Synthesis of polyurethane from glycolysis product of PET using ZnO as catalyst

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Abstract

In this work, zinc oxide (ZnO) nanoparticles were applied as solid catalysts for studying a glycolysis reaction of disposal PET plastic bottles. The effects of temperature, time and concentration of ethylene glycol and ZnO catalyst on % conversion and % yield of Bis(2-Hydroxyethyl) terephthalate (BHET) product were investigated. The chemical structures of the product were confirmed using melting point, Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^{1}H-NMR) analysis. The glycolysis product was applied with a different ratio of isophorone diisocyanate (IPDI) and polyethylene glycol 400 (PEG_{400}) for the synthesis of polyurethane (PU). The results revealed the optimal condition for the glycolysis, which was conducted at 200 °C for 2 h with the ratio of PET: EG of 1:5 in the presence of 1% wt catalyst to obtain the BHET of about 60% yield. The addition of BHET into PU formulations was to increase their molecular weight, hardness and glass transition temperature (T_g) of prepared PU. This research reveals the possibility of using ZnO nanoparticles as the glycolysis catalysts, and the application of the glycolysis product as an alternative method for reducing plastic waste and preserving the environment.

Keywords: PET, ZnO nanoparticle, glycolysis, BHET, polyurethane

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Introduction

Environmental problems from human consumption waste have been increasing continuously, especially from plastics waste that has long degradation time. Bottle-grade polyethylene terephthalate (PET) is a thermoplastic, which can be recycled by physical and chemical method (Welle, 2011). For the physical method, PET bottles are disintegrated and then melted to obtain recycled plastic pellets. However, the quality of these recycled plastics drops due to thermal degradation and impurities from labels and adhesives. The expense for melting plastics is very high due to expensive machines and the need to run in large-scale. Recycle using chemical methods such as, hydrolysis, methanolysis, aminolysis and glycolysis, is a better way due to ease of installation and flexibility to utilize from a laboratory-scale to a factory-scale. Glycolysis is an interesting reaction to convert PET to monomer using glycol, particularly ethylene glycol (EG), which is a non-toxic compound and a mild reaction condition to provide a solid monomer of bis (2-hydroxyethyl terephthalate) (BHET) (Abdelaa, Sobahi, & Makki, 2011).

A catalyst is necessary for glycolysis, typically metal salt (López-Fonseca, Duque-Ingunza, de Rivas, Arnaiz, & Gutiérrez-Ortiz, 2010), especially zinc salt, (Chen, Chen, & Cheng, 1999) is used. However, soluble catalysts might cause impurities in monomer products. These catalysts could not be separated for reuse and they contain toxic from heavy metal ion (Al-Sabagh, Yehia, Eshaq, Rabie, & ElMetwally, 2016). Thus, solid phase catalysts are more attractive choices as they can be reused several times. However, these solid catalysts need specific preparation steps that lead to increasing cost of recycling process. Zinc oxide nanoparticles (ZnO) could be a better choice for glycolysis catalyst due to high surface area, high mechanical strength, thermally stable, and cost-effective. 1% wt ZnO was used as a glycolysis catalyst with EG: PET mole ratio of 17.2 under the temperature of 230 ^{o}C for 80 min to obtain BHET of approximately 60% yield (Imran et al., 2013). Well distributed ZnO nanoparticles were prepared by depositing on fabricated silica nanoparticle, which improved % yield of BHET depending on the size of silica support (Imran et al., 2011). However, the optimization of ZnO nanoparticles for glycolysis of PET has not yet found in previous literatures. The resulted BHET could be used to synthesis variety of products, for example, softeners, dyes, polyesters and polyurethanes.

Polyurethane (PU) is a versatile material with a wide range of mechanical properties, from flexible to rigid materials, depending on their chemical structures. PU is mostly utilized in the production of foams, insulators, furniture, synthetic leathers, engineering plastics, sealants, adhesives, and coatings. Polymerization of PU generally undergoes through step-growth polymerization reactions of diisocyanate and diol, which are mainly obtained from petrochemical industries. BHET is used as diol for the production of PU. Glycolysis products from the reaction of PET with neopentyl glycol and dipropylene glycol are subjected to react with isophorone diisocyanate (IPDI) to produce waterborne PU coating (Zhou et al., 2017). Polyethylene glycol (PEG) was used for glycolysis of PET and applied the resulting product for the synthesis of PU dispersion (Cakić et al., 2015). Methylene diisocyanate (MDI) with mixed diol forms the glycolysis reaction and uses hexadiyne 1, 6-diol as a chain extender to obtain crosslink PU with mechanochromism property (Phuangngamphan, & Thongpin, 2014).

In this work, we investigate the optimum condition of using ZnO nanoparticles as solid catalysts for the glycolysis reaction of PET waste bottles with EG. The glycolysis product is utilized by the reaction of diol with IPDI and PEG to reduce the cost of the synthesis of PU. The obtained PU samples with different ratio of IPDI: PEG: BHET are characterized by their chemical, thermal and mechanical properties to study the role of BHET on properties of PU.

Methodology

Materials

Isophorone diisocyanate 98% (IPDI, Aldrich, Singapore) and dibutyltin dilaurate (DBTDL, Aldrich, Singapore) were stored under N_2 gas and kept in a desiccator to avoid humidity. Ethylene glycol (EG, POCH, Poland), tetrahydrofuran (THF, Thailand India), polyethylene glycol with an average molecular weight of 400 g/mol (PEG_{400}) and chloroform-d ($CDCl_3$, Aldrich, Singapore) were used as received. ZnO nanoparticles, each with a round shape with a crystallite size of 65 nm, were kindly obtained from the college of nanotechnology, King Mongkut's Institute of Technology Ladkrabang (KMITL). PET bottles were clean with detergent and tap water, then air dried and cut into chips (size 1×1 cm). PET chips were dried at 60 °C in an oven to remove moisture and stored in a zip bag.

Glycoysis of PET to BHET

PET chips were mixed with EG and ZnO nanoparticles (0.5-3% wt), which were subjected to reflux for a given temperature and time. The obtained mixture was filtered using Buchner funnel. The solid fraction was dried at 110 °C in an oven. The solid was collected and then weighed for calculating % conversion of PET ($\%C_{PET}$), as followed;

$$\%C_{PET} = \frac{w_0 - w_s}{w_0} \times 100 \qquad (1)$$

Where w_0 was the weight of PET and w_s was the weight of the solid fraction. For the filtered fraction, 200 ml of distilled water was added and stirred using a magnetic bar for 45 min. Then, water was removed using a rotary vacuum evaporator until the volume of the remaining mixture was about

60 ml. The mixture was transferred to a conical flask, closed the lid with parafilm and then placed in a refrigerator (4 °C) to crystallize BHET for 24 h. The white solid of BHET was filtered using Buchner funnel and washed with cold distilled water several times. The product was placed in an oven at 60 °C for 24 h. The weight of BHET was recorded for calculating % yield of BHET (%Y_{BHET}) as the equation below, where w_p was the weight of BHET product.

$$\%Y_{BHET} = \frac{w_0 - w_p}{w_0} \times 100 \tag{2}$$

Synthesis of polyurethane

Diol compound (BHET and PEG_{400}) was dissolved with THF in a round bottom flask with a magnetic bar. The reflux apparatus was set and heated the mixture to 60 °C for 30 min. IPDI was dissolved in THF and then added to the reaction, followed by the addition of catalyst. % Solid of the reaction mixture was controlled to be 60% w/v of the solvent. The reaction was refluxed at 70 °C for 3 h. Then, the resulting reaction was cooled down to room temperature. PU solution was cast by pouring the solution on the Petri dish. To test the pencil hardness, a layer of thin adhesive tape (3M tape) was stuck on both sides of the glass substrate for controlling a thickness of the coating. The PU solution was dropped, then uniformly and slowly scraped back and forth on the surface of the tape as showned in (Figure 1). The PU sample was left for solvent evaporation at room temperature for 24 h and then dried at 60 °C for 24 in an oven.

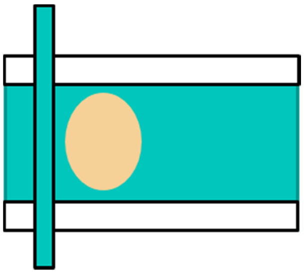


Figure 1 Cast of the PU coating using a modified blade method.

Characterizations

^1H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded on a Bruker 300 MHz using $CDCl_3$ as a solvent with tetramethylsilane (TMS) as an internal standard. Fourier transform infrared (FTIR) spectra were measured on a PerkinElmer system 2,000 infrared spectrometers in a range of 400-4,000 cm^{-1} with a resolution of 4 cm^{-1}. The number and weight average molecular weights (M_n and M_w, respectively) of PUs were determined by gel permeation chromatography (GPC) using the Styragel column (Styragel HR5E, 7.8×9×300 mm). Tetrahydrofuran (THF) was applied as a solvent for PU sample and an eluent for polystyrene standards. The flow rate of the carrier solvent was 1.00 ml/min. Pencil hardness was tested using a modified method of ASTM D-3363 (ASTAS) (ASTM, 2011).

Results and discussion

Glycolysis of PET waste bottles using ZnO nanoparticles as catalyst

The glycolysis of PET was examined using the weight ratio of PET: EG at 1:5 and 1:10. The amount of ZnO nanoparticle were kept constant at 1% wt of PET. The reaction was conducted at 200 °C under the atmosphere for 1-6 h to observe %C_{PET} and %Y_{BHET}. The results showed in (Figure 2) that both %C_{PET} and %Y_{BHET} were gradually increased and then kept constant after 3 h of the reaction time. %Y_{BHET} lower than %C_{PET} was due to the loss of some product during crystallization. However, the reaction at 2 h was selected for further investigation because the slight increase of %Y_{BHET} comparing to the response at 3 h. It was found that the ratio of PET: EG affected the reaction process. When using the ratio lower than 1:5, the reaction could not be thoroughly completed. After adjusting the ratio to 1:10, the catalyst could be diluted and led to a decrease in the rate of reaction. Thus, the reaction condition using for glycolysis of PET was 200 °C for 2 h to obtain %C_{PET} and %Y_{BHET} at 97.36 and 60.18, respectively.

ZnO nanoparticles with a concentration of 0.5, 1, 2 and 3% wt were studied. The result showed the optimum point when using the catalyst concentration at 1% wt, which was used for investigating the effect of temperature in the range of 180-220 °C as presented in (Figure 3). At 180 °C, the reaction was not occurred due to an insufficient heat for EG to penetrate and swell PET chips (Sangalang, Bartolome, & Kim, 2015). %C_{PET} and %Y_{BHET} were kept constant at about 60% at the temperature of 200-220°C. The result was correlated to the literature that used 1% ZnO particles as catalyst to get %Y_{BHET} of 65%, but the reaction condition occurred at much higher temperature at 260 °C, and under pressure of 5 atm, (Imran et al., 2013).

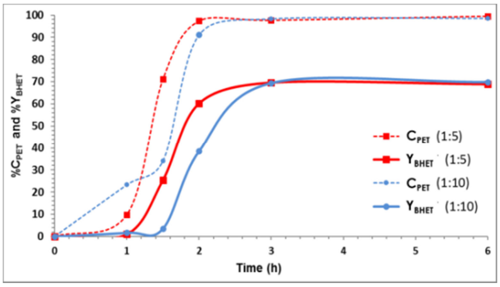


Figure 2 % Conversion (%C_{PET}) and % yield of BHET (%Y_{BHET}) at 200 °C with 1% wt of ZnO catalyst.

Characterization of BHET

The melting point of BHET was 106.7-107.4 °C with resembling the data in the literature (m.p. of BHET=110 °C) (Imran et al., 2013). The chemical structure of BHET was further confirmed using FTIR and ^{1}H-NMR technique. FTIR was used to examine the functional groups that showed the signals at wavenumber of 3292 cm^{-1} (O-H stretching of hydroxy group), 2955-2873 cm^{-1} (C-H stretching of alkane), 1721 cm^{-1} (C=O stretching of conjugated ester) and 1546 cm^{-1} (C=C stretching of aromatic ring) as presented in (Figure 4). ^{1}H-NMR spectrum of the product in (Figure 5) exhibited the chemical shift signals (ppm) at 8.14 (m, 4H, aromatic protons), 4.53 (t, 1H, hydroxyl proton), 4.51 (t, 2H, COO-CH$_2$-) and 4.00 (q, 2H, -CH$_2$-OH). The other signals came from a solvent that was used for dissolving sample for NMR experiment.

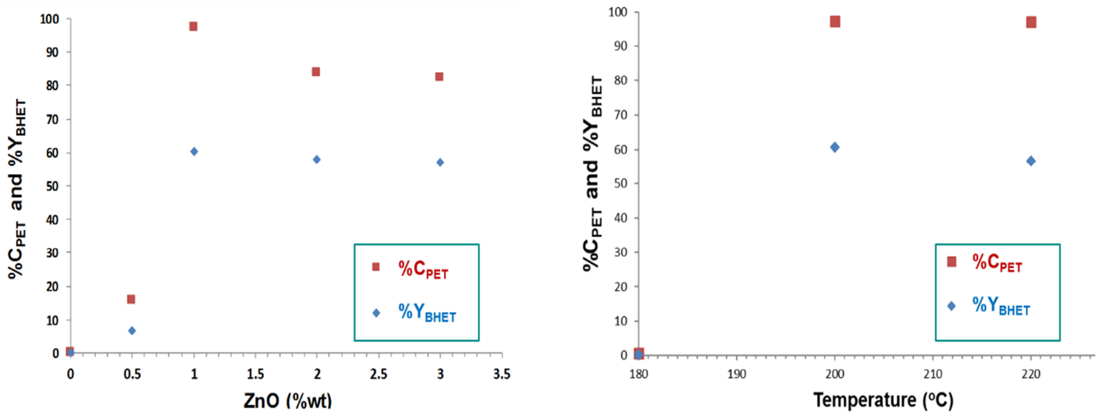


Figure 3 %C$_{PET}$ and %Y$_{BHET}$ with condition (left) 200 °C for 2 h (right) 1% wt ZnO nanoparticle for 2 h.

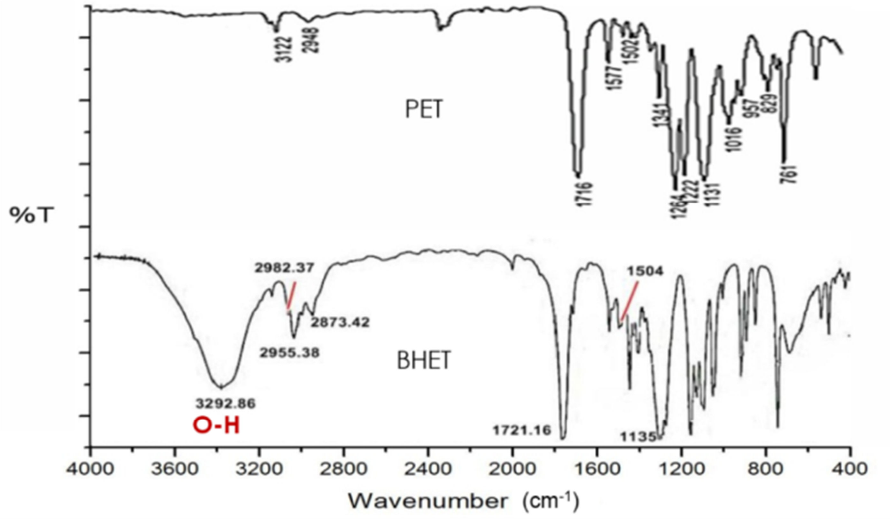


Figure 4 FTIR spectrum (KBr disc) of BHET.

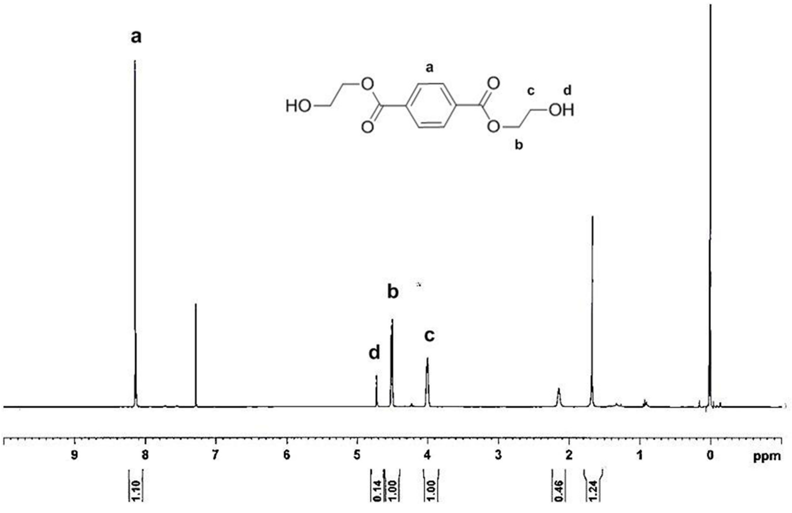
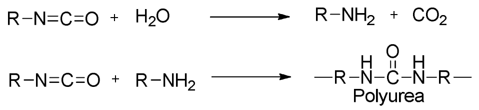


Figure 5 ^{1}H-NMR spectrum ($CDCl_3$) of BHET.

Synthesis of PU

BHET was applied as a diol compound for synthesis of PU with PEG_{400} and IPDI. The mole ratio of IPDI: diol was controlled at 1:1, 1.5:1 and 2:1. THF was used as a solvent, which the % solid of the reaction mixture was adjusted to 60% w/v of the solvent. PU was cast as a film, which had an appearance as presented in (Table 1). The result showed that the PU with the mole ratio at 2:1 gave a good film that could be peeled off, whereas the mole ratio of 1.5:1 and 1:1 reduced a film's strength. The problem maybe due to the competitive reaction between diol and water reacting with IPDI to generate carbon dioxide (CO_2) and the amine compound ($R\text{-}NH_2$) as byproducts (Ma et al., 2016). The amine could further react with the isocyanate group to give the urea group as shown in (Figure 6). Thus, the mole ratio of IPDI should be greater than 1:1 to avoid this problem.



$$R{-}N{=}C{=}O + H_2O \longrightarrow R{-}NH_2 + CO_2$$

$$R{-}N{=}C{=}O + R{-}NH_2 \longrightarrow \underset{\text{Polyurea}}{{-}R{-}\overset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}\overset{H}{N}{-}R{-}}$$

Figure 6 Reaction of isocyanate with water.

The bubble trapped inside PU film could also come from CO_2 byproducts. However, some conditions provided a smooth film surface without bubbles. It could be explained by the viscosity of the obtaining PU solution, which depended on the molecular weight of PU. The air trapped occurred when using BHET as diol only. This evidence showed that at high viscosity of PU solution, the air bubble from the side reaction could not migrate out of the film. The high viscosity was related to the high molecular weight of the

PU, which was confirmed by GPC technique later. The addition of PEG_{400} decreased a viscosity of the PU solution allowing the air to migrate out of the film. Thus, the synthesis condition with the mole ratio of IPDI: diol at 2:1 was selected for further studies due to the uniformity and strength of prepared PU films. Besides, all samples were clear without yellowness and the opacity of the film increased with increasing the content of BHET as presented in (Figure 7).

Table 1 Appearance of prepared PU films.

code	IPDI : BHET : PEG_{400}	film's appearance
-	1 : 0 : 1	sticky/ unpeeled film
-	1 : 0.25 : 0.75	sticky/ unpeeled film
-	1 : 0.50 : 0.50	sticky/ unpeeled film
-	1 : 0.75 : 0.25	sticky/ unpeeled film
-	1 : 1 : 0	brittle/ no film forming
-	1.5 : 0 : 1	sticky/ unpeeled film
-	1.5 : 0.25 : 0.75	sticky/ peeled film
-	1.5 : 0.50 : 0.50	peeled film
-	1.5 : 0.75 : 0.25	peeled film
-	1.5 : 1 : 0	peeled film/ air bubble trap
PU1	2 : 0 : 1	peeled film
PU2	2 : 0.25 : 0.75	peeled film
PU3	2 : 0.50 : 0.50	peeled film
PU4	2 : 0.75 : 0.25	peeled film
PU5	2 : 1 : 0	peeled film/ air bubble trap

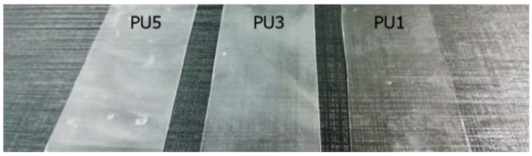


Figure 7 The appearance of the PU films with 2:1 ratio of NCO:OH with showing an increasing of the opacity with the amount of BHET.

ATR-FTIR of PU films

ATR-FTIR was applied to confirm the formation of PU chain. The FTIR spectrum of PU films in (Figure 8) showed the signals of urethane functional group at wavenumber of 3330 cm^{-1} (N-H stretching), 1712-1707 cm^{-1} (C=O stretching of the urethane group) and 1662-1618 cm^{-1} (C=O stretching of urea group) as presented in (Figure 6). PU4 and PU5 showed the signal of the isocyanate group (-N=C=O) at a wavenumber of 2265 cm^{-1}, which revealed the residue of the IPDI monomer in PU film. The addition of the PEG_{400}, a hygroscopic compound, showed the higher content of urea function than using BHET only.

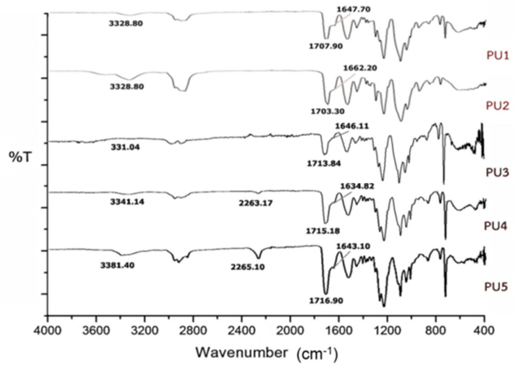


Figure 8 ATR-FTIR spectrum of the PU samples.

GPC of PU films

The GPC results showed the increase of the molecular weight of PU when increasing BHET content in the reaction as show in (Table 2). Applying BHET alone gave the highest molecular weight of PU up to 58,241 g/mol. This result correlated well with the presence of air trapped in the film, which revealed the high viscosity of the PU solution. The addition of PEG_{400} decreased the molecular weight of PU due to the side reaction as mention earlier. Besides, the molecular weight distribution of the PU samples was determined using the polydispersity index (PDI) and the values were about 1.40-1.50. The increasing of PDI value due to the side reaction with moisture can be solved by improving purity and decreasing moisture content of the monomers before the synthesis of PU. Also, M_w of thermoplastic PU is usually varied in the range of 25,000 to higher than 100,000 g/mol depending on the type of isocyanate and polyol (Datta, & Kasprzyk, 2018). Typically, the commercial PU uses an oligomer polyol or a prepolymer polyurethane to connect with a chain extender, which can provide a high M_w of PU.

Table 2 Analysis results from GPC, DSC and pencil hardness.

code	IPDI : BHET : PEG_{400}	M_w	M_n	PDI	T_g (°C)	pencil hardness
PU 1	2 : 0 : 1	23270	16787	1.39	6.41	B
PU 2	2 : 0.25 : 0.75	24785	17162	1.44	9.84	B
PU 3	2 : 0.50 : 0.50	42791	26930	1.59	64.29	HB
PU 4	2 : 0.75 : 0.25	37746	25203	1.50	92.54	HB
PU 5	2 : 1 : 0	58241	38396	1.52	138.69	2H

DSC of PU films

DSC technique was applied to determine the changing of heat flux on materials, which was measured at the temperature range of -30 to 180 °C. DSC. Thermogram revealed glass transition temperature (T_g) of prepared PU films, which increased when increasing the content of BHET. The presence of an aromatic ring, together with the short length molecular structure of BHET, made PU chain more rigid. This phenomenon could be described with the entanglement of the PU chain. The higher molecular weight reflected the longer chain length that led to the greater chain entanglement, which prevented the movement of PU chain when increasing T_g. Moreover, the short length molecule of BHET increased the content of the hard segment, the formation of the crystalline region due to H-bonding between PU chain through urethane and urea groups, which was also an obstruction to the dislocation of PU chains (Hood, Wang, Sands, La Scala, Beyer, & Li, 2010).

Pencil scratch hardness testing

Due to the PU films had some defects such as bubbles and pinholes, which could affect the tensile test, the mechanical property of PU samples was then investigated through pencil scratch hardness. The results were showed in (Table 2). PU films with the higher content of BHET exhibited the higher pencil hardness up to 2H, while the addition of PEG_{400} reduced the hardness down to 2B. These results correlated well with T_g and molecular weight of PU.

Conclusion

The depolymerization of PET by glycolysis reaction was done using ZnO nanoparticles as the catalyst. The optimum condition was using PET: EG of 1:5 by weight with 1% of ZnO catalyst, which was refluxed at 200 °C for 2 h to obtain BHET in moderate yield. The purity of the product was analyzed using several suitable spectroscopic methods. Synthesis of PU was studied using a mole ratio of IPDI: diol of 2:1 to obtain the uniformity film formation. Moisture in PEG_{400} posed a serious problem because it resulted in the side reaction, which led to the decreasing molecular weight of PU. Adding the content of BHET into the formula could provide higher molecular weight, better thermal and mechanical properties of PU product. This work showed the possibility of changing plastic waste into a valuable product using chemical reaction to obtain PU coating. The method could reduce the use of monomer from a petrochemical source that is soon to be depleted.

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