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INVESTIGATION OF POTENTIONAL USE OF RECYCLED POLY(ETHYLENE TEREPHTHALATE) IN POLYURETHANE SYNTHESIS

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Abstract: This paper presents an outline of developed methods for chemical recycling of postconsumer poly(ethylene terephthalate) (PET) waste bottles. Oligoesters (obtained by chemical recycled PET) with 2,2-bis (hydroxyl methyl) propionic acid, as hydrophobic monomer, and isophorone diisocyanate as cross-linker, in the presence of di-n-dibutyl tin(IV)dilaurate catalyst, were used for polyurethane dispersions. Molecular masses of obtained products were analyzed by gel permeation chromatography. Infra-red spectroscopy was used for molecular structures analysis. Thermal properties were evaluated by using differential scanning calorimetry and thermogravimetric analysis.

Keywords: recycling, poly(ethylene terephthalate), polyurethane dispersion.

1. INTRODUCTION

Various possibilities for utilizing poly(ethylene terephthalate), PET, product waste have been a subject of investigation for many years [1]. Due to low cost of PET polymer and its easy manufacture to get consumer products such as bottles, films or fibers, extensive use of these polymeric materials, i.e. their disposing after use, may present a threat to the environment. PET is polyester which is sensitive to some reagents, such as water (hydrolysis), alcohols (alcoholysis), acids (acidolysis), glycols (glycolysis) and amines (aminolysis). The main depolymerization processes that have reached commercial maturity up to now, because of their simple processing and valuable end products, include glycolysis and methanolysis. The glycolysis reaction is molecular degradation of PET polymer by glycols, in the presence of trans-esterification catalysts, mainly metal acetates [2], various chloride catalyst [3], and sodium sulfate [4]. The glycolysis products could be used for the synthesis of different resins, such as epoxy [5,6], unsaturated polyester resin [7,8,9], alkyd [10,11] or melamine formaldehyde resins [12].

Thanks to the environmental legislation such as the clean air act as well as technological advances, polyurethane dispersions (PUD) are a rapidly growing segment of polyurethane coatings industry [13]. In the wide range of applications such as adhesives and in the surface coatings industry [14], PUD have already been the main topic for many industrial and academic research centres. Their versatility and wide range of superior properties such as abrasion resistance, high flexibility at low temperature, excellent adhesion to many surface are the main reason for their continuously expanding use in many applications. They are free of isocyanate residues and have a zero or very low organic content (VOC), due to their processability with water. PUD can be tailor-made to have 30-65% solid content and a wide range of mechanical properties. The basic principle involved in producing PUD dispersions is to introduce solubilising groups, ionic centres, into the backbone of the polymer which render the polymer self-dispersible, such as carboxylic or sulfonic groups. The cationic PUD contains the quaternary ammonium moiety and is generally stable under acidic conditions. The non-ionic PUD has no ions in their structure and therefore is stable under a wide range of pH [15].

This paper primarily discusses a potential use of the recycled PET products in formulation of polyurethane dispersion coatings system. Recycled products of PET, olygoesters, were used for anionic polyurethane dispersions preparation with isophorone diisocyanate (IPDI), dimethylolpropionic acid (DMPA) as potential ionic centre which allow water

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dispersibility and ethylene dimine (EDA) as chain extender. Thermal properties were studied in detail in order to evaluate PUD dispersion composition.

2. EXPERIMENTAL

Postconsumer waste PET bottles with a number average molecular weight from 25000 to 30000, cut into 1 cm^2 pieces, were supplied from the local market. Propylene glycol, triethylene glycol and poly(ethylene glycol) were used as supplied. Zinc acetate was used as the transesterification catalyst for depolymerization of PET. Isophorone diisocyanate (IPDI) and dimethylolpropionic acid (DMPA) were used without further purification and were supplied by Aldrich Chemical Co. Ethylenediamine (EDA) was obtained from Zorka, Serbia. 1-methyl-2-pyrrolidone (NMP), dimethyl formamide (DMF) and triethyl amine (TEA) were received from Merk-Schuchardt. The dibutyltin dilaurate (DBTDL) was supplied by Bayer AG.

2.1. Glycolysis of PET

PET waste bottles (100 g) were added to 88.64 g PG, 173.07 g TEG or 461.5 g PEG, such that the molar ratio of PET repeating unit to glycol was 1:2. 0.5 wt.% zinc acetate (based on weight of PET as transesterification catalyst) was added to this mixture and charged into a glass reactor, which was equipped with a stirrer, reflux condenser, nitrogen inlet and temperature controller. Depolymerisation reaction was performed at 190 °C for 2 h, and after that the temperature was raised to 210 °C until all the solids disappeared.

Anionic polyurethane dispersions based on PET glycolyzed products were prepared by a modified acetone process. Acetone was added to the prepared prepolymer and the dispersion was formed by the addition of water to this solution. In order to prepare dispersion, the molar ratio of dimethylolpropionic acid (DMPA) as a hydrophilic monomer was adjusted to isophorone diisocyanate (IPDI). The appropriate ratio of DMPA to IPDI for polyurethane dispersion synthesis was 1:2.

The oligoester polyol and hydrophilic monomer was mixed in the co-solvent N, N-dimethylformamide (DMF) (50:50 w/w), in a 250-ml round four-neck glass reactor. The reaction was carried out at 70 °C for 30 min to obtain a homogeneous mixture and the uniform distribution of hydrophilic monomer to the polyurethane backbone. Isophorone diisocyanate and catalyst dibutyltin dilaurate were added to the homogenized mixture at 80 °C for 4h until the amount of residual NCO groups reached a theoretical value, as determined by the dibutyl amine back-titration method [20]. To reduce the viscosity and obtain a homogenous mixture of NCO prepolymers, acetone was added 50 wt% to the solid reaction mass. After obtaining completely NCO terminated prepolymer, the mixture was cooled to 60 °C and the carboxylic groups in hydrophilic monomer were completely neutralized by adding TEA dissolved in 1-methyl-2-pyrrolidone (5 wt% based on total solids) by stirring the solution for 60 min. The polyurethane anionomer was cooled to 30 °C then dispersed in water (50% of total mass) under high-speed stirring for 30 min. Upon completing the phase inversion, the ethylenediamine was added for 60 min at 35 °C. Polyurethane dispersion of about 30 wt% solids was obtained upon removal of acetone by rotary vacuum evaporation at 35 °C.

2.2. Characterization of obtained polymers

Fourier transform infrared spectra, FTIR, were recorded by Bomem Hartmann & Braun MB-series, in the wave band range from 400 to 4000 cm^{-1}. FTIR spectra were recorded as a film on KBr formed tablets under vacuum press.

The molecular mass distribution of glycolyzed products and obtained polyurethane dispersions were measured by gel permeation chromatography (GPC), using Agilent 1100 Series system with refractive index. ZORBAX PSM Columns 300, 250 × 6.2 mm, 5 μm was used and operated at temperature 25 °C with tetrahydrophuran as carrier solvent with 1.00 ml min^{-1} flow. The average molecular masses, M_n, M_w and polydispersity index Q were determined by software Agilent ChemStation. Poly(methyl metacrylate) standards were used to make calibration curve.

Thermogravimetric experiments were performed in a Perkin-Elmer TG-7 analyser. Film samples about 10 mg were placed in a platinum sample pan and heated from 30 to 600 °C, with an air flow of 200 mL min^{-1} and heating rates of 10 °C min^{-1}. During the heating period, the weight loss and temperature difference were recorded as a function of temperature.

Thermal properties of the samples were investigated by Differential scanning calorimetry (DSC) using Setaram 151R instrument (software SETSOFT 2000 from Setaram).

Table 1 The compositions of synthesized urethane prepolymers

Sample	PET /glycol molar ratio	Oligoester polyol (g)	DMPA (mol)	IPDI (mol)	TEA (mol)	EDA (mol)
PUD 1	PET/PG (1:2)	15.0	0.1	0.2	0.1	0.03
PUD 2	PET/TEG (1:2)	20.0	0.1	0.2	0.1	0.03
PUD 3	PET/PEG (1:2)	25.0	0.1	0.2	0.1	0.03

3. RESULTS AND DISCUSSIONS

The molecular structures of glycolyzed PET oligoesters and synthesized polyurethane dispersions were estimated by FTIR spectroscopy. Figure 1 shows the comparative FTIR spectra of PET oligoesters obtained by glycolysis with triethylene glycol and corresponding polyurethane dispersion.

The assignment of the most characteristic IR bands is presented in the Table 2. Bands from –C=O stretching which appears at 1720 cm^{-1} is a key band and confirmed ester bond formation during the glycolysis of PET using different glycols. This can be compared with used glycols FT-IR spectra which does not contain any band around 1750 cm^{-1}. Band around 3400 cm^{-1} is due to free hydroxyl group present in glycolyzed PET oligoesters. The most relevant bands correspond to N–H stretching at about 3400 cm^{-1}, CN stretching and δ NH stretching at about 1540 cm^{-1}, C–H stretching at 2950 cm^{-1} and C=O stretchings due to urea (1662–1618 cm^{-1}) and ester-urethane (1712-1707 cm^{-1}). FT-IR spectra show the characteristic C–O and N–CO–O stretchings (at about 1250 and 1040 cm^{-1}) and C–O stretching (at about 1110 cm^{-1}). According to these characteristics peaks formation of urethane group (–NHCOO–) was confirmed.

Glycolysis of PET and obtaining of polyurethane dispersions were confirmed by GPC analysis. Figure 2 shows the GPC chromatograms of the glycolyzed PET products. The number average molecular masses (M_n) of waste PET used for soft drink bottles are generally in the range of 25000 to 30000 g mol^{-1}. Molecular mass of PET in glycolysis (as depolymerization process) reduces and has values between 200 and 700 g mol^{-1}.The molecular masses of the oligoester polyols obtained by GPC and calculated according to the hydroxyl number value are summarised in Table 3. Also, the weight average molecular mass (M_w) and polydispersity index of oligoester polyol obtained from GPC were included. The results of molecular mass of oliogoester polyols obtained from GPC were higher than the corresponding value from the hydroxyl number. The polydispersityes of oligoester polyols based on molar ratio PET/glycol 1:2, were higher than 1.5 which was higher than polydispersity of obtained polyurethane dispersions. The molecular masses of the polyurethane dispersions were also determined using GPC and presented in Table 3.

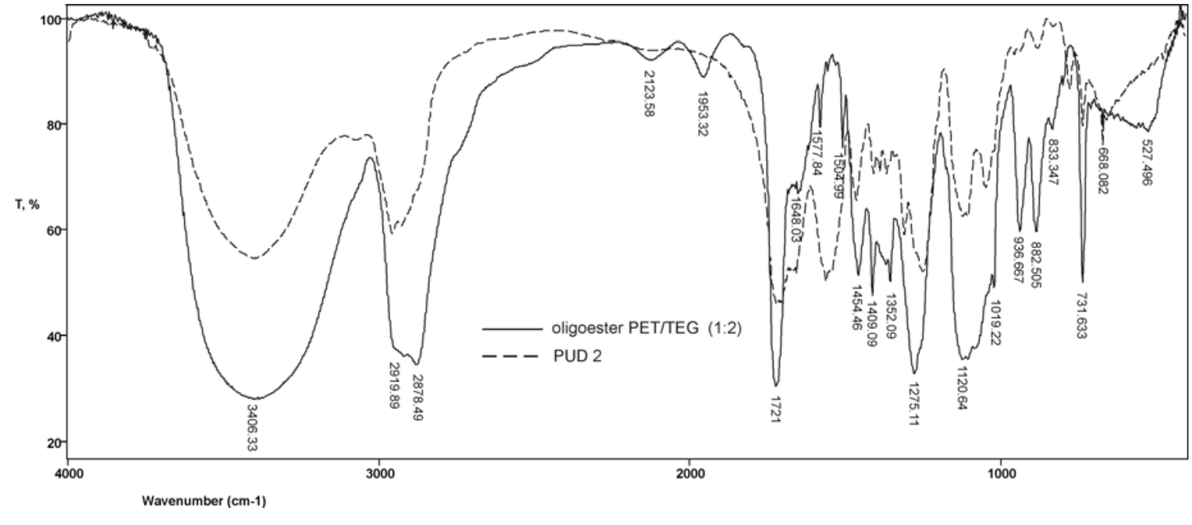

Figure 1. FT-IR spectra of PET oligoesters, PET/TEG 1:2, and polyurethane dispersion PUD 2

Table 2 Characteristic IR bands of the polyurethane dispersions [16]

Wavelength (cm^{-1})	Assignment
3420	st N–H (free)
3330	st N–H (bonded)
3000–2840	st C–H
1712-1707	st C = O (bonded ester and urethane)
1662–1618	st C = O (bonded disordered urea)
1610–1550	st C–N + δN–H
1470–1430	δ asym CH3
1475–1450	δ CH$_2$
1450–1400	st sy (COO$^-$)
1395–1365	δ sy CH3
1255–1247	st asym N–CO–O +st (C–O–C)
1124–1101	st (C–O–C)
1046–1040	st sy N–CO–O +st (C–O–C)
770	out-of-plane δ aromatic ring
st: stretching, δ: bending, sy: symmetric, asym: non-symmetric; bonded disordered urea: C=O of urea bonded to only one NH group nearby an urea o urethane.	

Table 3 Average molecular masses and polydispersity index of PET oligoesters and polyurethane dispersions.

Different PET/glycol	PET oligoesters				PUD dispersions		
	M_w	M_n	M_w/M_n	M_n^a	M_w	M_n	M_w/M_n
PET/PG (1:2)	209	190	1.65	230	2944	2982	1.01
PET/TEG (1:2)	210	223	1.52	303	3033	2960	1.02
PET/PEG (1:2)	215	201	1.64	378	3251	3204	1.00

[a] Calculated from OH values

Thermogravimetric analysis was used to analyse decomposition behaviour of cured polyurethane dispersion synthesized with glycolized products obtained from PET waste. The thermal stability of polyurethane dispersions is generally low, especially above their softening temperatures and the degradation mechanism is very complex due to the variety of products formed in the process [13, 17]. It was proposed that the thermal degradation of polyurethane is primarily a depolycondensation process, which starts at about 200 °C, and presents a multimodal profile. Polyurethane with different backbone structures has different thermal stabilities [18]. TG results were summarised in Table 4 which presents the degradation temperatures of polyurethane dispersions influenced by the variation of oligoester polyols. It was verified that thermal stability was influenced by glycol type, which can be ascribed to the increasing length of glycol in glycolyzed oligoester polyol (poly (ethylene glycol) (PEG 400) > triethylene glycol > propylene glycol).

Further information about phase structure of obtained polyurethane dispersion could be obtained from the analysis of DSC results. The low temperature of crystalline domains melting of the aliphatic soft segments and the transition of the soft and hard segments could be detected in the thermograms. Their positions are influenced by the types and quantity of segments. Transition temperatures of hard and soft segments measured by DSC are presented in Table 5. The transition of the hard segment is extremely weak since the heat capacity change of the stiff molecules upon glass transition is very small [19].

The observed melting peaks indicate some order in the soft domains influenced by diol quantity, Figure 4. With an increase of diol contents phase separation occurs, which is confirmed by increasing on hard segment Tg (from 83 °C to 92.5 °C).

The samples (PUD 1, PUD 2 and PUD 3) based on oligoester polyol, PET/glycol(1:2) exhibit two distinct T_g, which indicate that in these cases two kinds of segments are not mixed at molecular level. A possible explanation for this could be in the appearance of two or three peaks of first decomposition and higher value of polydispersity of GPC results. Glass transition temperature of hard segment decreases with the increasing of soft segment content (which allowed ordering of diols) due to limited mobility. Distribution of hard segments length and energy dissipation among hard segments, influenced by higher cross-linkage density, is responsible for this phenomenon [20].

DSC measurements prove that phase separation occurs, which is not very surprising, but the results also indicate changes in the properties of the phases influenced by types of diols.

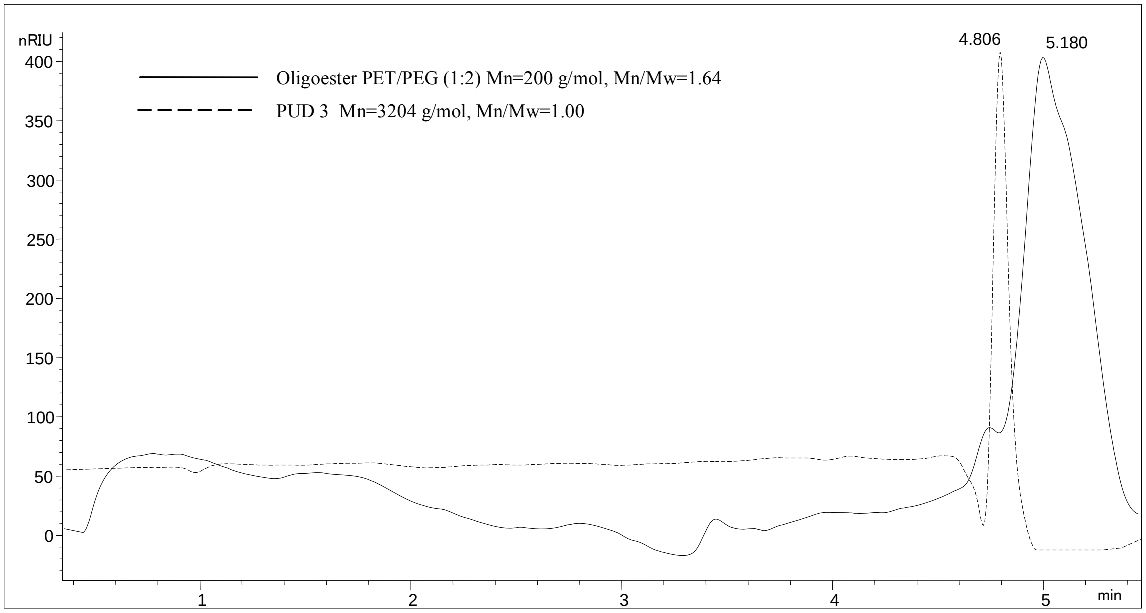

Figure 3. GPC chromatograms of glycolyzed oligoester polyol, PET/PEG, and polyurethane dispersion, PUD 3.

Table 4 Temperature of decomposition of the polyurethane dispersions.

Sample	First decomposition		Second decomposition	Third decomposition
	T_{1on} (°C)	T_{1max} (°C)	T_2 (°C)	T_3 (°C)
PUD 1	190.2	270.7	349.7	400.3
PUD 2	-	288.0	335.1	401.9
PUD 3	248.6	-	316.5	403.4

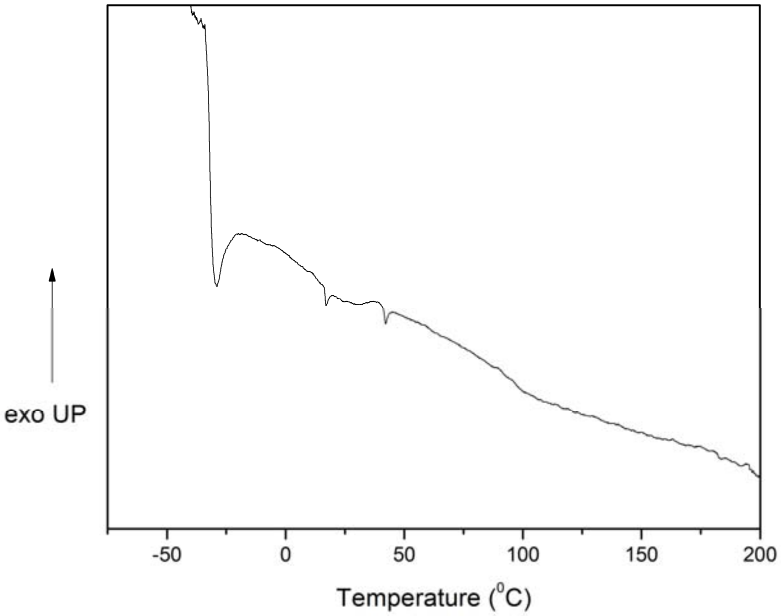

Figure 4. DSC thermogram of polyurethane dispersion PUD 1

Table 5 Thermal properties of synthesised polyurethane dispersion (obtained by DSC method).

Sample	Different PET /glycol	Tg °C	Tm °C
PUD 1	PET/PG (1:2)	-30.2, 92.5	17.2, 40.0
PUD 2	PET/TEG (1:2)	87.6	56.09
PUD 3	PET/PEG 400 (1:2)	–35.0, 38.0	61.87

4. CONCLUSIONS

Waste PET flakes were depolymerised by using different molar ratio PET/ propylene glycol (PG), triethylene glycol (TEG) and poly(ethylene glycol) (PEG 400) as 1:2. The main purpose of this study is to investigate the possibility of using glycolysis products of waste PET in polyurethane dispersions manufacturing. The effects of glycol type and the different mole ratios of PET to glycol on thermal and coating properties of polyurethane dispersions have been described. The degradation profile of the dispersions was dependent on mole ratios of PET to glycol in glycolyzed products. The samples based molar ratio, PET/glycol(1:2) exhibit two distinct T_g, which indicate that in these cases two kinds of hard segments are formed and not mixed at molecular level. Therefore, it is thought that glycolized products obtained from recycled PET would be applicable to the polyurethane dispersions.

5. ACKNOWLEDGEMENTS

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ИСПИТИВАЊЕ МОГУЋНОСТИ КОРИШЋЕЊА ПРОДУКАТА РЕЦИКЛАЖЕ ПОЛИ(ЕТИЛЕН ТЕРЕФТАЛАТА) ЗА СИНТЕЗУ ПОЛИУРЕТАНСКИХ ДИСПЕРЗИЈА

Сажетак: У раду су приказани поступци хемијске разградње искоришћених боца (на основу поли(етилен терефталата) (ПЕТ)) у циљу добијања продуката који би се могли искористити за добијање анјонских полиуретанских дисперзија. Синтеза анјонских полиуретанских дисперзија изведена је коришћењем гликолизованих ПЕТ олигоестара, 2,2-бис(хидроксиметил) пропионске киселине, као хидрофилног мономера, и изофорон диизоцијаната као умреживача. Анализа молских маса добијених продуката је рађена методом гел пропусне хроматографије, док је инфрацрвена спектроскопија са Фуријеовом трансфорамцијом искоришћена за потврду структуре добијених продуката. Топлотна својства добијених полиуретанских дисперзија су проучавана методама диференцијалне скенирајуће калориметрије и термогравиметријске анализе.

Кључне ријечи: рециклажа, поли(етилен терефталата), полиуретанске дисперзије.

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