Synthesis of Waterborne Polyurethane Coatings Using A Surfactant Derived From Recycling of Waste PET Bottles

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Waterborne polyurethane coatings were synthesized by emulsion polymerization of linseed oil-modified polyurethane and acrylic monomers using various amounts of surfactant prepared from the reaction of poly (ethylene glycol), toluene diisocyanate, ethylene glycol and castor oil. The ethylene glycol used in this research was a byproduct from alkali decomposition of PET bottles using sodium hydroxide in anhydrous media. It was found that at 180°C and with a reaction time of 1 hour, the percent decomposition of PET was 94.9%. The obtained ethylene glycol had a purity of 92.7% and the prepared surfactant had a critical micelle concentration of 0.003 mol/l. All coatings synthesized from this surfactant were milk-like liquids and gave films with good flexibility, good adhesion, excellent water resistance but fair alkali and acid resistances. Furthermore, the results also showed that at 0.003 mol/l of the surfactant, the coating exhibited better properties than those prepared with other surfactant concentrations.

Keywords: PET, ethylene glycol, surfactant, polyurethane, waterborne coating.

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การสังเคราะห์สารเคลือบผิวพอลิยูรีเทนสูตรน้ำโดยใช้สารลดแรงตึงผิวที่เตรียมได้จากการรีไซเคิลขยะขวดเพท

เสาวรจน์ ช่วยจุลจิตร์ วิมลวรรณ พิมพ์พันธุ์ พรทิพย์ แซ่เบ๊ รัตนวดี ถิตย์สถาน และ รัตนา สุรชัยเกษม (2546)

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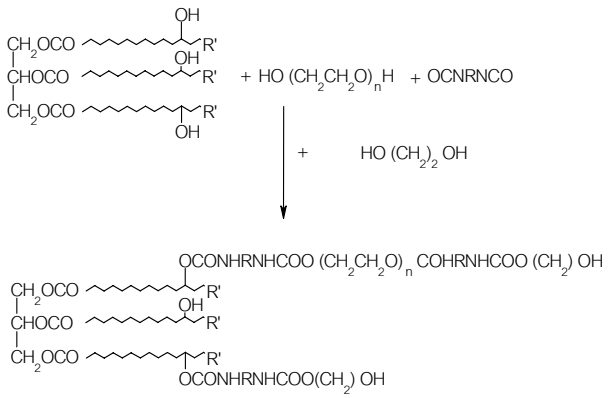
สารเคลือบผิวพอลิยูรีเทนสูตรน้ำถูกสังเคราะห์ด้วยกระบวนการอิมัลชันพอลิเมอไรเซชันจากพอลิยูรีเทนที่ดัดแปรด้วยน้ำมันลินสีดและอะคริลิกมอนอเมอร์ โดยใช้สารลดแรงตึงผิวในปริมาณต่างๆ กัน ซึ่งสารลดแรงตึงผิวนี้เตรียมได้จากปฏิกิริยาระหว่างพอลิเอทิลีนไกลคอล โทลูอีนไดไอโซไซยาเนต เอทิลีนไกลคอลและน้ำมันละหุ่ง โดยเอทิลีนไกลคอลที่ใช้ในงานวิจัยนี้เป็นผลพลอยได้จากการย่อยสลายขวดเพทที่ใช้แล้วด้วยกระบวนการอัลคาไลน์ดีคอมโพซิชัน ซึ่งใช้โซเดียมไฮดรอกไซด์ในตัวกลางที่ปราศจากน้ำ จากการทดลองพบว่า สามารถย่อยสลายขวดเพทได้ร้อยละ 94.9 ที่อุณหภูมิ 180 องศาเซลเซียส ภายในเวลา 1 ชั่วโมง เอทิลีนไกลคอลที่ได้มีความบริสุทธิ์ร้อยละ 92.7 และสารลดแรงตึงผิวที่เตรียมได้มีค่าความเข้มข้นไมเซลวิกฤต 0.003 โมล/ลิตร สำหรับสารเคลือบผิวที่สังเคราะห์จากสารลดแรงตึงผิวดังกล่าวทุกสูตรมีลักษณะเหมือนน้ำนมและฟิล์มของสารเคลือบผิวมีความอ่อนตัว สามารถติดแน่นได้ดี มีความทนน้ำดีเยี่ยม มีความทนด่างและทนกรดปานกลาง ทั้งนี้สารเคลือบผิวที่สังเคราะห์จากสูตรซึ่งใช้ความเข้มข้นของสารลดแรงตึงผิวเป็น 0.003 โมล/ลิตร จะให้ฟิล์มที่มีสมบัติต่างๆ ดีกว่าสารเคลือบผิวที่สังเคราะห์จากสูตรอื่น

คำสำคัญ เพท เอทิลีนไกลคอล สารลดแรงตึงผิว พอลิยูรีเทน สารเคลือบผิวสูตรน้ำ

INTRODUCTION

It is known that the waste management of post-consumer products made from synthetic polymers can be difficult. Burning of these products may result in releasing dangerous gases to the atmosphere while burying them in soil cannot destroy the products because they are only slowly biodegradable. Therefore, alternative methods are being currently developed.

One method is to convert high molecular weight polymers into low molecular weight substances via chemical reactions, called "chemical recycling." Poly (ethylene terephthalate) or 'PET' is one of the synthetic polymers being extensively chemically recycled. This is because it is widely used in packaging applications especially in water and soft-drink bottle industries due to its clarity, light weight and selective gas permeability.[1] Consequently, its waste is continuously increasing. Previous studies have found that PET can be depolymerized by various reactions such as glycolysis,[2-4] alcoholysis,[5-7] hydrolysis[8-10] and alkali decomposition.[11,12] 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).[2, 12] These products can be used as the reactants for preparations of other chemicals and polymers such as dioctyl terephthalate, a plasticizer for PVC,[12] and unsaturated polyester resin.[2,4]



Scheme 1. Synthesis of PU Surfactant.

A chemical of interest is the polyurethane (PU) surfactant which is generally synthesized from EG, toluene diisocyanate, poly(ethylene glycol) and castor oil as shown in Scheme 1.[13] In this research, the EG used in the surfactant synthesis was obtained from alkali decomposition of waste PET bottles using NaOH as a catalyst in non-aqueous EG.[11, 12] The depolymerization yields EG and sodium terephthalate which can be changed into TPA by reacting with an acid. EG is recovered by distillation as shown in Scheme 2.[12]

PET + excess EG

↓ NaOH

$Na^+ {}^-O_2CC_6H_4CO_2^- Na^+$ + EG

↓ H^+

$HOOCC_6H_4COOH$

Scheme 2. Alkali Decomposition of PET.

The obtained polyurethane surfactant can be used as emulsifier in preparation of a waterborne polyurethane coating via an emulsion system. In general, normal coatings are organic solvent-based coatings. The curing process involving the evaporation of an organic solvent causes air pollution. On the other hand, waterborne coating is more environmentally friendly since water is the component that evaporates. However, the dispersion of hydrophobic components in water in the preparation process is difficult to achieve. Therefore, an emulsifier is needed in order to obtain a well dispersed and stable mixture.

This research also emphasizes the determination of the proper amount of the surfactant which should be used in order to obtain the coating with suitable properties.

MATERIALS AND METHODS

Materials

Waste PET bottles, both water and soft-drink bottles, were used in this research. Ethylene glycol (EG) (commercial grade) was obtained from Tuntex (Thailand) Co., Ltd., while poly(ethylene glycol) (PEG) having molecular weight of 4,600 was donated from Union Carbide Thailand Co. Castor oil, linseed modified polyurethane (OMPU), dibutyltin dilaurate and toluene diisocyanate (TDI) which were commercial grade were donated by Siam Chemical Industries Co. Methyl methacrylate (MMA), acrylic acid (AA) and butyl acrylate (BA) were commercial grade and were obtained from Lenso Asia Co. Sodium hydroxide (NaOH), acetone, potassium persulfate and benzoyl peroxide (BPO) were laboratory grade and were purchased from Fluka Co. All chemicals were used as received without further purification.

Methods

Depolymerization of PET

Ground PET bottles 38.4 g, EG 200 ml and NaOH 16.8 g were mixed in 500 ml 4-necked round bottom flask connecting with a stirrer, a thermometer, a condenser and a N_2 gas inlet. The reaction was carried out at 180°C under reflux for 1 hour under nitrogen. The solution was allowed to cool down to room temperature. The precipitated unreacted PET was

removed from the solution by filtration. This unreacted PET was dried at 100°C for 6 hours and weighed. EG was distilled from the remaining solution at 190°C.

Percent decomposition (%D) was calculated from the following equation:

$$\%D = [(PET_i - PET_t) / PET_i] \times 100$$

when PET_i = Initial weight of PET used for the reaction

PET_t = Weight of unreacted PET

Characterization of EG

The chemical structure of EG was characterized by FT-IR spectroscopy using FT-IR spectrometer Model Nicolet-Impact 400.

Its purity was determined by gas chromatography using nitrogen as carrier gas at a rate of 50 mm/min and a temperature of 250°C.

Synthesis and Characterization of Polyurethane Surfactant

PEG 46 g and castor oil 2.98 g were mixed in 500 ml 4-necked round bottom flask fitted with a stirrer, a thermometer, a condenser and a N_2 gas inlet. Acetone 150 ml was poured into the flask and the mixture was heated at 50°C and stirred until PEG completely dissolved. TDI 5.22 g and dibutyltin dilaurate 0.001 g were added to the flask. The mixture was heated at 50°C for 3 hours under nitrogen. 1.24 g of EG was then poured into the flask and the reaction was maintained at 50°C for 1 hour. Acetone was evaporated from the solution and the solid polyurethane (PU) surfactant was obtained.

Critical micelle concentration (CMC) and the chemical structure of the obtained PU surfactant were analyzed using KRUSS surface tension analyzer Model K8 and FT-IR spectrometer Model Nicolet-Impact 400.

Synthesis and Characterization of Waterborne Polyurethane (PU) Coatings

The amounts of all chemicals used in this step are given in Table 1. In this step, MMA, AA, BA, OMPU and BPO were mixed together using a mechanical stirrer for 3 hours. The aqueous solution of PU surfactant was added to the mixture. After stirring with a mechanical stirrer for 5 minutes, the mixture was ultrasonicated at a frequency of 47 kHz for 45 minutes in order to make the mixure homogeneous. After that, the mixture was poured into a 500 ml 4-necked round bottom flask fitted with a stirrer, a thermometer, a condenser and a N_2 gas inlet. An aqueous solution of potassium persulfate was added to the mixture and the mixture was heated at 80°C for 3 hour under nitrogen. After cooling down to room temperature, a waterborne PU coating was obtained.

Its chemical structure was determined by FT-IR spectroscopy using FT-IR spectrometer Model Nicolet-Impact 400.

Table 1. The amounts of the chemicals used in synthesis of waterborne PU coatings.

Chemicals	Formula No.				
	1	**2**	**3**	**4**	**5**
OMPU (g)	30	30	30	30	30
MMA (g)	49	49	49	49	49
AA (g)	1	1	1	1	1
BA (g)	50	50	50	50	50
BPO (g)	0.5	0.5	0.5	0.5	0.5
Water (g)	300	300	300	300	300
Potassium Persulfate (g)	2.7	2.7	2.7	2.7	2.7
PU Surfactant (mol/l)	0.01	0.003	0.001	0.0003	0.0001

Film Formation and Properties of Waterborne PU Coating Film

Drying Time

PU coating was applied to a metal plate using an applicator to give a wet film with a thickness of 90 microns. The drying time was determined based on ASTM D1640-95.

Hardness

PU coating was applied to a tin-coated metal plate using an applicator to give a wet film with a thickness of 90 microns and it was left to dry at room temperature. It was subjected to a mechanical scratch test. The hardness of a film is defined as the minimum weight that makes the needle of the tester penetrate the film.

Flexibility

Test samples prepared using the same method as for hardness test were bent around cones of a conical mandrel tester. These cones have diameters of 3-37 mm and length of 200 mm. The flexibility of a film is defined as a diameter that causes defects on the film.

Adhesion

Test samples prepared using the same method as for hardness test were subjected to a cross-cut tape test using a cross hatch cutter based on ASTM D 3359-95 Method B in order to determine the adhesive property.

Impact Resistance

Test samples prepared using the same method as for hardness test were placed in an impact tester. A weight of 4 pounds was droped on the test samples from different heights.

Water Resistance

Water resistance of the test samples prepared using the same method as for hardness test were determined based on ASTM D 1647-89.

Acid and Alkali Resistances

Acid and alkali resistances of test samples prepared using the same method as for hardness test were determined based on ASTM D 1647-89.

RESULTS AND DISCUSSION

94.9% alkali decomposition of waste PET bottles resulted in a transparent and slightly yellow liquid before distillation. After distillation at 190°C, a transparent colorless liquid was obtained. When FT-IR spectra of both liquids were compared to that of standard EG as shown in Figure 1, it can be seen that their spectra are similar. They exhibit peaks at wavenumbers of 3,400 cm^{-1}, 2,925 cm^{-1} and 1,091 cm^{-1} which correspond to OH, CH_2 and CO stretchings, respectively. This suggests that both liquids were EG. Since the latter liquid has higher purity (92.7%), it was used for synthesis of PU surfactant.

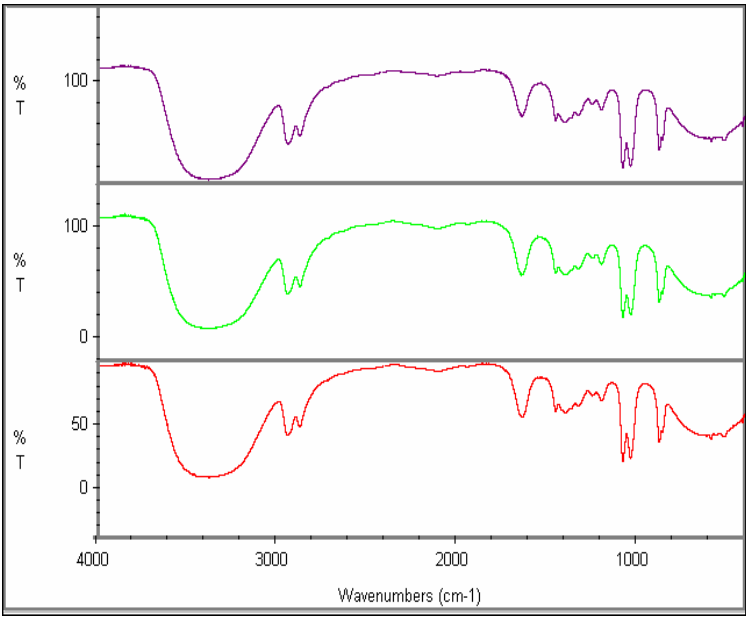


Figure 1. FT-IR spectra of standard EG (top), EG before distillation (middle) and EG after distillation.

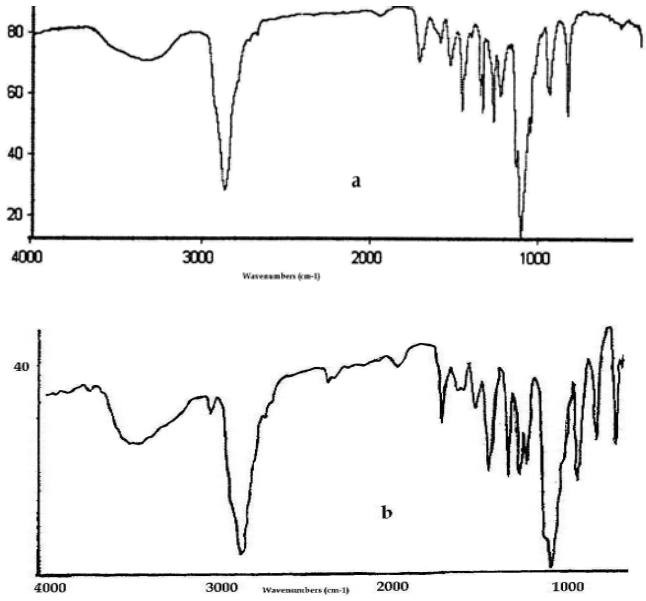


Figure 2. FT-IR spectra of polyurethane surfactants synthesized from recycled EG (a) and pure EG[13] (b).

The PU surfactant obtained from the reaction between PEG, TDI and castor oil using dibutyltin dilaurate as a catalyst and acetone as a solvent followed by termination of the chain ends with EG and evaporation of acetone was a yellow solid. Its FT-IR spectrum in Figure 2-a shows a peak at wavenumber around 3,400 cm^{-1} corresponding to OH stretching, indicating the presence of OH groups at the chain ends resulting from the termination with EG as previously mentioned. While peaks at 1,723 cm^{-1} which corresponds to C=O and around 3,200 cm^{-1} which corresponds to NH stretching indicates the presence of urethane linkages (-NHCOO-). Furthermore, peaks at 2,925 cm^{-1} and 1,112 cm^{-1} which correspond to CH_2 and CN stretchings were also observed. These resemble those of PU surfactant prepared from pure EG previously reported by Ismail[13] as shown in Figure 2-b.

The CMC of this surfactant determined from a plot of surface tension and surfactant concentration, as shown in Figure 3, is 0.003 mol/l.

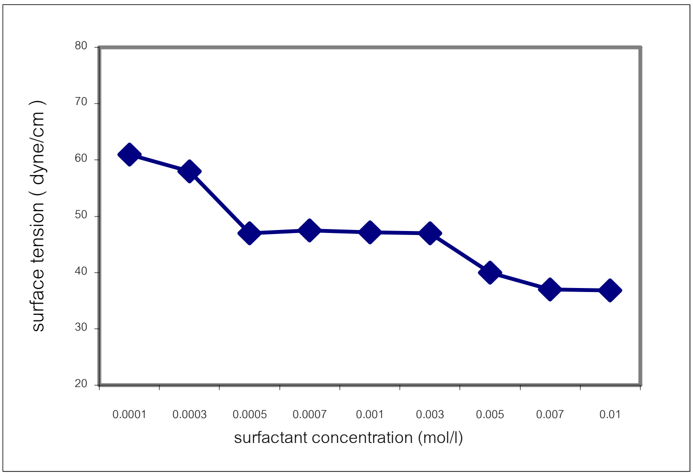


Figure 3. Relationship between surfactant concentration and its surface tension.

All waterborne PU coatings synthesized from OMPU and acrylic monomers via emulsion polymerization using the prepared PU surfactant as an emulsifier were milk-like liquids. An example of the FT-IR spectrum of the coating is shown in Figure 4. It can be seen that peak corresponding to C=O of urethane linkage of PU components is observed at wavenumber of 1,715 cm^{-1} while the peak corresponding to the C=O of an ester linkage of acrylic monomers is observed at wavenumber of 1,600 cm^{-1}. The peak at wavenumber of 1,183 cm^{-1} corresponds to the CN stretching which indicates the presence of PU components in the coating. The broad peak at wavenumber range 3,200-3,600 cm^{-1} is due to water contamination since this coating is water-based.

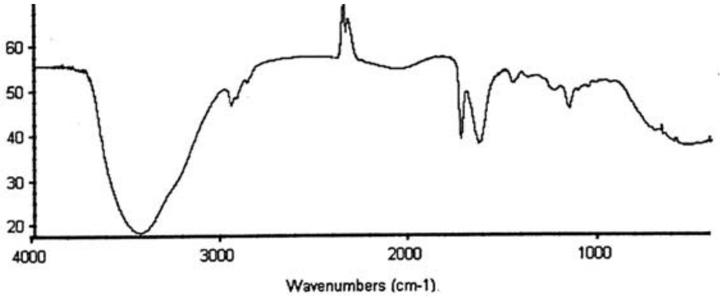


Figure 4. FT-IR spectrum of synthesized waterborne polyurethane coating.

After applying all waterborne PU coatings onto tin-coated metal plates and allowing them to dry at room temperature, it was found that the drying time for all coating was 3 days. Unfortunately, coatings No. 4 and 5 did not form the films but exhibited aggregation of the solid components. This may because the concentrations of PU surfactant used were not enough to emulsify the polymers in the water phase. Therefore, only coatings No. 1-3 were selected for futher studies.

Tables 2 and 3 show the properties of the films prepared from the synthesized waterborne PU coatings and from a commercial PU coating. It can be seen that synthesized PU films exhibit mechanical properties which are comparable to those of commercial PU except for hardness. All PU films show excellent water resistance. However, synthesized PU films have lower acid resistance than commercial PU film but their alkali resistance was comparable. The differences in mechanical and chemical properties between synthesized and commercial PU films may be caused by the differences in reactant compositions of these films. [14]

Furthermore, the results also suggest that a proper concentration of PU surfactant should be used for the synthesis of PU coatings in order to obtain PU films with properties that are comparable to those of the film prepared from commercial PU coating (0.003 mol/l). This concentration is also the CMC of this PU surfactant.

Table 2. Mechanical Properties of PU Coating Films.

Properties	Formula No.			
	1	2	3	Com*
Hardness (g)	100	100	100	200
Flexibility (mm)	3	3	3	3
Adhesion	5B	5B	4B	5B
Impact Resistance (N)	40	40	40	40

*Com = commercial PU coating

Table 3. Water, Acid and Alkali Resistances of PU Coating Films.

Resistances	Formula No.			
	1	2	3	Com*
Water	EX**	EX	EX	EX
Acid	30 min	60 min	10 min	24 hrs
Alkali	30 min	30 min	30 min	30 min

*Com = commercial PU coating
**EX = excellent

CONCLUSIONS

Waste PET bottles can be depolymerized by alkaline decomposition in excess ethylene glycol using NaOH as a catalyst. The obtained transparent colorless EG was further used to synthesize a PU surfactant which was then used as an emulsifier for the synthesis of a waterborne polyurethane coating from linseed oil-modified polyurethane and acrylic monomers via emulsion polymerization. It was found that the film prepared from the synthesized PU coating based on PU surfactant 0.003 mol/l exhibited better properties than those prepared with other surfactant concentrations.

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