to 50°C and xylene at half of the amount in Table I was added. A solution of TDI and drier in another half amount of xylene was then slowly added. The mixture was heated at 75–80°C for 2 h to obtain the urethane oil.

In case of using methanol as a blocking agent, after preparing urethane oils according to the earlier method, methanol was added at the final step of the preparation.

Characterization of urethane oils

The chemical structures of all the prepared urethane oils were characterized using a Nicolet FTIR spectrophotometer (Model Impact 400). Their molecular weights and molecular weight distributions were also determined by GPC (Shimadzu Model 10 AVP; Duisburg, Germany) using THF as solvent and standard polystyrene as reference.

The viscosities were determined using Brookfield Viscometer. The colors were determined by comparison with the colors of standard Gardner solutions.

Acid values of these urethane oils were calculated based on ASTM D 1639. The drying times (with wet film thickness of 60 μm) were determined based on ASTM D 1640. Their solubilities in several solvents were also tested.

% Nonvolatile content (%NV) were calculated from the following equation after drying the sample at 105°C for 3 h.

$$\% \text{ NV} = 100 - [(A - B)/A \times 100]$$

where A is the weight of the sample before drying and B is the weight of the sample after drying.

Determination of film properties

Urethane oil films were formed by applying the oils on tin plate or glass panels depending on each standard test method using a film applicator. The samples were then subjected to the following tests including hardness (using a mechanical scratch test appara-

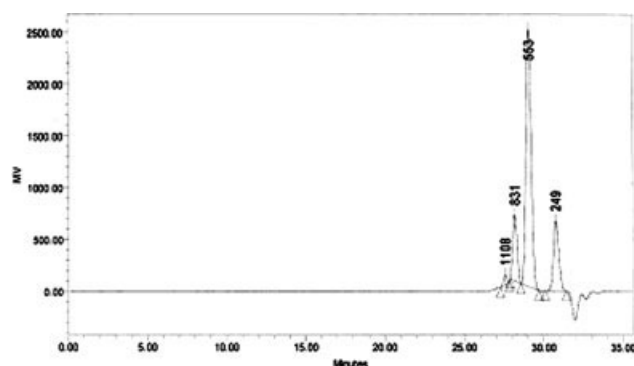


Figure 2 GPC chromatogram of the glycolized product.

tus; Sheen Instruments, Surrey, UK), flexibility (using a conical mandrel test apparatus; Sheen Instruments), adhesion (using crosscut tape method based on ASTM D 3359 Method B), and impact resistance (using impact tester; Sheen Instruments). Furthermore, water, acid, and alkali resistances were also analyzed based on ASTM D 1647. Their properties were then compared with those of commercial urethane oil "Burnock UL-65," which is a linseed oil-modified polyurethane resin supplied by Siam Chemical Industries.

RESULTS AND DISCUSSION

Glycolized product obtained from glycolysis of waste PET bottles in excess PG was a blue-green transparent viscous liquid. Its FTIR spectrum shown

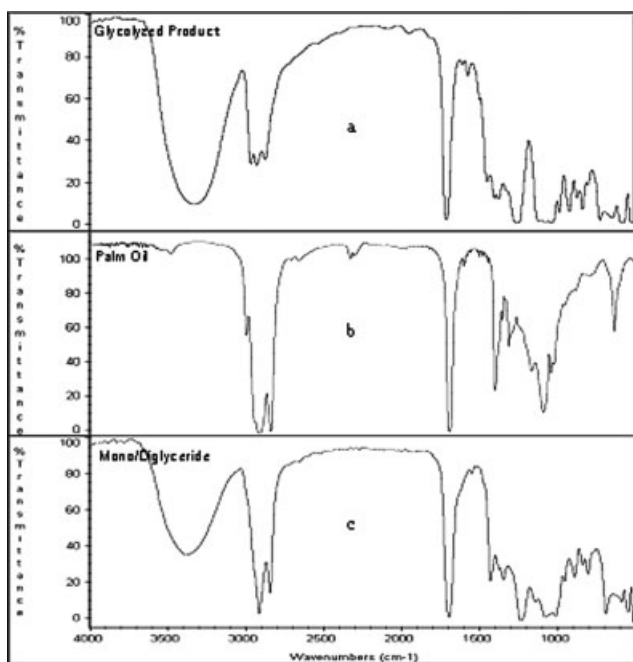


Figure 1 FTIR spectra of glycolized product (a), palm oil (b), and mono/diglycerides (c).

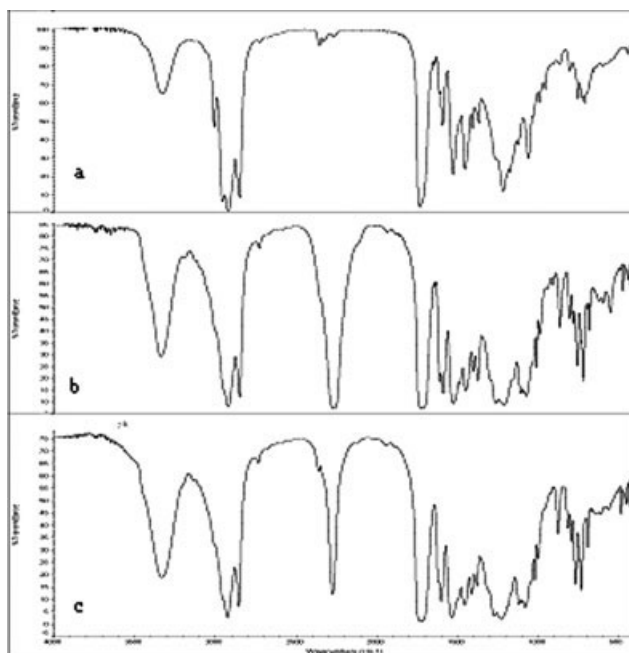


Figure 3 FTIR spectra of commercial urethane oil (a), synthesized urethane oils formula No. 1-0.8 (b), and 1-0.8b (c).

TABLE II
Molecular Weights and Molecular Weight Distributions of Synthesized and Commercial Urethane Oils

Parameter	Formula number						
	1-1	1-0.9	1-0.8	1-1b	1-0.9b	1-0.8b	Com ^a
M_n	897	1,052	1,227	1,100	1,148	1,861	6,158
M_w	1,422	1,879	2,613	2,069	2,823	5,533	75,113
MWD	1.59	1.79	2.13	1.88	2.46	2.97	12.20

^a Com, commercial urethane oil.

in Figure 1(a) exhibits peaks corresponding to OH stretching, CH stretching, C=O stretching, C—O—C stretching and C—OH stretching at wavenumber of 3358, 2972, 1720, 1275, and 1046 cm^{-1} , respectively. This indicates the presence of compound and/or compounds having hydroxyl and ester groups. It was previously reported that glycolized products of PET and PG usually composed of BHET, BHPT, α -(2-hydroxyethyl)- α' -(2-hydroxypropyl) terephthalate, and their dimers, trimers, and oligomers.^{4,5} GPC chromatogram of this glycolized product exhibits four peaks of low molecular weight compounds as shown in Figure 2. The peak corresponding to the number-average molecular weight of 240 (molecular weight at peak, $\overline{M}_p = 249$) can be attributed to BHET, BHPT, and α -(2-hydroxyethyl)- α' -(2-hydroxypropyl) terephthalate, whereas those of 548 ($\overline{M}_p = 553$), 828 ($\overline{M}_p = 831$), and 1107 ($\overline{M}_p = 1108$) are possibly assigned to dimers and oligomers of these monomers, respectively. This glycolized product had a hydroxyl value of 759.47 mg KOH/g, which is higher than that of BHET (441.5 mg KOH/g)³; hence, there are unreacted PG present in the product. This observation is in good agreement with that previously reported in the literature.⁷

The mixture of monoglycerides and diglycerides obtained from alcoholysis of palm oil with the glycolized product using CaO as a catalyst exhibits FTIR spectrum having peaks corresponding to those observed in FTIR spectra of glycolized product and

palm oil as shown in Figure 1. Confirmation of the existence of monoglycerides and diglycerides was done by solubility test in ethanol. It was found that the mixture completely dissolved in ethanol.

Urethane oils obtained from the reaction between TDI and the mixture of monoglycerides and diglycerides at various ratios exhibit FTIR spectra similar to that of the commercial urethane oil as shown in Figure 3. The characteristic peaks of urethane bonds occur at wavenumbers of 3341, 1732, and 1538 cm^{-1} . However, the FTIR spectra of the synthesized urethane oil show the characteristic peak of unreacted NCO groups at 2273 cm^{-1} , which was barely observed in the FTIR spectrum of the commercial urethane oil. This indicates that commercial urethane oil had the lowest amount of unreacted NCO groups. Moreover, when Formulae No. 1-0.8 and No. 1-0.8b were compared, the result also suggests that added methanol reacted with some NCO groups as same as previously reported⁴; consequently, less unreacted NCO groups were found in Formula No. 1-0.8b.

The molecular weights and molecular weight distributions of these urethane oils are given in Table II. It can be seen that as the amount of TDI decreases, the molecular weights of urethane oils increases. Furthermore, it can be seen that methanol-blocked urethane oils have slightly higher molecular weights than unblocked urethane oils. This may be

TABLE III
Characteristics of Synthesized and Commercial Urethane Oils

Formula no.	Color ^a (gardner)	Viscosity (cP)	% NV	Acid value	Solubility ^b			
					Xylene	White spirit	Butyl acetate	<i>n</i> -Butanol
1-1	3.5	40	49.78	4	√	X	√	X
1-0.9	2+	50	50.00	4	√	X	√	X
1-0.8	3-	111	50.90	3	√	X	√	X
1-1b	3-	52	49.76	4	√	X	√	X
1-0.9b	3-	53	52.40	4	√	X	√	X
1-0.8b	3-	420	53.73	3	√	X	√	X
Com ^c	3.5	1700	65.17	0.5	√	√	√	X

^a Colors from lighter to darker are in the order of 2+, 3-, 3, 3.5, and 3+, respectively.

^b √, soluble; X, insoluble.

^c Com, commercial urethane oil.

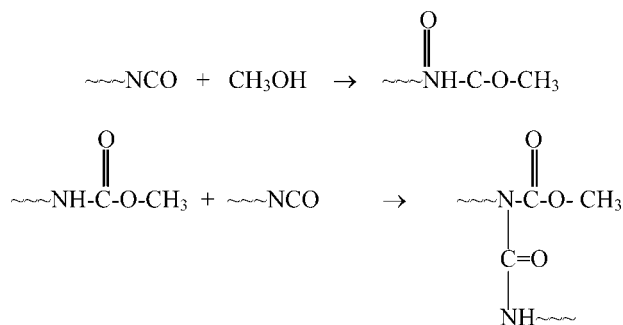
TABLE IV
Drying Time of Urethane Oil Films (h:min)

Formula no.	Drying time (hard dry) ^a
1-1	25:10
1-0.9	23:50
1-0.8	23:00
1-1b	23:40
1-0.9b	20:30
1-0.8b	19:50
Com ^b	18:06

^a Hard dry, after pressing and rotating finger on the film, no damage is observed.

^b Com, commercial urethane oil.

caused by adding methanol to polyurethane molecules, resulting in the following chain ends. These chain ends can further connect with other molecules via allophanate bonds as shown below:



However, it can be seen from this table that the molecular weights of all synthesized urethane oils are lower than that of the commercial one. This may be due to the differences in the reactants and the conditions that were used to synthesize urethane oils. As a result, the chemical structure as shown in Figure 3 and the molecular weight of the latter are different from those of the formers.

All synthesized urethane oils were transparent yellowish liquids with different viscosities depending on their molecular weights as indicated in Table III. These synthesized urethane oils have %NV in the range of 49.76–53.73%, which are lower than that of the commercial urethane oil, whereas their acid val-

ues are in the range of 3–4, which indicates that they are higher. They can dissolve in aromatic nonpolar solvent such as xylene and medium polar solvent such as butyl acetate but not dissolve in aliphatic nonpolar solvent such as white spirit and high polar solvent such as *n*-butanol. These characteristics of all synthesized urethane oils are slightly different from those of commercial oils as shown in Table III. This may be due to the difference in the compositions and the types of reactants used in urethane oil synthesis. This can be clearly seen from solubility properties, which indicate that the chemical structure of commercial urethane oil consists of both aliphatic and aromatic constituents; as a result, it can dissolve in both aliphatic and aromatic nonpolar solvents (white spirit and xylene). On the other hand, the chemical structures of synthesized urethane oils consist mainly of aromatic constituents (from glycolized product and TDI); therefore, they can dissolve only in aromatic nonpolar solvent, but not in aliphatic nonpolar solvent.

It was found, as shown in Table IV, that the drying time of urethane oil depends on the ratio between hydroxyl and isocyanate groups. It is clearly seen that as the amount of isocyanate decreases, the drying time also decreases. This is due to the fact that the formulae having lower amount of TDI have higher molecular weight (Table II), thus, they need less time to complete the reaction.^{8–10} In addition, the formulae having shorter drying time have lower amount of palm oil which is a nondrying oil (Table I). However, it can be seen that the synthesized urethane oils took longer time to dry than the commercial urethane oil. Since the commercial urethane oil has higher molecular weight and composed of linseed oil, which is a drying oil; consequently, it has the shortest drying time. It can be also seen that adding of methanol also decreases the drying time. This is because methanol can react with NCO groups as previously explained so the formulae containing methanol would take shorter time to dry than the formulae having no methanol.

From Tables V and VI, it can be seen that the films derived from synthesized urethane oils have good

TABLE V
Mechanical Properties of Urethane Oil Films

Property	Formula number						
	1-1	1-0.9	1-0.8	1-1b	1-0.9b	1-0.8b	Com ^a
Hardness (g)	600	700	600	600	600	700	700
Flexibility (ϕ , mm)	3	3	3	3	3	3	3
Adhesion	5B	5B	5B	5B	5B	5B	0B
Impact resistance (inch-pound)	160	160	160	160	160	160	160

^a Com, commercial urethane oil.

TABLE VI
Water, Acid, and Alkali Resistances of Urethane Oil Films

Substance	Formula number						
	1-1	1-0.9	1-0.8	1-1b	1-0.9b	1-0.8b	Com ^a
Water ^b	Ex ^c	Ex	Ex	Ex	Ex	Ex	Ex
Acid ^b	14 : 00	14 : 15	14 : 30	14 : 15	14 : 15	14 : 30	15 : 40
Alkali ^d	2 : 10	2 : 15	2 : 20	2 : 15	2 : 15	2 : 30	3 : 30

^a Com, commercial urethane oil.

^b Testing conditions, 24 h at room temperature.

^c Ex, excellent.

^d Time detected when films exhibited blistering after immersing in 5% NaOH.

hardness, excellent flexibility, high impact strength, excellent water resistance, good acid resistance but only fair alkali resistance. These properties are comparable with those of the film prepared from commercial urethane oil. Moreover, they exhibit superior adhesion than the commercial one.

All of these results suggest that it is possible to use waste PET bottles and palm oil, which is a non-drying oil to synthesize urethane oil that has the properties comparable to the commercial urethane oils that are currently used.

CONCLUSIONS

Waste PET bottles were depolymerized by glycolysis in excess propylene glycol using zinc acetate as a catalyst. The obtained glycolyzed product was then reacted with palm oil to form monoglycerides and triglycerides, which further reacted with TDI to obtain urethane oil. Results showed that all synthesized urethane oils are of low molecular weights and the properties in both liquid and dry film were comparable with those of commercial urethane oil. The results also showed that the ratio of hydroxyl to isocyanate groups and the presence of a blocking agent have significant effects on the drying time and the

molecular weights of the synthesized urethane oils, but they slightly affect other characteristics and properties.

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