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PET Recycling by Diethylene Glycol-Diethanol Amine Binary Mixture and Application of Product in Rigid Polyurethane Foam Formulation

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Polyethylene terephthalate (PET) wastes were depolymerized by diethylene glycol (DEG)-diethanol amine (DEA) binary mixtures as a solvent system in various DEG:DEA ratios and sodium hydroxide as the trans-esterification catalyst. The obtained product was vacuum filtered for separation and characterization of resulting phases by using spectroscopic and chromatographic techniques. Liquid phase of recyclate was an OH containing product and was used as a portion of polyol content, being compared with virgin polyol in rigid polyurethane foam formulation.

Keywords: polyethylene terephthalate; polyurethane foam; recycle; trans-esterification; diethylene glycol; diethanol amine

1 Introduction

Over the last several decades, recycling of polymer waste has been attracting the attention of many polymer scientists. Polymer recycling is very important for at least two main reasons: 1) to reduce the ever increasing volumes of polymers waste produced from any sources such as daily life packaging and materials and, 2) to generate valuable materials from low cost sources by converting them in to some extent similar to virgin materials.

While polymer applications are expanded daily, PET is one of the most consumed polymers as its noticeable physical properties in the manufacture of high strength fibers, soft drink bottles and photographic films and its consumption increased to more than 3,000,000 tons per year at the end of the last century (1).

In the polymer recycling industry, there are several recycling methods which have been investigated during much research. Four main approaches have been proposed namely primary or in-plant recycle of the scrap material of controlled history, secondary or mechanical, tertiary or chemical and quaternary or recovery of plastic energy recycling (2–6).

Among recycling techniques, the only acceptable one according to the principles of sustainable development is the tertiary or chemical recycling since it leads to the formation of the raw materials or monomers. Chemical recycling processes for PET are divided as follows: (i) glycolysis, (ii) methanolysis, (iii) hydrolysis and, (iv) other processes. The main depolymerization processes that have reached commercial maturity are glycolysis and methanolysis (3, 6).

Essentially, glycolysis involves the insertion of glycols in PET chains to give bis(hydroxyethyl) terephthalate (BHET) which is a precursor for PET synthesis and its oligomers. Kinetics of the glycolysis reaction of PET have been studied by several researchers (7–11) and reviewed by Bisio and Xanthos (12), Brandrup (13), Paszun (6), and Schiers (3). Glycolysis of PET yields the true monomer which has been used in polyester condensation, namely BHET with its oligomers (n = 2–10). The main advantage of this method is that it can be easily integrated into a conventional PET production plant and the recovered BHET can be blended with fresh BHET. However, there is always a risk of contaminants. On the other hand, the main disadvantage is that the reaction products are not pure chemicals but contain BHET, along with higher oligomers which are difficult to be purified by conventional techniques.

Methanolysis is the degradation of PET by methanol at high temperatures and high pressures with dimethyl terephthalate (DMT) and a glycol as the main products (6, 12–15).

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Hydrolysis is a chemical method of waste PET processing leading to TPA and EG. The growing interest in this method is connected to the development of new factories for PET synthesis directly from TPA and EG. In this method, the production of methanol is eliminated from the technical cycle. Commercial hydrolysis is not widely used to produce food-grade recycled PET because of the cost associated with purification of the recycled TPA. Hydrolysis of PET flakes can be carried out as (a) alkaline hydrolysis (b) acid hydrolysis and (c) neutral hydrolysis (3, 6, 12, 13, 16).

Other processes include some newly developed techniques for the depolymerization of PET waste such as aminolysis and ammonolysis (6, 17). Aminolysis is the reaction of PET with different amine aqueous solutions to yield the corresponding diamides of TPA and EG. There are no known reports for the utilization of this process in a commercial scale. However partial aminolysis has found its application in the improvement of PET properties in the manufacture of fibers with defined processing properties. The amines used include methylamine, ethylamine and ethanolamine temperatures of 20–100°C.

Ammonolysis is the reaction of anhydrous ammonia with PET to produce a terephthaldiamide which can be converted to terephthalonitrile and further to other chemical substances. In addition, the reaction is carried out with post consumer PET bottles at 120–180°C and pressure of about 2 MPa for 1–7 h.

From all the above techniques, we focused on a specific method which conforms to the sustainable development principles and makes new trends in industrial recycling of PET. In other words, chemical recycling by glycol/amine binary mixture leads to new materials, which are interesting enough to be further investigated.

Much research has been carried out in the glycolysis method field. Oku et al. investigated the glycolysis of PET by anhydrous ethylene glycol, applying NaOH as the catalyst, yielding a solid terephthalate salt and an ethylene glycol similar liquid product (18). PET is also glycol treatable by ethylene or propylene glycol in a xylene medium (19). A mixture of alcohol and ether has been reported as a good solvent media for the glycolysis reaction (20). But in much of the research, the main solvent has been a glycol, producing a more applicable product (1, 21–24). Structural effects of diacidic and glycolic moieties on physicochemical properties of aromatic polyesterdiols from glycolysis/esterification of poly(ethylene terephthalate) wastes have been investigated, resulting in many useful facts, e.g. the viscosity of the polyols increases greatly with decreasing the hydroxyl value or increasing the proportion of aromatic diacidic residues (25).

Much research was also concerned with the process, utilizing the products obtained by using glycolysis. The PET glycolysates have been applied in the manufacture of unsaturated polyesters (26), polymer concrete resins for unsaturated polyesters (27) and polyurethane foams (28). Murayama and co-workers designed a process in which PET and raw polyol are allowed to react in a reaction vessel to produce polyester polyol and also ethylene glycol which is a byproduct of the reaction (29). On the other hand, it is important to define an appropriate application for the recyclate. Of course, the main aim of a recycling process is to make a reusable material. For example, in the case of PET glycolysis, the obtained OH containing recyclate has been blended with virgin polyol in polyurethane systems (30). Another research project deals with PUF production via a process using some hydrocarbons as the blowing agent (31).

In this study, diethylene glycol (DEG), in combination with diethanol amine (DEA) has been used as a recycling agent and sodium hydroxide was added as the catalyst. An attempt was made to recycle the PET waste in different glycol/amine ratios and to characterize the final product due to the amine portion. A hybrid process utilizing both glycol and amine recycling abilities was aimed to be designed in order to find the best agent portions and investigate the effect of different agent portions on product characteristics. As mentioned before, recyclate consists of OH containing oligomers and is applicable in a polyurethane structure as a portion of polyol in rigid polyurethane foam formulation.

2 Experimental

2.1 Materials and Apparatus

Waste PET scraps from soft drink bottles were used with intrinsic viscosity of 0.8dl/g and a melting point of 254°C. Sodium hydroxide from Merck® and commercially available diethylene glycol (DEG), and diethanol amine (DEA) were purchased. The polyol (Daltofoam® TA 14066) and MDI (Suprasec® 5005) were from Huntsman® Co. and their technical data are listed in Tables 1 and 2. The recycling process was carried out in a three-necked round bottom glass flask, equipped with a stirrer, a thermometer and a reflux condenser. Gel permeation chromatograms (GPC) were obtained, using a 6A Shimadzu instrument. Water contents were measured by a Metler DL-18 automated Karl Fischer titrator. Mechanical properties were determined using an Instron 1122 tensometer. Infrared spectroscopic studies were performed by a Bruker® Tensor 27 mid-FTIR spectrometer and NMR spectra were recorded by an Avance 300 Bruker®.

Table 1. Technical data of virgin polyol used in PUF formulations

DALTOFOAM® TA 14066	
Appearance	Viscous yellow liquid
Viscosity	5940 cPs @ 20°C 5263 cPs @ 25°C
Specific gravity	$1.06\ g \cdot cm^{-3}$ @ 25°C
Water content	2.3%
pH	9.45
OH number	430 ± 20

Table 2. Technical data of MDI used in PUF formulations

SUPRASEC® 5005	
Appearance	Dark brown liquid
Viscosity	220 cPs @ 25°C
Specific gravity	$1.23\ g \cdot cm^{-3}$ @ 25°C
NCO value	30.9% by wt NCO groups (group wt:42)
Average functionality	2.7
Flash point	233°C
Fire point	245°C

Table 3. Solvent binary mixture's ratio in recycling reactions

	DEG (%)	DEA (%)	Complete digestion time (hr:min)
Reaction 1	100	0	0:54
Reaction 2	95	5	1:25
Reaction 3	83.33	16.67	7:20
Reaction 4	66.67	33.33	13:00
Reaction 5	50	50	20:00
Reaction 6	30	70	26:00

2.2 Glycolysis of PET Waste

Waste PET flakes were depolymerized by the binary mixture of DEG and DEA (polymer:solvent ratio was 1:1) using 1.5 w/w% of NaOH as the catalyst. The glycolysis was carried out at 190–200°C under reflux at six different DEG:DEA ratios of 6:0, 5.7:0.3, 5:1, 4:2, 3:3 and 1.8:4.2, respectively, according to Table 3. The recycling reactions were allowed to proceed up to the complete polymer digestion at 190–200°C. Surprisingly, by increasing the amine content, end point of digestion was achieved later and in other words, recycling was more time consuming.

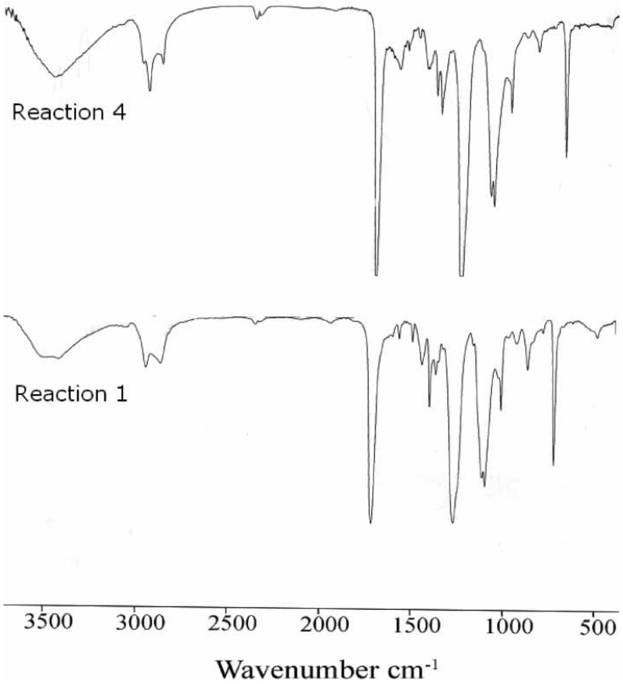

Fig. 1. Typical FT-IR spectra of PET recycylate.

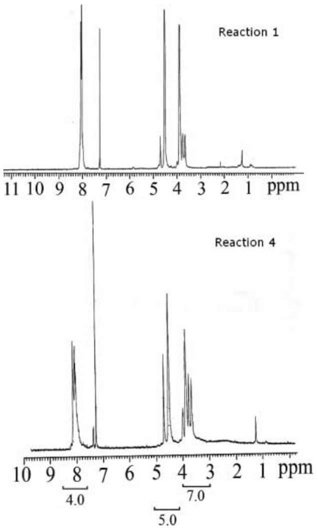

Fig. 2. Typical ^{1}H-NMR spectra of PET recyclate.

3 Results and Discussion

All samples were vacuum distilled in order to determine the amount of free solvent and recyclate structure. During

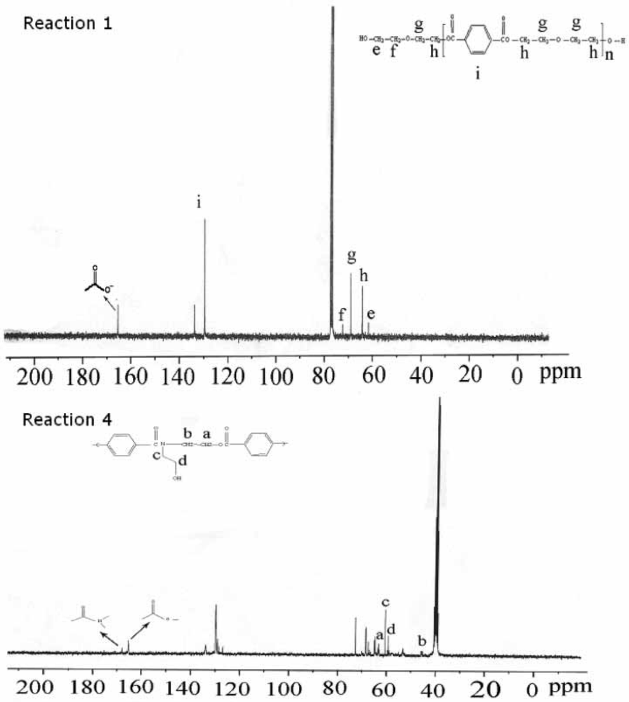

Fig. 3. Typical ^{13}C-NMR spectra of PET recyclate.

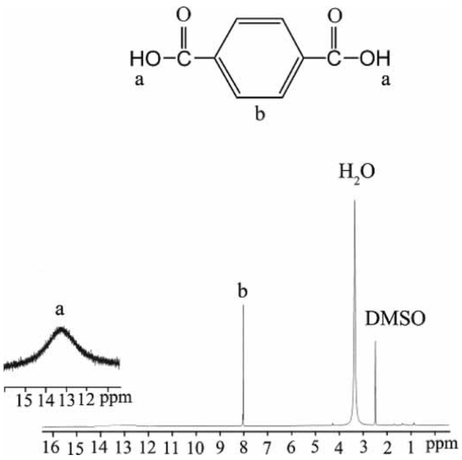

Fig. 4. The ^{1}H-NMR spectrum of solid phase of recyclate.

vacuum filtration of the recyclate, a white powder remained on the filter which was shown to contain terephthalate structure. All fractions were studied by FT-IR and NMR spectroscopy.

3.1 *IR Spectra of Recyclate*

The recyclate was studied by infrared spectroscopy. Figure 1 shows two typical FT-IR spectra of recyclate. All IR spectra showed an intensive broad band in 3200–3600 cm^{-1} region related to stretching frequency of hydroxyl groups. A sharp band at 1719 cm^{-1}, probably due to the stretching frequency of the ester carbonyl group, two signals at 2956 and 1450 cm^{-1} may stand for stretching and bending of CH$_2$ group. A signal at 1580 cm^{-1}, is, to a certain extent, due to aromatic C=C stretching. The bending frequencies at 690 and 900cm^{-1} strongly suggest the presence of an aromatic

Table 4. Distribution of molecular weight in recyclate of reaction 2 during the time

MW range		Abundance of MW range (%)							
		Reaction time (min)							
From	To	30	60	90	120	150	180	210	240
Highest MW	1600	0	0.22	0.82	0.37	0.68	0.54	0.33	0.11
1600	1400	0	0.75	1.61	1.1	1.28	1.24	1.02	0.59
1400	1200	0	2.16	3.98	3.19	3.32	3.38	3.04	2.15
1200	1000	0.18	5.78	9.43	8.47	8.51	8.75	8.28	6.65
1000	900	0.76	5.51	8.35	7.91	7.8	7.92	7.69	6.72
900	800	3.42	8.43	11.21	11.14	11.22	11.64	11.35	10.26
800	700	8.83	12.8	15.86	16.18	15.97	16.02	16.02	15.68
700	600	21.42	19.7	17.9	18.55	18.84	19.32	19.07	18.86
600	500	50.3	35.27	24.97	26.57	26.39	26.06	26.97	29.98
500	400	17.1	11.52	8.05	8.65	8.16	7.37	8.36	10.9
400	300	0.01	0.01	0.03	0.08	0.04	0.03	0.09	0.25
300	0	0	0	0	0	0	0	0	0

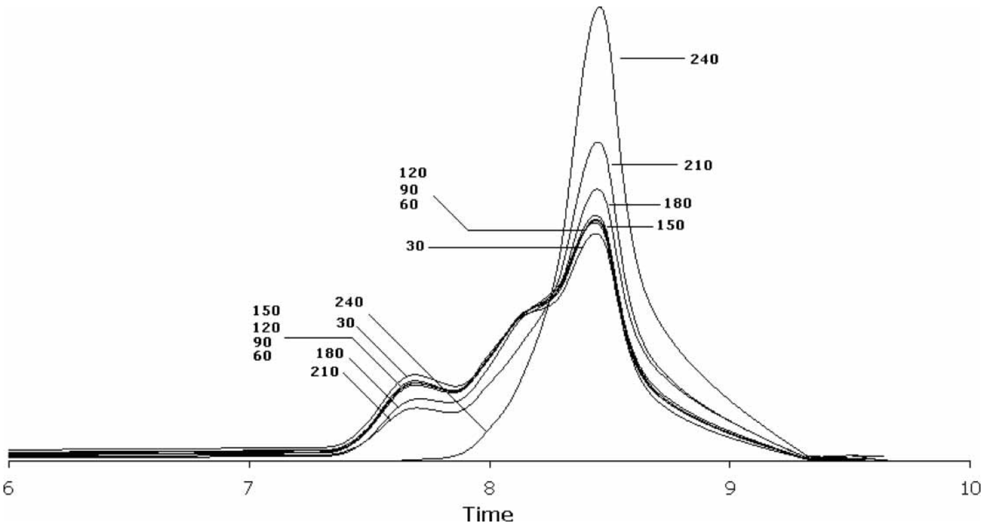

Fig. 5. Gel permeation chromatograms of recycled PET during 4 h of reaction time.

Table 5. Formulation of PUF samples containing PET recyclate as a portion of polyol

Foam sample	Polyol daltofoam TA 14066	MDI suprasec 5005	PET recyclate	Water
S_1	100	100	0	0
S_2	90	100	10	0.2
S_3	80	100	20	0.4
S_4	70	100	30	0.6
S_5	70	115	30	1.0
S_6	60	100	40	0.8
S_7	60	120	40	1.2
S_8	60	120	40	1.5
S_9	50	125	50	1.0
S_{10}	50	125	50	1.8

residue in the recycling product. The signal at 1275 cm^{-1} is probably due to the stretching frequency of ester C-O.

3.2 *NMR Spectra of Recyclate*

The solvent free recyclate was also studied by ^{1}H-NMR and ^{13}C-NMR spectroscopy. Figure 2 shows the ^{1}H-NMR spectra for the recyclate. The signal at δ 7.98 corresponds to aromatic ring protons, δ 3-4 corresponds to the methylene protons of DEG and DEA residue, δ 4.5 is due to the carboxyl methylene group C-O-CH_2 and δ 4.7 corresponds to -OH groups. Results, made of ^{13}C-NMR were in accordance with those predicted in ^{1}H-NMR (Figure 3). In addition, the signal at δ 167 ppm corresponds to an amide functional group and it can be concluded that an amide functional group in glycolysis products is obtained.

The ^{1}H-NMR spectrum of white powder which remained on the filter, which indicates a TPA structure and is shown in Figure 4.

3.3 *GPC of Recyclate*

Reaction 2 was selected as a sample for molecular weight investigation. After about 85 min, PET flakes were completely digested, but the reaction was continued in the following 4 h. Sampling was performed for gel permeation chromatography every 30 min in order to monitor the rate of depolymerization. The recycling stage shows the conversion of PET flakes to lower molecular weight fragments. The gel permeation chromatography results initially indicate the average molecular weight to be about 700. The longer reaction leads to a further decrease in molecular weight, but after 4 h, the decrease in molecular weight is quite moderate (Table 4 and Figure 5). It can be concluded from the combined results obtained in the above discussion, that the glycolysis product mainly consists of DEG-TPA-

Table 6. Reaction time parameters of rigid PUF in cup testing

Foam sample	Cream time	Gel time	String time	End of rise	Tack free time	Foam quality
S_1	5	6	28	41	59	Excellent
S_2	5	6	27	40	56	Excellent
S_3	6	7	26	40	54	Good
S_4	6	7	26	36	48	Good
S_5	6	8	30	43	55	Excellent
S_6	5	7	25	35	46	Medium
S_7	6	8	29	40	49	Good
S_8	5	7	26	45	52	Excellent
S_9	4	5	—	31	36	Medium
S_{10}	5	6	25	40	49	Good

Table 7. Comparing the quality control results of foam sample

Properties	Sample				
	S_1	S_2	S_3	S_5	S_8
Core density ($kg \cdot m^{-3}$)	35	37	40	39	46
Tensile strength @ horizontally (kPa)	108.23	225.64	233.23	244.46	175.42
Elongation @ break (%) @ horizontally	9.20	8.64	9.79	9.38	7.50
E-Modulus (kPa) @ horizontally	1388	3849	3419	4074	2867
Compression set (%)	14	8.3	10	3.44	5.56
Water absorption (%) (24 hours)	1.5	1.6	1.4	1.8	2
Dimensional stability (−30°C/24 h) (%)	OK	OK	OK	OK	OK
Dimensional stability (70°C/24 h) (%)	OK	OK	OK	OK	OK

EG-TPA-EG-TPA-DEG and DEG-[TPA-DEG$)_{n:2,3}$. It is noteworthy that the signal at the 7–8 min region is due to a solvent system that interestingly decreases during the reaction in accordance.

3.4 Rigid Polyurethane Foam Preparation

The main aim of this study was to achieve a product which is usable in polyurethane rigid foam formulation and shows no destructive effect on foam quality. A sample of recyclate from reaction 2 was selected to be examined during polyurethane foam formulating experiments. Blended polyols containing 10–40% PET recyclate were prepared and mixed well to be homogenized and then were used in a RIM machine. (Table 5) Urethane reaction time parameters were recorded during a cup testing in laboratory. Results are compared in Table 6. The quality control results are detailed in Table 7.

4 Conclusions

Recycling of waste PET flakes is performable using different DEG:DEA ratios, but more DEA leads to more time consuming process. The recyclate consists of some unreacted solvent mixture; a TPA based solid residue and an OH containing liquid product which is applicable in rigid PUF formulation. It is mentionable that contaminants exiting in the PET scrap are not able to affect the proposed recycling process. One of the most important results of this study was the hybrid process containing both glycol and amine agents and application of the OH containing recyclate in PUF production up to 50% of polyol blend.

The rigid PUF is formulated free of CFC blowing agents and water is utilized as the co-blowing agent. Improvement in some mechanical properties of rigid PUF would be another advantage of this product which is completely compatible with virgin polyol. The next step on this field might be a recycling agent which its product would be 100% useable instead of virgin polyol in PUF.

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