

Synthesis of Urethane Oils from Waste Poly(ethylene terephthalate) Bottles

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ABSTRACT: Waste poly(ethylene terephthalate) (PET) bottles were glycolyzed by propylene glycol (PG) at a weight ratio of PET to PG 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 458–844, was obtained. It was further reacted with soybean oil and toluene diisocyanate to obtain urethane oils at hydroxyl to isocyanate ratios from 1 : 1 to 1 : 0.7, with and without methanol acting as a blocking agent. All the synthesized urethane oils were yellowish, transparent, low-viscosity liquids of low molecular weights. A lower diisocyanate

content and 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 and adhesion. They also showed excellent water and acid resistance but only fair alkali resistance. However, these prepared urethane oils had lower flexibility and poorer wear resistance compared to those of the commercial urethane oil. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3040–3045, 2004

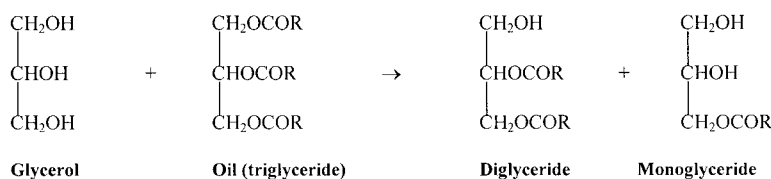
Key words: waste PET bottles; glycolysis; urethane oil

INTRODUCTION

Poly(ethylene terephthalate) (PET) wastes, including postconsumer wastes and wastes from manufacturing processes, have been chemically recycled by various methods. It can be depolymerized from high molecular weight molecules into low molecular weight substances by reactions such as glycolysis,^{1–3} alcoholysis,^{4–6} hydrolysis,^{7–9} and alkali decomposition.^{10,11} The products obtained from these reactions are predominantly the monomers of PET such as terephthalic acid (TPA), ethylene glycol (EG), or bis(hydroxyethyl)terephthalate (BHET).^{1–11} These products were found to be useful as reactants for preparations of other chemicals and polymers. For example, TPA obtained from alkali decomposition of PET was directly esterified with 2-ethyl-1-hexanol to obtain dioctyl terephthalate (DOTP), which can be

used as a plasticizer for poly(vinyl chloride).¹¹ Alternatively, disodium terephthalate and calcium terephthalate, obtained from the same reaction, are used as nucleating agents for isotactic polypropylene.¹² Furthermore, it was also found that BHET, obtained from glycolysis of PET, was reacted with maleic anhydride and then dissolved in styrene monomer to prepare unsaturated polyester resin.^{1–3} For this research, the possibility of preparing other products from these chemically recycled monomers was investigated. A product that has such potential to be developed is a urethane oil for surface coating.

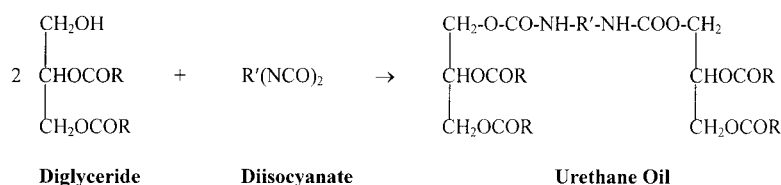
In general, urethane oil is prepared from the reaction between diisocyanate and a mixture of mono- and diglycerides resulting from alcoholysis of oils such as linseed oil and sunflower oil, for example.^{13–15} The following reactions constitute one example of urethane oil synthesis¹³:



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

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In glycolysis of PET, high molecular weight PET is depolymerized in excess glycols to yield glycolized products. The components of these glycolized products, depending on the type of glycol used, are predominantly the monomers and dimers of bis(hydroxyalkyl)terephthalate and terephthalates having fragments of different glycols in the same molecule.¹⁻³ By substituting glycerol in the previous reaction with these glycolized products, urethane oils are expected to be obtained.

Therefore, the main objective of this research was to synthesize urethane oils for surface coatings using glycolized products obtained from glycolysis of PET instead of commercial polyols. The properties of the synthesized urethane oils were also studied and compared with those of commercial urethane oil.

EXPERIMENTAL

Materials

Waste PET flakes were obtained from grinding of postconsumer bottles. Laboratory-grade propylene glycol (PG, 1,2-propane diol) was purchased from Ajax Chemical (Auburn, NSW, Australia). Zinc acetate, calcium oxide (CaO), and methanol were purchased from Fluka (Buchs, Switzerland). Soybean oil, a drier, and toluene diisocyanate (TDI 80/20; consisting of 80% 2,4- and 20% 2,6-isomers) were supplied by Siam Chemical Industries Co. (Samutprakarn, Thailand). Xylene was purchased from Labscan Asia (Bangkok, Thailand). Whereas xylene was distilled before use, all other 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 four-neck round-bottom flask equipped with a stirrer, a thermometer, a reflux condenser, and N₂ 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 a 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 D4274-94 Method C. The molecular weight and molecular weight distribution were also characterized by GPC using THF as solvent with an injection rate of 1 mL/min at 30°C.

Synthesis of urethane oils

The glycolized product and soybean oil were mixed in a 500-mL four-neck round-bottom flask equipped with a stirrer, a thermometer, a reflux condenser, and 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, after which xylene was added.

A solution of TDI and drier in xylene was added. The mixture was heated at 75 to 80°C for 2 h to obtain the urethane oil.

The amounts of all materials used in this step are given in Table I.

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 (Waters Model 150-cv; Milford, MA) using THF as solvent with an injection rate of 1 mL/min at 30°C.

The viscosities were determined using a Garner-Holdt bubble viscometer (Pacific Scientific, Silver Spring, MD). The colors were determined by comparison with the colors of standard Gardner solutions.

Acid values of these urethane oils were calculated based on ASTM D1639. The drying times (with wet film thickness of 60 μm) were determined based on ASTM D1640-95. Their solubilities in several solvents were also tested.

Percentage nonvolatile content (%NV) was calculated from the following equation, after drying the sample at 105°C for 3 h.

TABLE I
Formulas for Synthesizing Urethane Oils

Formula no. ^a	Glycolized product (g)	Soybean oil (g)	TDI (g)	Xylene (g)	CaO (g)	Drier (g)	Methanol (g)
1-1	50	44.89	42.65	116.72	0.0337	0.1347	—
1-1b	50	44.89	42.65	116.72	0.0337	0.1347	1
1-0.9	50	40.40	38.38	105.04	0.0303	0.1212	—
1-0.9b	50	40.40	38.38	105.04	0.0303	0.1212	1
1-0.8	50	35.92	34.12	93.38	0.0269	0.1077	—
1-0.8b	50	35.92	34.12	93.38	0.0269	0.1077	1
1-0.7	50	31.42	29.85	81.70	0.0236	0.0943	—
1-0.7b	50	31.42	29.85	81.70	0.0236	0.0943	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.

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

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 onto 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 apparatus; Sheen Instruments Ltd., Surrey, UK), flexibility (using a conical mandrel test apparatus; Sheen Instruments Ltd.), adhesion (using a crosscut tape method based on ASTM D3359-95 Method B), and wear resistance (using wet abrasion scrub tester; Sheen Instruments Ltd.). Furthermore, water, acid, and alkali resistances were also analyzed based on ASTM D1647-89. Their properties were then compared with those of commercial urethane oil supplied by Siam Chemical Industries Co.

RESULTS AND DISCUSSION

The glycolized product, obtained from glycolysis of waste PET bottles in excess PG, was a blue-green transparent viscous liquid. Its FTIR spectrum shows peaks corresponding to OH stretching, CH stretching, C=O stretching, C—O—C stretching, and C—OH stretching at wavenumbers of 3355, 2925, 1723, 1266, and 1111 cm^{-1} , respectively. This indicates the presence of compound and/or compounds having hydroxyl and ester groups. Analysis of this glycolized product by GPC indicated that it consists of low molecular weight compounds in which the number-average molecular weight varied between 458 and 844, as shown in Figure 1. It was previously reported that glycolized products of PET and PG are usually composed of BHET, bis(hydroxypropyl)terephthalate (BHPT), α -(2-

hydroxyethyl)- α' -(2-hydroxypropyl)terephthalate and their dimers, trimers, and oligomers.¹ By calculating the molecular weights of these monomers and their oligomers and comparing them with those obtained from this research, the results suggest that the glycolized product also consists of these compounds. This glycolized product had a hydroxyl value of 549.93 mg KOH/g, which is higher than that of BHET (441.5 mg KOH/g)³; thus, there is unreacted PG present in the product. This observation is in good agreement with that previously reported in the literature.³

The FTIR spectrum of the mixture of monoglycerides and diglycerides, obtained from alcoholysis of soybean oil with the glycolized product using CaO as a catalyst, exhibits peaks corresponding to those observed in the FTIR spectra of glycolized product and soybean oil. Confirmation of the existence of monoglycerides and diglycerides was done by solubility testing in ethanol. It was found that the mixture completely dissolved in ethanol.

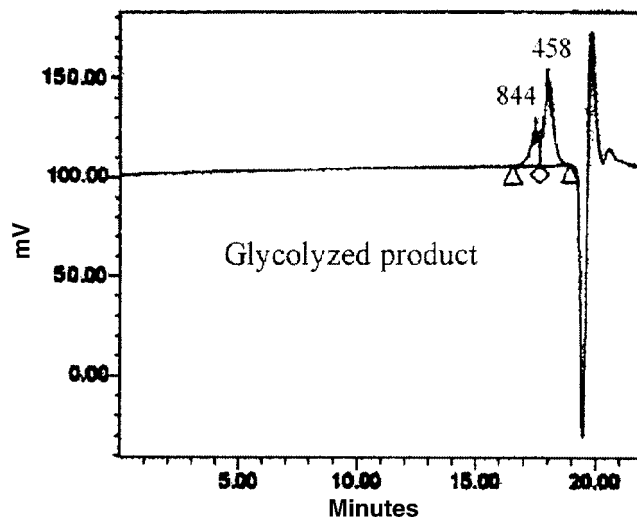


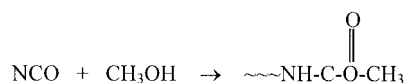
Figure 1 GPC chromatogram of the glycolized product.

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	1-0.7	1-1b	1-0.9b	1-0.8b	1-0.7b	Com ^a
\bar{M}_n	1621	2033	2303	2459	1648	2059	2125	2669	48,281 2882
\bar{M}_w	2668	4668	6107	8364	2757	5581	6709	9564	126,411 4346
MWD	1.65	2.30	2.65	3.40	1.65	2.71	3.16	3.58	2.62 1.51

^a Com, commercial urethane oil.

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 commercial urethane oil. For example, the FTIR spectra of commercial and synthesized urethane oils Formula No. 1-1 and No. 1-1b show characteristic peaks of urethane bonds at wavenumbers of 3328, 1723, and 1528 cm^{-1} . They also exhibit a characteristic peak of unreacted NCO groups at 2273 cm^{-1} . However, the intensities of this peak decrease in the order of Formula no. 1-1 > no. 1-1b > commercial. This indicates that commercial urethane oil had the lowest amount of unreacted NCO groups. Moreover, when Formula no. 1-1 and no. 1-1b were compared, the result also suggests that added methanol reacted with some NCO groups as shown below; consequently, fewer unreacted NCO groups were found in Formula no. 1-1b.



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 increases, the molecular weights of urethane oils decrease. Furthermore, it can be seen that methanol-blocked urethane oils have slightly higher molecular weights than those of unblocked urethane oils. This may be caused by adding methanol to polyurethane molecules, resulting in urethane chain ends, as shown in the previous reaction, which slightly increases their molecular weights. In addition, these chain ends can further connect with other molecules by allophanate bonds as shown in the following scheme:

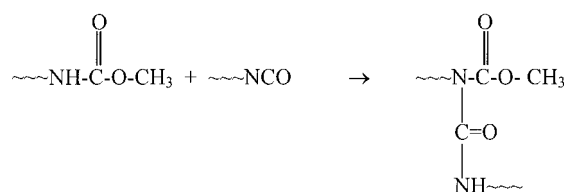


Table II also shows that commercial urethane oil has two different average molecular weights, whereas each of the remaining synthesized urethane oils has a single average molecular weight. This phenomenon may be attributable to the difference in the composi-

TABLE III
Characteristics of Synthesized and Commercial Urethane Oils

Formula no.	Color ^a (Gardner)	Viscosity (Stokes)	%NV	Acid value	Solubility ^b			
					Xylene	White spirit	Butyl acetate	<i>n</i> -Butanol
1-1	4	A = 0.50	49.49	3	✓	X	✓	X
1-0.9	3+	O = 3.70	51.34	2	✓	X	✓	X
1-0.8	3+	S = 5.00	52.23	2	✓	X	✓	X
1-0.7	3.5	U = 6.27	52.86	2	✓	X	✓	X
1-1b	3.5	B = 0.65	50.88	2	✓	X	✓	X
1-0.9b	3.5	R = 4.70	51.43	2	✓	X	✓	X
1-0.8b	3-	T = 5.50	53.05	1	✓	X	✓	X
1-0.7b	3-	V = 8.84	52.90	2	✓	X	✓	X
Com ^c	4	Z-Z ₃ = 22.7-46.3	59.0-61.0	1	✓	✓	✓	X

^a Colors from lighter to darker are in the order of 3-, 3, 3.5, 3+, 4-, and 4, respectively.

^b ✓, soluble, X, insoluble.

^c Com, commercial urethane oil.

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

Condition	Formula number								
	1-1	1-0.9	1-0.8	1-0.7	1-1b	1-0.9b	1-0.8b	1-0.7b	Com ^a
Touch dry ^b	1 : 47	0 : 13	0 : 11	0 : 10	1 : 18	0 : 10	0 : 09	0 : 07	0 : 06
Tack-free dry ^c	3 : 48	0 : 48	0 : 36	0 : 31	3 : 18	0 : 24	0 : 18	0 : 13	0 : 13
Hard dry ^d	7 : 07	4 : 37	2 : 00	1 : 50	5 : 08	1 : 44	1 : 38	1 : 35	1 : 08

^a Com, commercial urethane oil.

^b Touch dry: after soft touching of the film by finger, no fingerprint is observed.

^c Tack-free dry: after soft pressing of the film by finger, no fingerprint is observed.

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

tions and the types of reactants used in urethane oil synthesis.

All synthesized urethane oils were transparent yellowish liquids with different viscosities, depending on their molecular weights. It can be seen that as the molecular weight increases, the viscosity also increases. These urethane oils have acid values in the range of 1–3 and %NV in the range of 49.49–53.05%. They can dissolve in an aromatic nonpolar solvent such as xylene and a medium polar solvent such as butyl acetate but cannot dissolve in an aliphatic nonpolar solvent such as white spirit or in a 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 attributed 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 an aromatic nonpolar solvent but not in an 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 attributed to the fact that drying of urethane oil film occurs from the oxidation of soybean oil and the reaction between the remaining NCO groups and moisture in the atmosphere.^{16–18} Therefore, the formulas having lesser amounts of soybean oil and TDI took a shorter time to dry than did the formulas having greater amounts of soybean oil and TDI (Table I). In addition, the formulas having a shorter drying time have less volatile content (higher %NV, Table III); thus, they need less time for solvent evaporation. Because commercial urethane oil has the lowest amount of unreacted NCO groups and the highest %NV, it consequently has the shortest drying time. Moreover, it can be seen that the addition of methanol also decreases the drying time. This is because methanol can react with NCO groups, as previously explained, so the formulas containing methanol would take a shorter time to dry than would the formulas having no methanol.

From Tables V and VI, it can be seen that the films derived from synthesized urethane oils have good adhesion, good hardness, excellent water and acid resistance, but only fair alkali resistance. These properties are comparable to those of the film prepared from commercial urethane oil. However, they exhibit poorer flexibility and wear resistance than those of the commercial urethane oil-derived film. This may be a result of the higher amount of stiff aromatic structure present in the former, whereas the latter have higher amounts of flexible aliphatic structure, as previously mentioned.

TABLE V
Mechanical Properties of Urethane Oil Films

Property	Formula number								
	1-1	1-0.9	1-0.8	1-0.7	1-1b	1-0.9b	1-0.8b	1-0.7b	Com ^a
Hardness (g)	200	200	100	100	100	100	100	100	100
Flexibility (\varnothing , mm)	20	20	20	20	20	20	20	20	3
Adhesion	5B	5B	4B	3B	4B	4B	4B	4B	5B
Wear resistance (cycle)	50	40	40	45	49	50	52	50	147

^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	1-0.7	1-1b	1-0.9b	1-0.8b	1-0.7b	Com ^a
Water ^b	Ex ^c	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
Acid ^b	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex	Ex
Alkali ^d	30 min	30 min	35 min	25 min	30 min	30 min	25 min	25 min	30 min

^a Com, commercial urethane oil.

^b Testing conditions: 24 h at room temperature.

^c Ex, excellent.

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

All of these results suggest that it is possible to synthesize urethane oil for surface coating using glycolized product obtained from chemical recycling of waste PET bottles. By further modification of some properties, the synthesized urethane oil can be replaced by 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 glycolized product was then reacted with soybean oil to form monoglycerides and diglycerides, which further reacted with TDI to obtain urethane oil. Results showed that all synthesized urethane oils are of low molecular weight and the properties in both liquid and dry film were comparable to those of a 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 only slightly affect other characteristics and properties.

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