

Epoxy Resin and Polyurethane Compositions from Glycolized Poly (ethylene terephthalate) Wastes

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The possibility to use poly(ethylene terephthalate) (PET) bottles production waste as raw material for compositions with high adhesion ability has been investigated. PET waste was glycolized with polypropylene glycol and three kinds of oligoesters were formed after depolymerization reaction. The polydispersity of product formed was 1.05. The possibilities to use PET glycolysis products – oligoesters for epoxy resin and polyurethanes were studied. Two-step reaction of oligoesters with epichlorohydrin was chosen for epoxy resin synthesis, while glycolized PET reaction with aliphatic isocyanate was used for polyurethane synthesis. The structure and properties of the obtained polymers were investigated.

Keywords: PET waste, glycolysis, glycolized oligoesters, epoxy resin, polyurethane.

1. INTRODUCTION

Poly(ethylene terephthalate) (PET) is thermoplastic polyester widely used in diverse application as textile fibres, films, bottles and other moulded products [1]. One of the main reasons for the PET widespread use is their possibility of producing a number of different grades over a broad range of molecular weights in a single multiproduct polymerization plant [2]. Moreover, among all plastics PET has received particular attention in terms of post-consumer recycling due to the relatively large availability of PET bottles from special collection scheme [3]. PET occupies the top of the list of polymers to be recycled due to its easy recycling by different ways and receive variable products [2].

PET can be chemically processed by total depolymerization into monomers or partial depolymerization into oligomers and other products [2]. Chemical recycling of PET includes chemolysis of the polyester with an excess of reactants such as water (hydrolysis), alcohols (alcoholysis), glycols (glycolysis) amines (aminolysis) and ammonia (ammonolysis) [4].

PET waste depolymerized by glycolysis to obtain oligomeric diols and polyols, or glycolized into monomeric units to obtain bis(2-hydroxyethyl) terephthalate (BHET) or dimethyl terephthalate [3–5]. BHET can be used as a substrate to create PET and other polymers [4–8].

Glycolysis reaction is the molecular degradation of PET polymer by glycols, in the presence of trans-esterification catalysts, mainly metal acetates, where ester linkages are broken and replaced with hydroxyl terminals. Nowadays the focus mainly is made on new trends of glycolysis reactions, as this process is more advantageous from the economical point of view than other kinds of chemolysis [9].

The products of PET chemical recycling are widely used in the production of unsaturated polyesters, polyester moulding compounds, topcoats of reinforced plastics, varnishes, binders for glass-fabrics, pre-pregs, polymer plasters, mortars, and concrete materials with mineral fillers

as well as fibres, polyoles for polyurethane elastomers, foams, and polyurethanes of low flammability [4–5].

Application of the products of PET chemical degradation to epoxy resins technology has also been the subject of research [10]. Products of aminolysis with tertiary alkanolamines of PET wastes are used as a new group of hardeners for epoxy resins. Mixtures of derivatives of terephthalic acid and suitable alkanolamines show high reactivity toward liquid epoxy resins. Epoxy resins cured with amino-glycolysis products exhibit improved impact strength, high mechanical strength, and thermal stability [11, 12]. Moreover, epoxy compositions with the products of PET amino-glycolysis are very good binders characterized by high shear strength. Czup P. in [13] describes application of the product of PET amino-glycolysis and glycerol as the modifiers for low-molecular-weight epoxy resin. In the PET recycling procedure obtained oligoesters can be further reacted with aliphatic diacids to form polyester polyols that can be used as a starting material in the polyurethane industry, also [3, 14]. Rigid polyurethane foams prepared from the product of PET degradation with triethanolamine can be considered as insulation materials [15]. The depolymerization products of PET by ethylene glycol, diethylene glycol, polyethylene glycol and glycerin were transesterified with the glycolized products of soy bean oil and glycerine. The films of all synthesized urethane oils exhibit good hardness, excellent flexibility, and high impact strength. Moreover, these prepared urethane oils have better adhesion properties compared with those of the commercial urethane oil [17].

Glycolized PET oligoesters can be reacted directly as a polyol component with isocyanate compounds to build up a urethane groups [14, 18, 19].

Thus, the aim of this study was to investigate the possibilities to use of the oligoester diols produced from PET bottles production waste recycling as potential raw materials for high adhesion ability compositions, such as epoxy resin and polyurethanes, suitable for various surfaces (i. e. wood, metal) coating.

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2. EXPERIMENTAL

2.1. Materials

PET production waste was collected from beverage bottles, produced by Join Stock Company "Selita" (Lithuania). Main characteristics of PET waste are presented in Table 1.

Table 1. Main properties of PET waste to be used

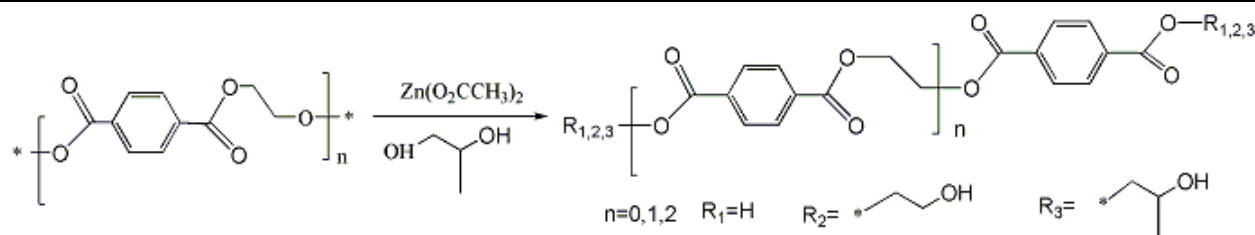
Characteristic	Value	
Melting point T_m , °C	265	
Glass transition temperature T_g , °C	77	
Mechanical properties at tension:	transverse direction	perpendicular direction
– yield point, MPa	104	62
– tensile strength, MPa	124	85
– Young's modulus, MPa	1258	891
– elongation at break, %	50	80

The depolymerization of PET waste using propylene glycol was used to produce hydroxyl-oligomers. For polymeric compositions with high adhesion capability synthesis hydroxyl-oligomer reaction with epichlorohydrin and aliphatic isocyanate Kendor C (specific gravity at $T = 25^\circ\text{C}$ is 1.17, viscosity at $T = 20^\circ\text{C}$ is 50 cps, NCO groups amount – 7 %) from Kenda Farben (Italy) were chosen. It is free from water and alcohols and is soluble in ketones, ethyl acetate, trichloroethylene, xylene, etc.

Main properties of materials to be used for PET waste decomposition and polymers synthesis are listed in Table 2.

Table 2. Main properties of materials to be used

Materials	Producer	Purity, %	Molar mass, g/mol	Melting point, °C	Boiling point, °C
PET glycolysis					
Propylene glycol	Sigma-Aldrich Inc. (Germany)	99.50	76.09	-59.0	188.2
Zinc acetate	Sigma-Aldrich (Germany)	99.99	183.48	–	–
Synthesis of epoxy resin					
Epichlorohydrin	Sigma-Aldrich (Germany)	99.00	92.52	-25.6	117.9
Toluene	Eko Plon (Poland)	99.90	92.14	-93.0	110.0
Sulphuric acid	Eko Plon (Poland)	93.50	98.06	10.0	337.0
Sodium hydroxide	Eko Plon (Poland)	98.80	40.00	–	–
Calcium carbonate	Eko Plon (Poland)	99.00	100.09	–	–
2-Ethylhexyl glycidyl ether	Sigma-Aldrich (Germany)	98.00	186.29	–	62.0
Triethylamine	Sigma-Aldrich (Germany)	99.00	101.19	-115.0	88.9
Isophorondiamine	Sigma-Aldrich (Germany)	99.00	170.30	10.0	247.0
Synthesis of polyurethane					
Isobutyl acetate	Eko Plon (Poland)	99.50	116.16	-99.0	118.0
Acetone	Eko Plon (Poland)	99.50	58.08	-94.9	56.5



Scheme 1. Glycolysis of PET waste (PET-Gly)

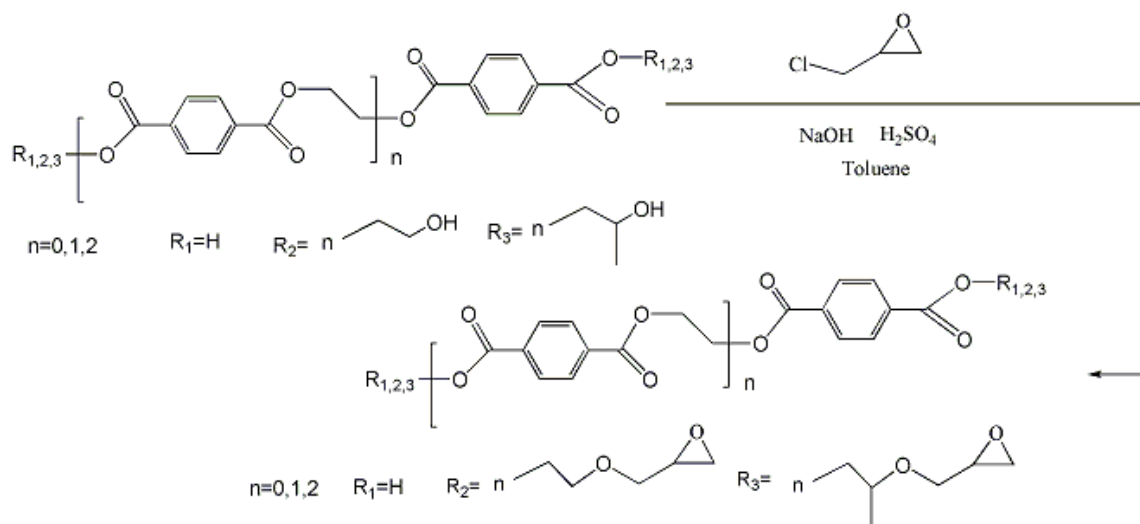
2.2. PET glycolysis

The glycolysis of PET depends on the reaction conditions represented in the glycolysis time and temperature, catalyst concentration and glycol concentration [17–19]. When glycols are used as destructing agent, the oligoester obtained have two hydroxyl end groups, i.e. oligoester diols were formed.

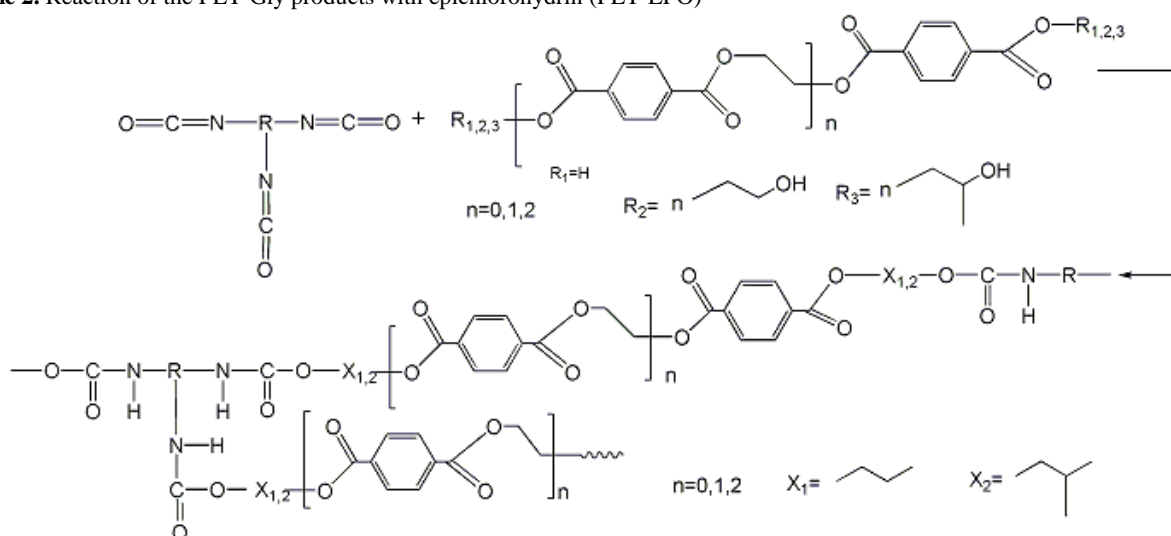
The temperature of glycolysis reaction of PET with propylene glycol was fixed at 210°C throughout the reaction to prevent the formation of cyclic derivatives between hydroxyl groups of the produced poly-hydroxy glycolized PET [23–24]. The glycolysis of PET waste was accomplished using the amount of the glycol sufficient for effective depolymerization of PET, but also as low as possible to leave some amount of glycol in the degradation products for the reaction with epichlorohydrin and isocyanate.

PET waste flakes, totalling 76.8 g equivalent to 0.4 mol repeating unit, 0.48 mol (36.52 g) propylene glycol and catalyst (0.2546 g, 0.001 mol of $\text{Zn}(\text{O}_2\text{CCH}_3)_2$) were charged into the flask such that the molar ratio of PET repeating unit to propylene glycol would be 1:1.2. Such mixture was charged into a three-neck, round-bottom 500 ml glass flask equipped with the reflux condenser, nitrogen inlet, thermometer, and mechanical stirrer there used for the glycolysis process.

Prior to addition of PET waste, the propylene glycol and the catalyst were charged into the flask and preheated at temperature of 85°C . After that the PET flakes were placed into the reactor. The glycolysis reaction was allowed to proceed for up to 8 h at temperature of 200°C under reflux in the nitrogen atmosphere.



Scheme 2. Reaction of the PET-Gly products with epichlorohydrin (PET-EPO)



Scheme 3. Reaction of the PET-Gly products with aliphatic isocyanate (PET-IZO)

The oligoester diols (PET-Gly) structure formed during the used reaction is shown in Scheme 1. This reaction product was used as it is for the next reaction for epoxy resin and polyurethanes synthesis.

2.3. Polymers synthesis methods

PET glycolysis product reaction with epichlorohydrin.

After decomposition obtained glycolysis products PET-Gly were applied in the two step reaction with epichlorohydrin. Because of the poor solubility of the glycolysis products in many organic solvents, the classical methods consisting of the halohydrin formation step and its dehydrohalogenation was chosen for the synthesis of epoxy resins [13]. Sulphuric acid was used as a catalyst for the opening of oxirane ring in the addition all step and sodium hydroxide was used for the dehydrochlorination process. The addition reaction was performed in toluene.

The synthesis of epoxy resin was carried out in the 500 ml three-neck round-bottom flask equipped with an efficient stirrer, a thermometer and a reflux condenser. The glycolyzed PET with propylene glycol and toluene was charged in the flask and heated up to the boiling temperature of toluene. When glycolyzed PET dissolved completely, 95 % of sulphuric acid (0.115 mol) was

poured. After that the epichlorohydrin (0.470 mol) was added dropwise with vigorous stirring, while keeping the reaction mixture refluxed (3–4 h). After the addition of epichlorohydrin stirring was continued for 1 h. Then sulphuric acid was neutralized using calcium carbonate (11.5 g, 0.115 mol). After that 30 % aqueous sodium hydroxide solution (18.8 g, 0.470 mol) was added dropwise and the reaction was continued for 4 h at $T = 100^\circ\text{C}$. Structure of product obtained during oligoester reaction with epichlorohydrin is presented in Scheme 2.

At the end of synthesis process the organic phase was separated from the water phase and washed three times with hot distilled water. The residual water, toluene, and excess of epichlorohydrin were distilled off. The mixture of synthesis product PET-EPO and 20 % of reactive solvent (ethyl glycidyl ether) as well as 3 % of triethylamine as a catalyst was prepared. The cross-linking of epoxy resin was performed at temperature of 80°C for a time of 24 h using isophorondiamine as a hardener.

PET glycolysis product reaction with aliphatic isocyanate. In that case for the crosslinking of glycolysis product PET-Gly the aliphatic isocyanate was used. The terminal hydroxy groups of PET-Gly molecules react with isocyanate groups forming urethane links in polyaddition

cross-linking reaction (PET-IZO) as can be seen from Scheme 3.

The best performance is achieved by choosing equivalent amounts of hydroxyl number and NCO% content: $n_{\text{NCO}} = n_{\text{OH}}$ [25]. The amount of isocyanate m_{NCO} necessary for equivalent cross-linking of 100 g of PET-Gly was determined according to the formula [25]:

$$m_{\text{NCO}} = \frac{\text{OH}_{nb} \cdot M_{\text{NCO}} \cdot 10}{\text{NCO}\% \cdot M_{\text{KOH}}}, \quad (1)$$

where M_{NCO} and M_{KOH} are molar masses of components (g/mol); OH_{nb} is OH number of PET-Gly; NCO% is amount of NCO groups in aliphatic isocyanate.

The samples after mixing the components were kept at room temperature for 24 h. The glycolyzed PET showed relatively high viscosity and, therefore, it was impossible to use it as coating primer. In order to solve this problem isobutyl acetate as the solvent was chosen.

2.3. Testing methods

The content of epoxy groups (epoxy value) in the resins obtained was determined by titration of the samples dissolved in 0.2 N HCl solution in acetone. The excess of acid was titrated with 0.1 N of NaOH solution in distilled water in presence of phenolphthalein as the indicator of acid value.

$^1\text{H-NMR}$ spectra of the glycolysis products and epoxy resins were recorded in CDCl_3 and analyzed using the spectrometer operating at 300 MHz. The chemical shifts were reported in ppm units using tetramethylsilane (TMS) as internal standard.

Thermal stability of polyurethane was studied using Linseis TGA PT1000 thermogravimetric analyser. The heating rate was set to $10^\circ\text{C}/\text{min}$ and the temperature range was from 30°C to 1000°C .

The amount of unreacted starting compounds was determined by extraction method using a Soxhlet apparatus and acetone as extragent. The extraction was performed for 8 h in boiling acetone.

FT-IR spectra were collected on a Perkin Elmer FT-IR (Perkin Elmer Spectrum-BX II) spectrometer by casting thin liquid samples between KBr plates.

Mass spectra were obtained on a Waters ZQ 2000 (Waters, Milford, USA) spectrometer.

Tensile tests were carried out at room temperature using universal testing machine H25KT with load cell of 250 N (Tinius Olsen, England). A cross-head speed of 50 mm/min was used. Measurements were performed at the room temperature with the specimens having gage area of 12 mm \times 20 mm and thickness of 0.2 mm \pm 0.1 mm. Four specimens were tested for each set of samples.

3. RESULTS AND DISCUSSIONS

3.1. PET glycolysis product PET-Gly characterization

In order to check the extent of depolymerization, PET-Gly was analyzed by mass spectrometry. The MS spectrum of glycolysis reaction products is shown in Fig. 1.

It clearly indicates that three kinds of oligoesters ($n = 0, 1,$ and 2), which are formed as the main products after glycolysis reaction. The spectrum also shows that very

small amount of $n = 3$ fraction was formed that due to the negligible amount it will be neglected. The number average molecular weight (M_n) and weight average molecular weight (M_w) of oligoester diols formed were calculated according to the mass spectra. Hydroxyl value was found to be 365 mg KOH/g, $M_n = 441$ g/mol, while $M_w = 419$ g/mol. Thus, polydispersity index of the formed PET-Gly is $M_w/M_n = 1.05$.

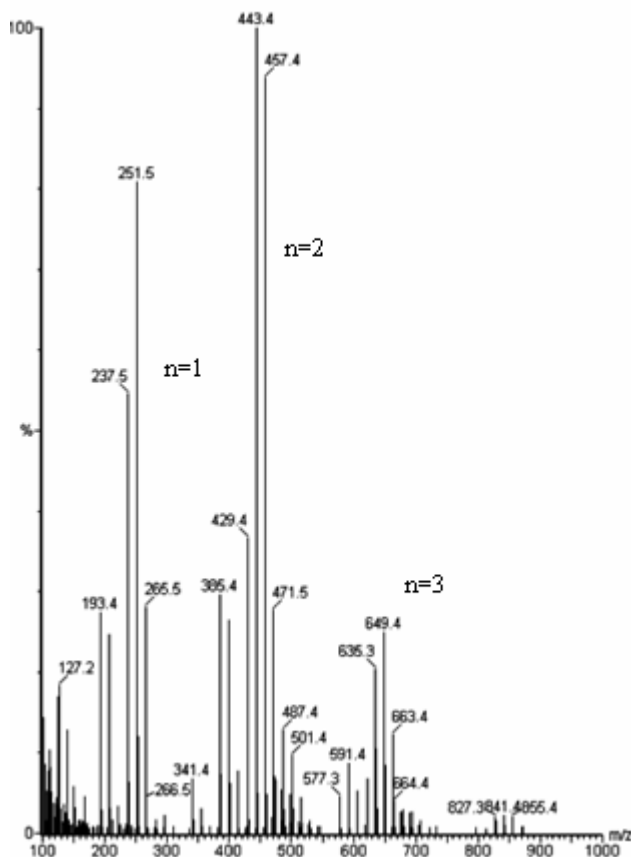


Fig. 1. Mass spectra of the PET-Gly product

The structure of the PET oligomers with propylene glycol was verified from FT-IR spectra (Fig. 2, curve 1). The presence of strong band at 3426 cm^{-1} indicates the termination of the glycolyzed products with hydroxyl groups. On the other hand, the bands observed at 728 cm^{-1} and 873 cm^{-1} for depolymerized PET is assigned to $-\text{CH}$ out-of-plane bending of phenyl. These bands confirm the presence of phenyl rings in depolymerized product. Strong peaks at 1716 and $1127, 1105,$ and 1078 cm^{-1} , which were assigned for $\text{C}=\text{O}$ stretching and $\text{C}-\text{O}$ stretching of ester groups, indicates the presence of ester groups in depolymerized PET product.

3.2. Epoxy resin formation and characterization

During the reaction of oligoesters with epichlorohydrin the halohydrin formation and its dehydrohalogenation proceeds. Structure of PET-EPO investigation performed by FT-IR spectroscopy is shown in Fig. 2, curve 2. Comparing the intensities of the bands at 3426 cm^{-1} of PET-Gly and PET-EPO it may be stated that the intensities of OH bands at 3426 cm^{-1} decrease and the absorption of the $\text{C}-\text{O}-\text{C}$ bonds at 1069 cm^{-1} and 1261 cm^{-1} increase,

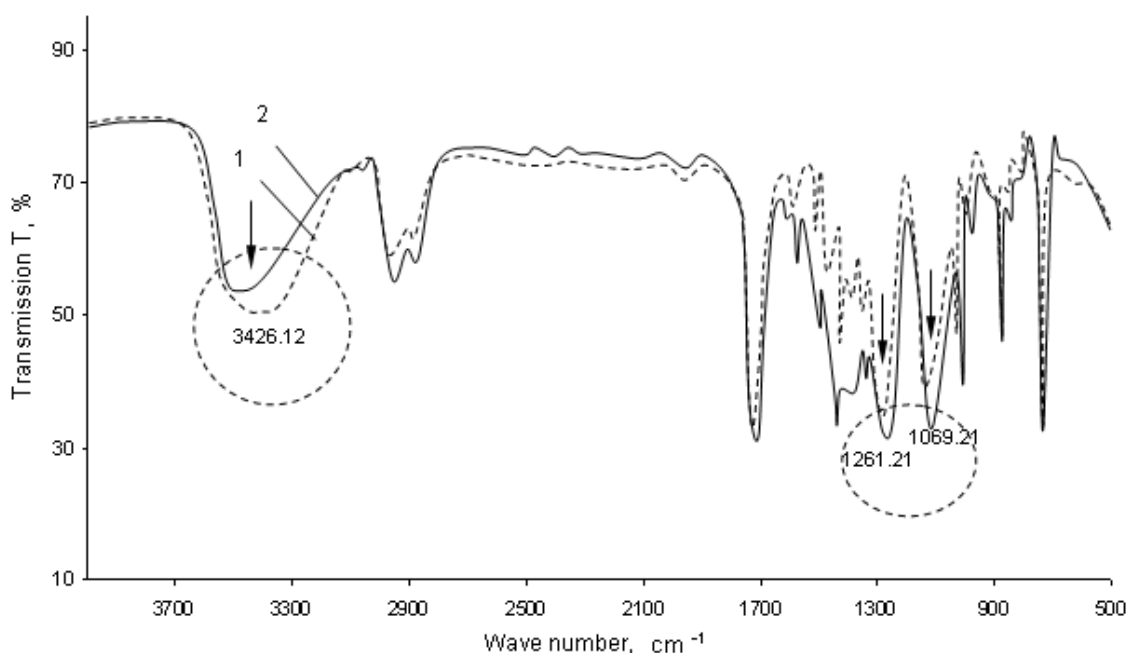


Fig. 2. FT-IR spectra of the depolymerized oligoester PET-Gly (1) and synthesized epoxy resin PET-EPO (2)

indicating that some of the OH groups reacted with epichlorohydrin.

The comparison of PET-Gly and PET-EPO SEC elution curves shows that average molecular weights of epoxy resin are very similar to the glycolyzed PET (Fig. 3).

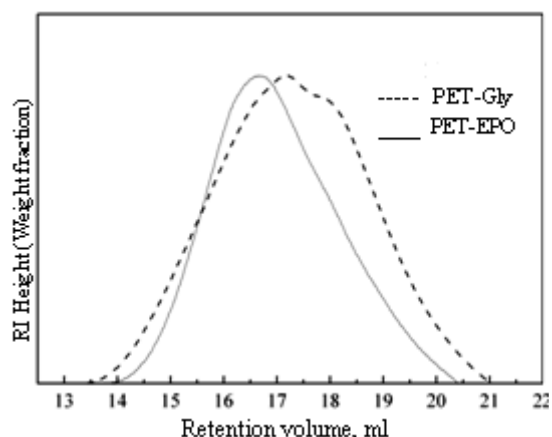


Fig. 3. SEC elution curves of PET-Gly and PET-EPO

The differences between $^1\text{H-NMR}$ spectra of PET-Gly and obtained PET-EPO are presented in Fig. 4. In the spectrum of the epoxy resin resonances at 8, 4.8 and 4.3 ppm represent phenyl groups $\text{HO-CH}_2\text{-CH-OH-CH}_3$ and $\text{HO-CH}_2\text{-CH}_2\text{-OH}$ of glycolyzed PET. The signal observed at 2.3 ppm represents OH group and indicates the presence of terminal OH in glycolyzed PET.

Epoxy resin PET-EPO synthesized from glycolyzed PET wastes was obtained with the 53.7 % yield of weight of initial reactants. The epoxy value determined by titration method shows that the polymer contains 9 % of epoxy groups of the total amount of resin.

The obtained epoxy resin PET-EPO showed relatively high viscosity, therefore, it was impossible to use obtained as coating polymer. In order to solve this problem the ethyl glycidyl ether as the reactive solvent was chosen. However,

further investigations show that PET-EPO with 9 % of epoxy groups was cured not effectively, because 88 % of unreacted starting components were extracted after cross-linking reaction. Thus, PET-EPO obtained as product of glycolyzed PET reaction with epichlorohydrin is not suitable for the formation of coating layer that would be resistant to the chemicals and temperature or humidity changes.

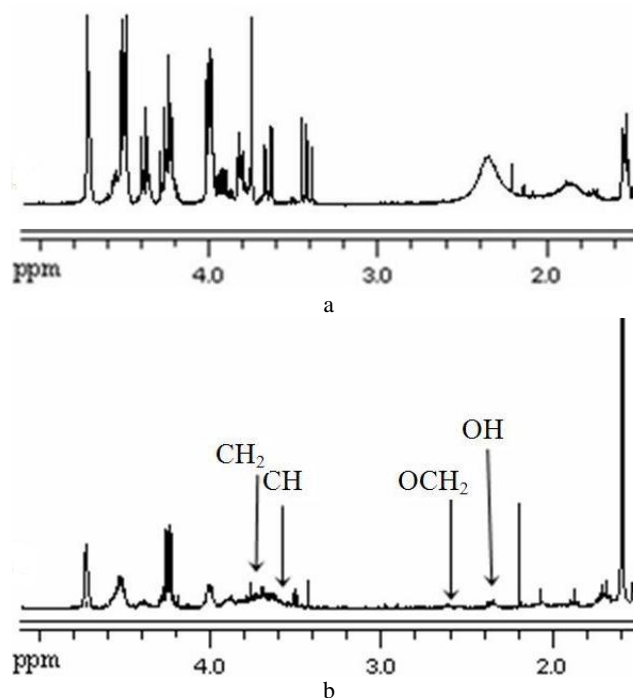


Fig. 4. $^1\text{H-NMR}$ spectra of the glycolysis product PET-Gly (a) and its reaction with epichlorohydrin (b)

3.3. Polyurethane synthesis and PET-IZO product characterization

In further investigations the ability of the directed reaction of the terminal groups of glycolyzed PET with aliphatic isocyanate was studied. Several compositions with that balance

the stoichiometric ratios of the aliphatic isocyanate for cross-linking were prepared for investigations. Their properties are listed in Table 3. The extraction results showed that composition that contains 77 % of isocyanate was cured most effectively, because only 3 % of unreacted starting components were extracted. However, in the cases of other compositions the amount of unreacted components is low, also.

Table 3. The compositions of polyurethanes

Parameter	Composition			
	I	II	III	IV
Amount of aliphatic isocyanate, %	74	76	77	79
Amount of NCO groups, %	8.9	9.1	9.2	9.5
Amount of unreacted components, %	8	4	3	4
The swelling in nonpolar solvent (toluene), %	19	19	16	13
The swelling in polar solvent (chloroform), %	20	20	19	18
Tensile strength, MPa	11.7	12.3	13.5	17.9
Elongation at break, %	14.2	12.0	5.8	5.0
Young's modulus, MPa	82.3	102.5	232.8	358.0

In order to analyse the completeness of the curing process the FT-IR spectra were taken of every composition, but in Fig. 5 only spectrum of mostly effective PET-IZO composition (composition III) is presented. The presence of strong band at 3300 cm^{-1} indicates N-H absorptions that show the formation of urethane links. As well as hydrogen bonds and no bonded N-H group absorption show band at 3446 cm^{-1} . IR spectrum also shows two carbonyl bands – one at 1707 cm^{-1} assigned to bonded C=O groups, and second at 1731 cm^{-1} assigned to free C=O groups. The weak absorption band at 2415 cm^{-1} indicates that some of N=C=O groups remain unreacted.

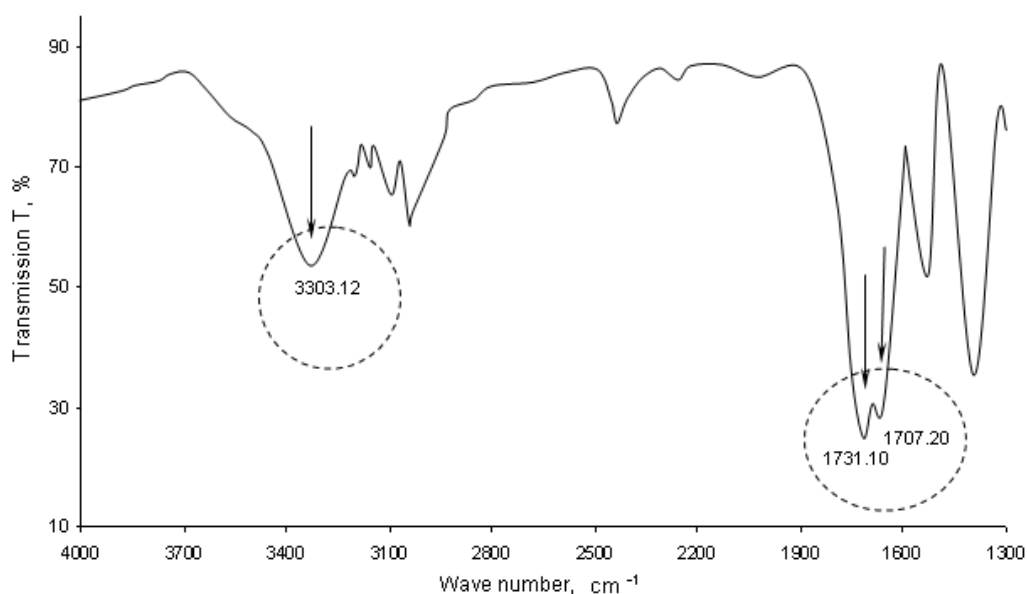


Fig. 5. FT-IR spectrum of synthesized PET-IZO polymer

The swelling of polymer in polar and nonpolar solvents is important in terms of the potential application as well as gives some information about the structure and properties of polymers [26]. The kinetic curves of swelling of the polyurethane compositions are presented in Fig. 6. As can be seen the swelling ability of PET-IZO compositions in nonpolar (toluene) and polar (chloroform) solvents slightly decreases as NCO groups amount increases from 8.9 % up to 9.5 % (Table 3). It can be explained by the different density of the cross-links and the formation of the longer molecular chains between crosslinking points in the polymer network when the concentration of the NCO groups in the composition increases. Furthermore, higher influence of network density of PET-IZO on the swelling process is observed in nonpolar solvent, i.e. toluene (Fig. 6, a).

Thermal analysis of the polyurethane composition enabled to determine some characteristics, such as the temperature of the beginning of the weight loss, the temperature of the beginning of the thermal degradation, the temperature of the highest rate of the weight loss. The studies show that NCO groups amount to be investigated does not have any significant effect on the thermal stability of the polyurethanes compositions.

Typical thermogravimetry (TGA) and differential thermogravimetric analyse (DTGA) curves of polyurethane PET-IZO (composition III) are presented in Fig. 7. The first step of the weight loss (about 8 % – 11 %) at temperature range $120^{\circ}\text{C} - 240^{\circ}\text{C}$ is related to the evaporation of the moisture and low molecular weight compounds. During the most intense degradation step that corresponds to the peaks 1 and 2 of DTGA curve at temperature range $240^{\circ}\text{C} - 300^{\circ}\text{C}$ the weight loss reaches 30 %.

Vitkauskiene I. et al. in [14] reported similar thermal profiles and mass loss of polyisocyanurate foams based on aromatic polyester polyols. The largest weight residue was characteristic for the polyurethane prepared from the branched polyol component. Usually, polyurethane structure decomposes at temperature around of $T = 200^{\circ}\text{C}$ giving a char yield about 20 % [14].

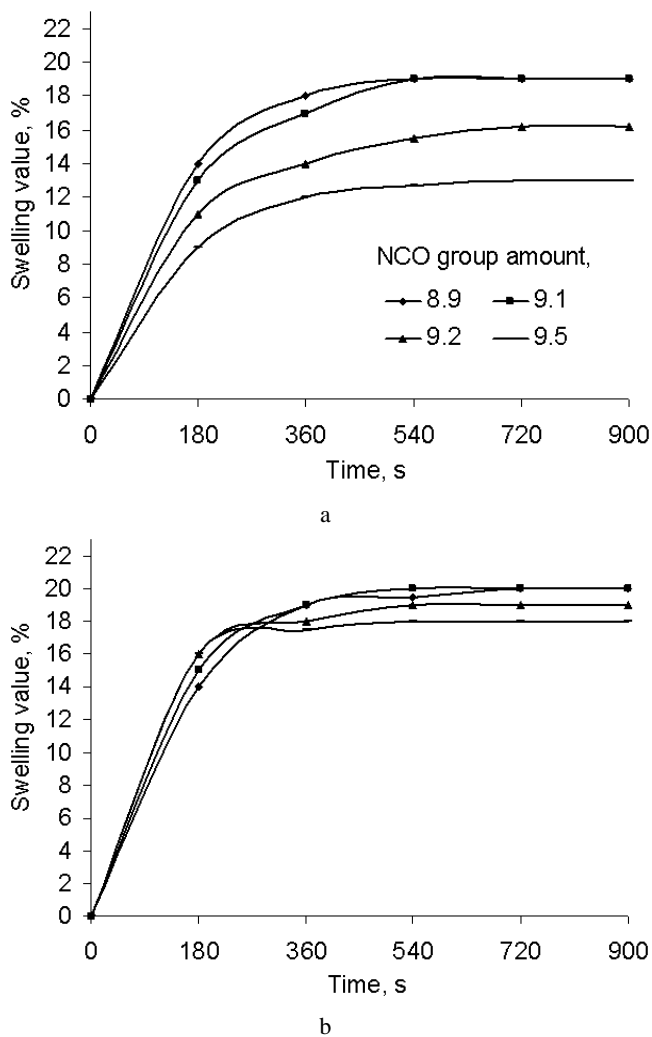


Fig. 6. The kinetic curves of PET-IZO compositions swelling in toluene (a) and chloroform (b) depending on the amount of NCO groups

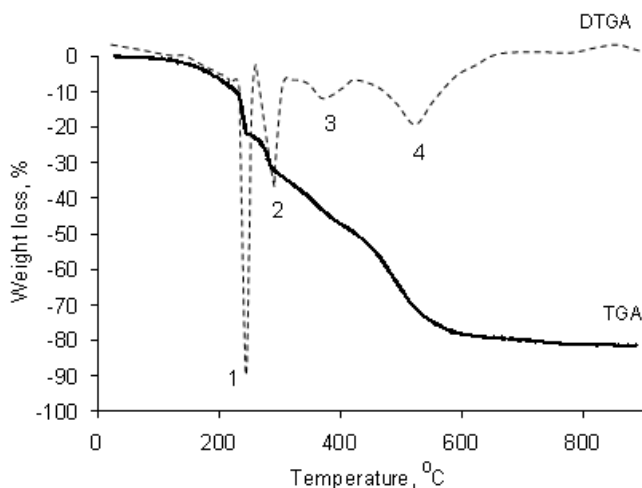


Fig. 7. TGA and DTGA curves of obtained PET-IZO polymer

Urethane bonds formed under the reaction of aliphatic isocyanate with polyols are characterized by the temperature of thermal dissociation at temperature of 200 °C [27, 28]. Dissociation or chain scission reactions in thermal degradation mechanisms of polyurethanes were summarized by D. K. Chattopad [29]: 1) dissociation to

isocyanate and alcohol; 2) formation of primary amino and olefin; 3) formation of secondary amine; 4) transesterification-type bimolecular displacement.

Thus, the peaks 1 and 2 DTGA curve trace are related to the polyurethane chain scission of polyol linkages, while peaks the 3 and 4 – chain scission of urethanes and carbodiimide linkages.

The investigations of mechanical behaviour at tensile show that high tensile strength and Young's modulus and sufficient elongation at break are characteristic for PET-IZO films (Table 3). Thus, it may be supposed that such PET-IZO compositions can form layers with properties required for high resistant coatings.

4. CONCLUSIONS

The PET oligoester from PET waste was prepared by glycolysis reaction with propylene glycol as raw material for epoxy and polyurethane compositions. The glycolyzed PET with molecular weights of $M_n = 419$ g/mol and $M_w = 441$ g/mol and polydispersity index 1.05 was obtained.

Two-step reaction of oligoesters with epichlorohydrin – halohydrin formation and its dehydrohalogenation – was applied for epoxy resin synthesis. Although obtained epoxy resin contains 9 % of epoxy groups, however, 88 % of resin starting components were extracted after cross-linking reaction. Such composition can not to form coating layers with proper properties.

Cross-linked polyurethane was obtained by synthesis of glycolyzed PET with high amount of aliphatic isocyanate. The composition that contains 75 % – 79 % of isocyanate was cured effectively and only 3 % – 8 % of unreacted starting components were extracted. Such composition can be used for formation of the coatings with high mechanical properties.

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