MICROWAVE-ASSISTED DEPOLYMERIZATION OF POST-CONSUMER PET BOTTLES FOR THE PRODUCTION OF RIGID THERMAL INSULATING POLYURETHANE FOAMS

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Abstract— Polyethylene terephthalate (PET) plastics are commonly used as water and soft drink bottles. Since these materials have poor biodegradability and high resistance to the atmosphere, it is not appropriate to dispose them by land-filling. Furthermore, these bottles contribute to the substantial plastic waste generation. Hence, this study aims to reduce the accumulation of waste PET bottles through chemical recycling, as well as find a waste alternative raw material for the production of rigid thermal insulating polyurethane (PU) foams. Post-consumer PET bottles were collected, dried and size-reduced. The PET flakes were subjected to microwave-assisted glycolysis in a modified microwave set-up with glycerine as depolymerizing agent to produce the glycolyzed product (GP). Glycolysis reaction time of 15 minutes yielded the highest percent conversion. The GP was then transesterified with castor oil to convert into polyester polyol. The derived polyester polyol was mixed with diisocyanate to produce rigid polyurethane. The GP, polyester polyol and PU foams were characterized using Fourier Transform Infrared spectroscopy (FTIR) to verify the presence of the expected functional groups. The final product was then analyzed by thermal gravimetric analysis (TGA) to determine its thermal stability as compared to that of commercial foam. The experimental foams were found to be more thermally stable compared to commercial polyurethane foams.

Keywords— Post-Consumer Pet Bottles; Rigid Polyurethane Foams; Glycolysis; Microwave-Assisted Depolymerization; Transesterification; Oligoester; Polyester Polyol; Diisocyanate; Thermal Stability

I. INTRODUCTION

Plastics play an important role in almost every aspect of our daily lives. They are used to manufacture everyday products such as food and beverage containers, furniture, and lightweight alternatives for glass and metal. The widespread use of plastics entails a rapid accumulation of plastic wastes that demands effective recycling. This has been given much attention for years in efforts to improve solid waste management.

Polyethylene terephthalate (PET) plastics are commonly manufactured as water and soft drink bottles. Post-consumer PET bottles contribute to substantial plastic waste generation. Since PET materials have poor biodegradability and high resistance to the atmosphere, it is not appropriate to dispose of PET wastes by land-filling (Sadeghi and Sayaf, 2012). Chemical process of recycling is found to be the best method to address the environmental concern.

Rigid polyurethane (PU) foams are common material used for thermal insulation and can significantly enhance the energy efficiency of residential and commercial buildings. In addition to save energy in the heating and cooling of buildings, PU can help make structures more durable, lessening the burden of using raw material resources to maintain or upgrade them. However, these PU foams are based on petrochemical raw materials and are no longer applied in construction industry on a large scale due to its high price; its price is higher than of foam polystyrene and mineral wool (Vitkauskiene and Makuska, 2008). If the cost of the rigid PU foam is reduced, it will be competitive to other materials commonly used for insulation which is possible with the use of PET wastes as raw materials. This study aims to produce rigid thermal insulating polyurethane foams derived from chemically recycled post-consumer PET bottles through microwave-assisted depolymerization. The thermal stability of the experimental foams is also studied and compared to commercial foams using thermal gravimetric analysis (TGA).

II. EXPERIMENTAL

2.1 Materials

The post-consumer PET bottles procured from Xavier University campus, after removing the labels and caps, were washed with water, dried, and cut into approximately 1mm x 1mm-sized flakes. Glycerin was kindly supplied by Pilipinas Kao, Inc. while sodium bicarbonate was obtained from XU Chemistry Department. The castor oil used in the transesterification was purchased from the local market while the potassium hydroxide catalyst was provided by the XU Unit Operations Laboratory. Diphenylmethane diisocyanate was purchased from Polymer Products Philippines.

2.2 Data Collection Procedures

II.2.1. Microwave-assisted Depolymerization of PET

A. Microwave-assisted Glycolysis of PET in Glycerine

After the raw material preparation, 30 grams of PET flakes were reacted with glycerin, in the presence of sodium bicarbonate as catalyst, in a microwaveable reaction flask fitted with a reflux condenser. The glycerin was obtained from Pilipinas Kao Inc. while the catalyst was readily available in the Xavier University Unit Operations Laboratory. The mixture was heated in a domestic microwave oven at an irradiation power of 600 watts, at three different heating times: 9, 12, and 15 minutes. The reaction was carried out at a PET to glycerol molar ratio of 1:4. After the glycolysis, all unreacted PET flakes were filtered out and weighed to estimate the conversion of PET using the equation:

$$\text{PET Conversion } (\%) = \frac{M_{PET,0} - M_{PET,1}}{M_{PET,0}} \times 100 \quad (eqn\ 1)$$

where, $M_{PET,0}$ represents the mass of PET initially taken for the experiment and $M_{PET,1}$ refers to the mass of unreacted PET. The conversion equation was used for the glycolyzed products at the three different reaction times. The mixture was then left to cool down to room temperature and the glycolyzed product was obtained.

B. Characterization of the Glycolyzed Products

The cooled glycolyzed products were in the form of a viscous white liquid. A 5 mL-sample was collected for each reaction time and was analyzed by a Fourier Transform Infrared Spectrometry located in the XU Chemistry Department. Hydroxyl values were also determined in Pilipinas Kao, Inc laboratory.

2.2.2. Production of Polyurethane Foams

A. Preparation of Polyester Polyol Mixture

The obtained glycolyzed PET (GP) from the previous section was mixed with castor oil at a GP:oil weight ratio of 1:2. Potassium hydroxide of 1.5 weight percent was used as catalyst for the trans-esterification reaction. The mixture was allowed to react in a microwave oven for 10 minutes at a low power setting (60-90°C). The resulting mixture, in the form of polyester polyol, was cooled to room temperature and was added with sulfuric acid to neutralize the basicity of the mixture.

B. Synthesis of Polyurethane from Glycolyzed-Product

The polyester polyol was added with water as the blowing agent and mixed using a mechanical stirrer for 60 seconds. An equal amount of diisocyanate was then added to the mixture and stirred for 90 seconds before transferring into a plastic mold. The mixture was allowed to rise at ambient conditions and was left to cure for 18 hours before further analysis.

C. Characterization of the Polyurethane Produced

The 1-inch x 1-inch x 0.5-inch sample of the produced polyurethane foam was characterized using FTIR Analysis available in the Chemistry Department of Xavier University. The thermal stability was then analyzed by obtaining percent residual weight using the thermogravimetric analysis in the Mindanao State University. – Iligan Institute of Technology.

III. RESULTS AND DISCUSSION

3. 1. Influence of Glycolysis Time

The conversion of the PET flakes through glycolysis is influenced by the reaction time. The 1:4 molar ratio of pre-washed PET flakes and glycerine with sodium bicarbonate as catalyst were depolymerized inside the microwave reactor for 9, 12 and 15 minutes. The temperatures of 600-W setting of the microwave were recorded right after the glycolysis time using FLUKE 568 IR Thermometer. Table 1 shows the recorded temperature of the microwave with respect to glycolysis time. The recorded temperatures are approximately the same throughout the time intervals. Thus, verifying the depolymerization temperature of PET in the range of 200 – 250^{o}C.

Table 1. Recorded temperatures for each glycolysis time

Glycolysis Time, minutes	Temperature, ^{o}C
9	237.20
12	236.56
15	236.23

A thin golden brown liquid was expected after the microwave heating and the temperatures recorded were in the 200-250^{o}C range. This was attained by the three glycolysis time. At this temperature, the solution is clear and there are no traces of unreacted PET flakes. However, at 9 and 12-min reaction time, the clear solution turned cloudy and traces of solids began to form upon cooling down to room temperature. The influence of glycolysis time on percentage conversion to glycolyzed product is shown in Table 2.

Table 2. Influence of glycolysis time on conversion of PET flakes

Glycolysis Time, minutes	Percent Conversion, %
9	43.15
12	81.80
15	100

Percentage conversion was determined from the initial and final masses of the PET in the glycolysis reaction. At 9 minutes, the conversion was almost 50% while at 12 minutes approximately 80% was converted. On the other hand, the samples from 15 minutes were all converted to glycolyzed PET product (GPP). As shown in Figure 4.2, the glycolysis conversion increases with respect to the glycolysis time and reaches a hundred percent conversion when the time reached 15 minutes.

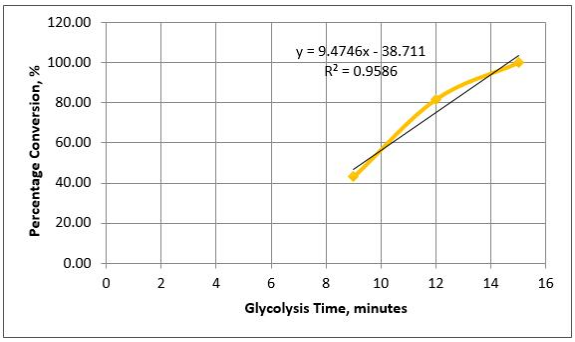

Figure 1. Relationship between the glycolysis time and conversion of PET at a 1:4 PET to glycerin molar ratio, under 600W microwave power setting.

Therefore, the relationship between glycolysis time and percentage conversion is directly proportional; thus, the longer the sample is heated inside the microwave the more effective is the conversion. The linear regression with an R^2 value of 0.9586 shows that the percent conversion to glycolyzed product has a strong relationship with respect to the glycolysis time. This signifies that an increase in the glycolysis time denotes an increase in the percent conversion. Since all the PET flakes were converted at the 15 minute-glycolysis time, this was the reaction time used for the production of the derived polyester polyol.

3. 2. Characterization of the glycolyzed products

Based on the effect of varying the reaction time of the glycolysis of PET flakes with glycerin and sodium bicarbonate catalyst, the optimum out of the stipulated three reaction times to give the highest glycolyzed product yield was determined to be 15 minutes. The mean hydroxyl value of the highest glycolyzed product percent yield was found to be 1,135.66 mg KOH/g of sample. The hydroxyl value of a polyol is associated to the physical and mechanical properties of the resultant structure of the polyurethane foam. The OH value is also important to gauge the extent of depolymerization of PET by glycolysis.

Theoretically, the preferred hydroxyl value of polyol in the preparation of rigid foams ranges from 250 to 1000 mg KOH/g of sample, while for semi-rigid, the OH value preferably ranges from 100 to 400 mg KOH/g of sample, as determined by ASTM D2849A. The determined hydroxyl value of the glycolyzed product is an implication that the produced polyurethane foam is rigid in bn structure. Although it surpassed the theoretical range of hydroxyl value, it did not cause any significant difference on the thermal stability of the produced foam from the commercial one as verified by the thermal gravimetric analysis (TGA).

FTIR analysis was also performed on the glycolyzed PET product using a Perkin-Elmer Spectrometer over a wavenumber range of 4000 - 400 cm^{-1} to confirm the structure of the products. The absorption peak at 3320 cm^{-1} is attributed to –OH functionality while absorptions at 2923 and 2863 cm^{-1} indicate alkyl C-H stretching. The presence of absorptions at 1719, 1510 and 1103 cm^{-1} were also observed due to ester carbonyl group C=O, aromatic group, and C-O stretching respectively. The absorption peaks imply that the glycolyzed products are compounds having hydroxyl and ester groups which are the main functional groups of an oligoester. The FTIR spectrum of the glycolyzed products is shown in Figure 2 (B).

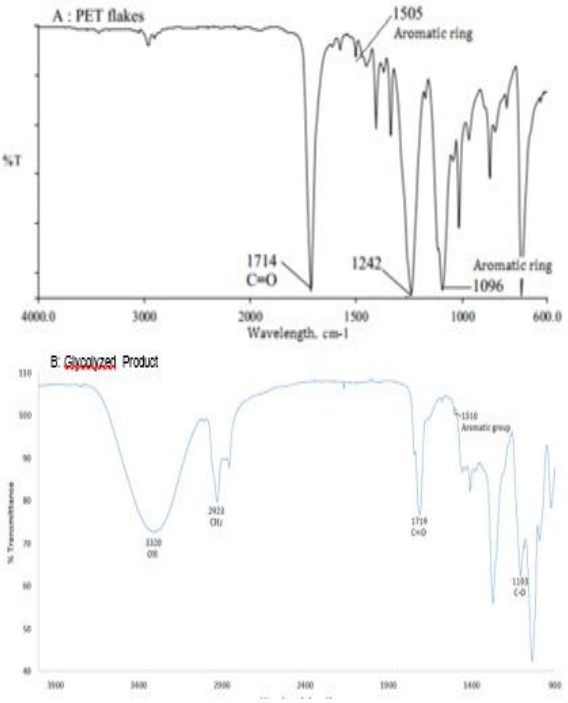

Figure 2. FTIR spectra of PET flakes (A) and glycolyzed PET products (B)

The FTIR spectra for the PET raw material, obtained from the study of Darus (2013), is shown in Figure 2. (A). Although the FTIR results for the glycolyzed product in (B) reveals a resemblance of the PET (A) in terms of the ester and the aromatic group appearance, an obvious band over 3000 to 3500 cm^{-1}can be observed in spectrum (B) which is due to strong hydrogen bonding in the glycolyzed product. The presence of this peak confirms the successful glycolysis of PET since the spectra of PET (A) does not display the same peak. The broad band is observed in all the FTIR analyses of the triplicate 15-minute PET glycolysis trials. The significance of other peaks present in the spectra was not covered in this study.

3.3. Characterization of the polyester polyol

Polyester polyol formation by reaction of GPP and castor oil was also confirmed by FTIR spectral analysis as shown in Figure 3. It shows that FTIR spectra of polyol formed on the trans-esterification glycolyzed PET with Castor oil. A strong sharp band at 1740 cm^{-1} confirms polyester formation due to the presence of C=O stretch which corresponds to the ester group. A medium broad band at 3390

cm^{-1}confirms the presence of free hydroxyl groups in the sample.

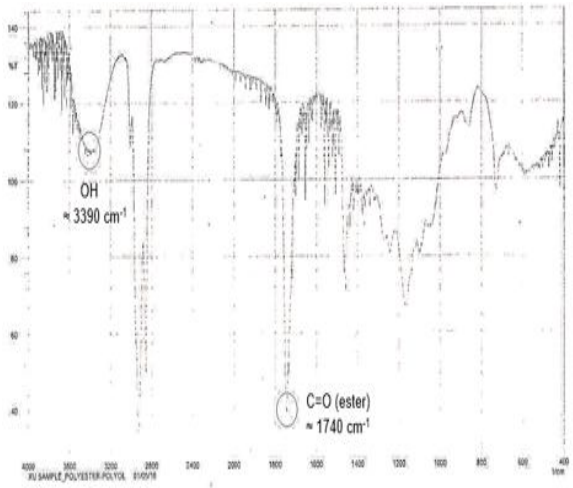

Figure 3. FTIR spectra of Polyester polyol

3.4. Characterization of the polyurethane foam

Figure 4 represents the FTIR spectra of the polyurethane foam indicating a weak sharp band at 3450 cm^{-1} was found and confirms the presence of N-H stretch. A strong and sharp peak of 1690 cm^{-1} confirms the presence of the functional group, amide group, of C=O stretch. This amide group is the main functional group of polyurethane that corresponds to the urethane linkages. The C-O stretch can be seen at a medium strong peak at 1112 cm^{-1}. Also, a weak sharp peak was also found at 2325 cm^{-1} that confirms the presence of N=C=O stretch.

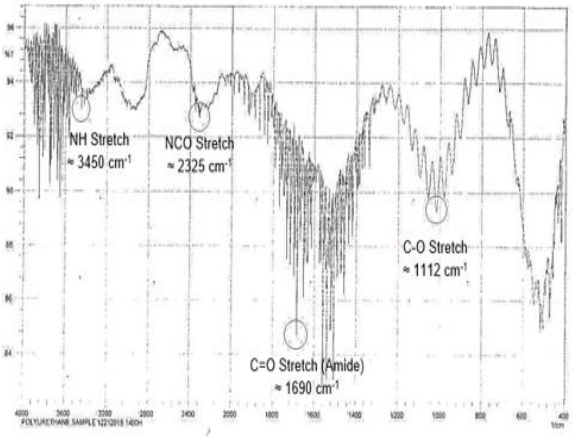

Figure 4. FTIR spectra of Polyurethane foam

3.5. Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was used to analyze decomposition behavior of the polyurethane foam synthesized with polyester polyol derived from the glycolyzed PET products. Thermal stability is the ability of a material at high temperatures and as an insulation material; it needs to withstand higher temperatures. The material that has higher stability has more resistance to decomposition at high temperatures. Thermal stability is important to test the thermal property of the experimental rigid foam and compare with an existing commercial foam.

Table 3. Percentage residual weight of the experimental and commercial foam in given temperatures

Residual Weight, %	Temperature, °C					
	100	200	300	400	500	600
Trial 1	98.36	95.721	84.064	62.431	38.645	1.268
Trial 2	98.524	95.664	82.886	61.812	42.002	1.707
Trial 3	96.407	92.289	82.184	62.448	40.398	4.395
Commercial	98.679	97.628	79.935	44.726	33.87	5.48

At 100^0C, both foams were not relatively affected by the heat blown in an air atmosphere. This was evident as the data projected approximately 98% residual weight. However, at 200^oC, the experimental foam began to project an approximate 5% weight loss.

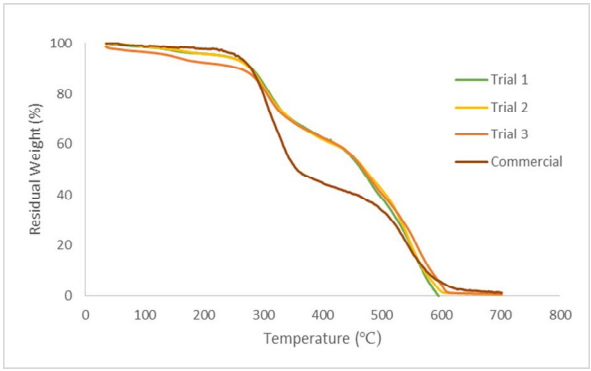

Figure 5. TGA Thermogram of the experimental and commercial polyurethane foams

Based from Figure 5, the average decomposition temperature of experimental foam was approximately 202^oC while the commercial foam started its decomposition process at 253.16^oC which is higher. On the other hand, as the temperature increases the percentage weight loss of the commercial foam decreases relatively. This was evident at higher temperatures of 300, 400 and 500^oC. The commercial foam's residual weights were approximately 4%, 17.5% and 7% lower than the experimental foam at the mentioned temperatures respectively.

CONCLUSION

PET wastes were depolymerized by glycolysis with glycerin, under microwave irradiation at 700 W at different reaction temperatures, i.e. 9, 12 and 15 minutes. The 15-minute glycolysis time yielded the highest conversion to glycolyzed product. Hydroxyl value analysis showed that the OH value for the obtained glycolyzed product was 1,135.66 mg KOH/g, which is within the range of hydroxyl value for preparation of rigid foams. Transesterification of the glycolyzed product with castor oil yielded polyester polyol which was then reacted with diphenylmethane diisocyanate to produce

polyurethane foams. The glycolyzed product, polyester polyol and polyurethane foams were characterized using Fourier Transform Infrared spectroscopy (FTIR) to verify the presence of the expected functional groups. From the thermal gravimetric analysis, the experimental foams produced were found to be comparable to that of commercial polyurethane foams, the experimental foams were found to be more thermally stable compared to the commercial. The application of the polyurethane foam is practical in insulation for heat transfer equipment, house and building construction as well as for automobiles and appliances.

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