

Glycolysis of industrial poly(ethylene terephthalate) waste directed to bis(hydroxyethylene) terephthalate and aromatic polyester polyols

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Industrial PET waste was recycled by glycolysis using both 1,2-ethanediol (ethylene glycol) to obtain bis(hydroxyethylene) terephthalate (BHET) and 2,2'-oxydiethanol (diethylene glycol) in the absence or presence of glycerol and adipic acid to obtain aromatic polyester polyols (APP). A high yield (ca 82%) of high quality BHET was obtained under 3 h of reflux at 190 °C. APP with the hydroxyl number in the range 290 to 430 mg KOH/g and viscosity in the range 3000 to 38000 mPa · s were prepared. APPs synthesized in the presence of functional additives were amorphous, more viscous and much more stable against crystallization. The effect of the amount and type of the organometallic catalyst on the properties of APP was investigated.

Key words: industrial PET waste, glycolysis, aromatic polyester polyols, recycling

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester showing excellent thermal and mechanical properties. PET is one of the versatile engineering plastics which is used to manufacture mainly textiles and bottles, as well as packaging, photographic films, video and audio tapes. The rapid development of PET production industry inevitably causes a continuously growing stream of post-consumed and industrial PET waste. The main PET waste source today is PET flakes taken from post-consumed soft drink bottles. In the manufacture of bottle-grade PET, industrial waste is generated at various stages of the production and includes PET prepolymers, oligomers, polymer dust and lumps, ill-conditioned products, etc. Recycling of industrial PET waste from the NEO GROUP bottle-grade PET plant (Lithuania) was studied with the aim to convert it to useful intermediates.

The chemical recycling of PET includes glycolysis, methanolysis, hydrolysis and similar processes. PET waste can be depolymerised by glycolysis obtaining oligomeric diols and polyols, or glycolysed into the constitutional repeating units of PET bis(hydroxyethylene) terephthalate (BHET) and a mixture of its oligomers (Scheme 1).

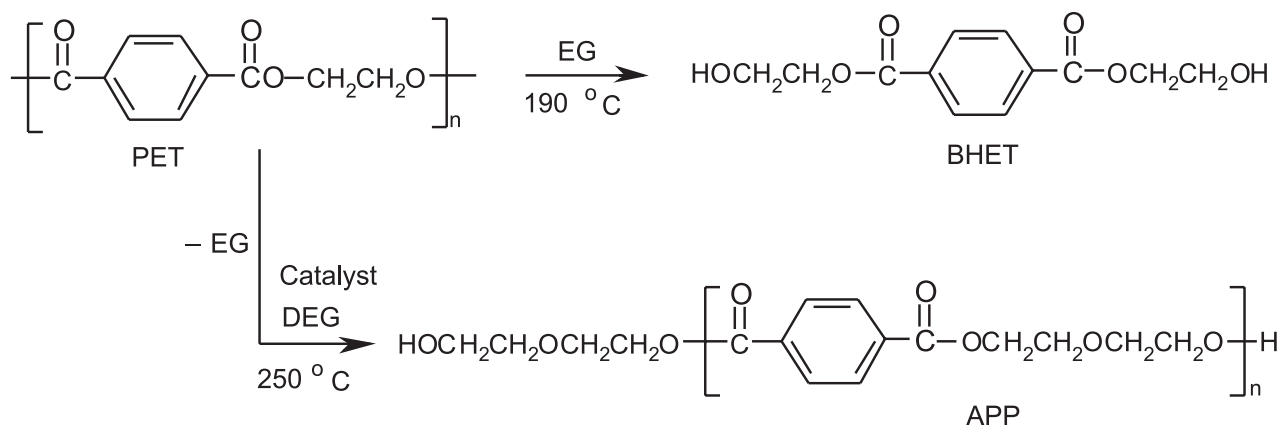
The oligomers and BHET can be returned back to the PET production process or used for the production of aromatic polyesters and rigid polyurethanes [1–4]. Oligoester polyols further can be reacted with dicarboxylic acids or monofunctional glycols to form polyester polyols that can be used as starting materials in the polyurethane industry [5].

The best studied glycolysis reaction of PET is the one with an excess of 1,2-ethanediol (ethylene glycol, EG) or 2,2'-oxydiethanol (diethylene glycol, DEG) resulting in polyols of high crystallinity which makes difficult their use after storage. This disadvantage can be avoided by introducing flexible fragments through the use of aliphatic acids such as adipic, sebacic or glutaric, or by addition of glycols with a higher functionality, followed by the polycondensation reaction resulting in oligoester polyols with increased functionality. The phenomenon of crystallization of polyols has been studied extensively by G. Colomines and coworkers [6]. The polyols obtained by glycolysis of PET using a mixture of DEG and different oligoesters were tested after two weeks of storage at room temperature. The oligoesters were the products of polyesterification (transesterification) of adipic acid or dimethyl isophthalate and neopentyl glycol or tetraethylene glycol. The polyols derived from PET using oligoesters were more amorphous as compared to the polyols obtained using DEG only [6, 7].

The preparation of polyester polyols usually includes two stages. In the first stage, depolymerization of PET takes place, resulting in a glycolysed product (GP) – a mixture of BHET, oligomers and unreacted glycols. In the second stage, GP is reacted with dicarboxylic acids, glycols and other additives resulting in polyester polyols. In the present paper, we describe one-stage synthesis of polyols in which all components (PET, glycols, dicarboxylic acids and other additives) are added at once, and the side product (distillate) is removed continuously from the reaction mixture.

The purpose of the present study is recycling of industrial PET waste by glycolysis with EG directed to BHET, and glycolysis with DEG in the presence of glycerol and adipic acid directed

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Scheme 1. Glycolysis of PET with EG and DEG

to polyester polyols with an increased stability against crystallization, and investigation of the properties of aromatic polyester polyols (APP) obtained using various amounts and types of catalysts.

EXPERIMENTAL

Materials

Industrial PET waste (T_m 246.3 °C, intrinsic viscosity (IV) 0.78 dl/g) and EG waste from the rectification column (water content 1.5%) were obtained from the Neo Group bottle-grade PET plant of (Lithuania). 2,2'-Oxydiethanol (diethylene glycol, DEG), adipic acid (ADA), glycerol (Gl), dibutyltin dilaurate (DBTL), tin 2-ethylhexanoate (TEH), tetrabutyltitanate (TBT), cobalt acetate, potassium hydroxide, phenolphthalein and ethanol were all purchased from Sigma-Aldrich and were used without further purification.

Methods

The melting point (T_m) of polyester polyols was determined by the DSC method using Mettler Toledo 822e apparatus calibrated with indium. The samples were heated from room temperature to 300 °C at the rate 10 °C/min under nitrogen flow. Intrinsic viscosity (IV) of PET and its oligomers was measured in the mixture of phenol and 1,2-dichlorobenzene (3 : 2, w/w) at 25 °C using an Ubbelohde viscometer in the PVS LAUDA automatic viscosity measuring system. The content of end-carboxylic groups of PET waste and acid number (AN) were determined by potentiometric titration with 0.05 M KOH solution in ethanol using the Metrohm Titrino 719 apparatus. Acetaldehyde (AA) and free EG in PET waste were tested by gas chromatography (GC). Water content was measured by coulometric titration using the Metrohm 832 KF Termoprep apparatus. The dynamic viscosity of polyester polyols was measured by both the rotation and the oscillation methods using a Haake Rheostress 300 apparatus. Hydroxyl number (HN) of polyester polyols was determined according to DIN 53240. The stability of APP against crystallization was evaluated as duration (in days) until a transparent oily 1-cm thick layer of APP turned to opaque (white) paste while storing it at room temperature.

Recycling of industrial PET waste into BHET

201 g (1.05 mol of the repeating unit) of PET dust was added to 654 g (10 mol) of secondary EG released from terephthalic acid (TPA) and the EG polycondensation process, the molar ratio of PET to EG approx. 1 : 10. The mixture, together with 1 g of cobalt acetate (transesterification catalyst, 0.5% by weight from PET), was charged to a four-necked flask which was fitted with a stirrer, reflux condenser, nitrogen inlet, and a thermometer. The reactor was heated, and the temperature was raised up to 190 °C. The glycolysis reaction was allowed to proceed for 4 h. During this stage, the samples were taken every 1 h. When the samples were cooled down, the glycolysed product (GP) turned into a white crystalline paste. Distilled water was added to GP to remove any unreacted EG and the catalyst which was gained by vigorous agitation and filtration. Aqueous extracts of GP were analysed by GC for determination of free EG content. Distilled water was poured on the solid residue, and the mixture was heated to boil. The boiling solution was filtered rapidly to separate the oligomer fraction from the BHET which remained soluble in water at 100 °C. The filtrate was cooled down to room temperature and then left in refrigerator at 4 °C for 48 h. BHET in the form of needle-shaped crystals was separated by filtration. BHET and oligomers were dried in an oven at 40 °C for 48 h.

Synthesis of aromatic polyester polyols from industrial PET waste

Synthesis of APP (APP1 and APP2) from industrial PET waste and DEG was carried out without any additives or in the presence of glycerol (Gl) or/and adipic acid (ADA). 225 g (2.1 mol) DEG, together with two drops of DBTL catalyst, was introduced into a four-necked flask which was fitted with a stirrer, condenser, nitrogen inlet and a thermometer. The flask was heated to 180 °C and left at this temperature for 20 min. The temperature was raised to 220 °C, and PET waste 212 g (1.1 mol) was added. After PET waste had been dissolved, the mixture was heated to a reaction temperature of 230–250 °C. The reaction was allowed to proceed for 4 h. The above experiment was repeated introducing various amounts of Gl or / and ADA, which were added before addition of PET. The distillate containing EG, water and other side products of the polycondensation re-

action was collected into flask. The experiments using different amounts of GI (1 to 12%) were carried out in a 10 l stainless steel reactor. A similar procedure for the synthesis of APP3 was used. APP3 was obtained by transesterification of PET waste with DEG (1 : 1.8, mol/mol) in the presence of fixed amounts of GI (1%) and ADA (16%) and using various organometallic catalysts – DBTL, TEH and TBT. The concentration of the catalyst was in the range 15 to 30 ppm.

RESULTS AND DISCUSSION

Characteristics of industrial PET waste

Waste generation in an efficient bottle grade PET chips manufacturing plant is about 0.3%. There are several reasons for the formation of industrial PET waste:

- inevitable part of the production process
- deviations from a technological mode
- periodic maintenance, service and cleaning of equipment
- unexpected repair of equipment
- waste in a place of sampling.

Industrial waste is generated at various stages of the PET production and includes PET oligomers, prepolymers, polymer lumps, dusts, etc. The biggest part of industrial PET waste – about 80% – is amorphous polymer lumps. Amorphous polymer lumps are produced during cleaning or repairing the granulators. Recycling of amorphous polymer lumps is relatively more complicated since they have to be crushed before the main process. A mixture of PET dust and chips is produced during cooling and dedusting processes following solid state polycondensation, and totals about 9%. The ratio of dust to chips depends on the technological parameters of PET production and has an effect on recycling time. The wet dust of amor-

phous PET amounts to 9%, but because of a high water content it contains 10% of PET only. Oligomers and prepolymers are a mixture of the products of the reaction between ethylene glycol and terephthalic acid and contain one, two, three, etc. constitutional repeating units of PET. According to the melting point of the prepolymers, the main part of this waste is the so called BHET monomer which contains one constitutional repeating unit of PET.

Industrial PET waste, differing in morphology and physical properties, was collected and analysed. Industrial PET waste was characterized by melting point, intrinsic viscosity, the content of water, acetaldehyde (AA), EG, end-carboxylic groups and acid number (AN). Characteristics of industrial PET waste are presented in Table 1.

The most suitable source of industrial PET waste is amorphous polymer lumps and mixes of PET dust and chips collected from different places. A mix of PET dust and chips No 2 (Table 1) with IV 0.78 dl/g and low content of AA, EG and water was used in this study.

Recycling of industrial PET waste producing BHET

Glycolysis is the most cost-effective viable process of the chemical recycling of PET waste. One possibility is degradation of polyester waste at high temperature (under reflux) in a large excess of EG and in the presence of transesterification catalysts such as acetates of Zn, Mn, Co, Na or Ca. During glycolysis, ester linkages are broken and replaced by hydroxyl terminals (Scheme 1). The process converts waste into BHET and its oligomers (dimmer, trimer, etc.). The extent of depolymerization of PET depends on the excess of EG taken for glycolysis [5, 8, 9].

Characteristics of primary glycolysed products (GP) as well as oligomers and BHET derived thereof are presented in Table 2.

Table 1. Characteristics of industrial PET waste

No	Waste type	IV, dl/g (±0.02)	AA, ppm	Water cont., %	Free EG, %	T _m , °C	COOH, mmol/kg	AN, mg KOH/g
1.	Oligomers of PET	0.10	33	0.20	80.0	–	150	8.4
2.	Prepolymers of PET	0.10–0.25	100	0.20	1.63	110.1	110	6.2
3.	Amorphous polymer lumps	0.60	< 60	0.20	0.02	250.1	30–45	1.7–2.5
4.	Wet dust of amorphous PET	0.60*	< 60*	90	0.02*	249.4	30–45*	1.7–2.5
5.	Mix of PET dust and chips (No 1)	0.60	4.0	0.05	0.02	252.0	39	2.2
6.	Mix of PET dust and chips (No 2)	0.78	1.0	0.10	0.02	248.1	32	1.8
7.	Mix of PET dust and chips (No 3)	1.04	0.5	0.20	0.02	245.6	25	1.4

IV – intrinsic viscosity, AA – acetaldehyde content, EG – ethylene glycol, T_m – melting point, COOH – content of end-carboxylic groups, AN – acid number
*characteristics of the dried sample.

Table 2. Characteristics of GP and the products derived thereof

Sample No and reaction time, h	GP		Oligomers			BHET	
	Free EG, %	Melting point, °C	Yield from PET, wt.%	Melting point, °C	IV, dl/g	Yield from PET, wt.%	Melting point, °C
GP1, 1	56.0	55.1	23.3	167.4, 241.0	0.12	31.4	111.2
GP2, 2	54.0	57.3	12.4	170.3	0.06	74.8	111.3
GP3, 3	54.5	56.7	12.4	171.4	0.07	82.4	111.7
GP4, 4	54.0	58.0	10.8	171.8	0.06	81.1	110.8

During the first hour of the process, EG content decreased from 75% to 56%, while the viscosity decreased from 0.78 to 0.12 dl/g. These parameters underwent certain changes during the second period and remained unchanged later. Oligomer content was relatively high after 1 h of glycolysis, decreased considerably during the second period and later remained almost unchanged. Analysis of GP characteristics evidenced that the glycolysis was almost complete within 3 h of the process, the yield of BHET being 81–82%. Thus, the glycolysed products contained mainly BHET.

The melting point of GPs was increasing slightly from 55° to 58 °C during the process. Separation of BHET from GP during crystallization from the hot aqueous solution was found to be relatively simple and complete. DSC analysis helped well in identification of separated BHET and oligomers. Oligomers separated after 1 h of the process had two melting peaks – at 167.4 °C and 241.0 °C. The temperature of the second peak (241.0 °C) was not much lower than the PET melting temperature, suggesting an incomplete depolymerization of the initial PET. After 2 h of glycolysis, the second peak in the DSC curve disappeared, confirming a distinct progress of the process. BHET melted at around 111 °C, whereas the mixture of oligomers melted at around 170 °C. According to the published data [2, 10, 11], pure BHET melts at 109–110 °C, and the dimer of BHET melts in the temperature range 170–174 °C. Thus, one could suppose that the main part of oligomers is just dimers BHET.

High purity BHET was obtained by recycling industrial PET waste. BHET produced in this way may be used alone or together with other monomers for the production of PET or aromatic copolyesters. BHET obtained from industrial PET waste can be used for various products, including food packing, which, in contrast to GP, is obtained from post-consumed PET not suitable because of impurities and contamination [12].

Synthesis of aromatic polyester polyols

a) Effect of glycerol and adipic acid on APP properties

Transesterification of PET waste with DEG and other glycols or their mixtures results in low viscosity and low functionality aromatic polyester polyols (Scheme 1). Due to its low cost the preferred glycol for transesterification is DEG. However, the process of PET glycolysis with DEG has several disadvantages: the reaction products – polyester polyols – are viscous liquids with

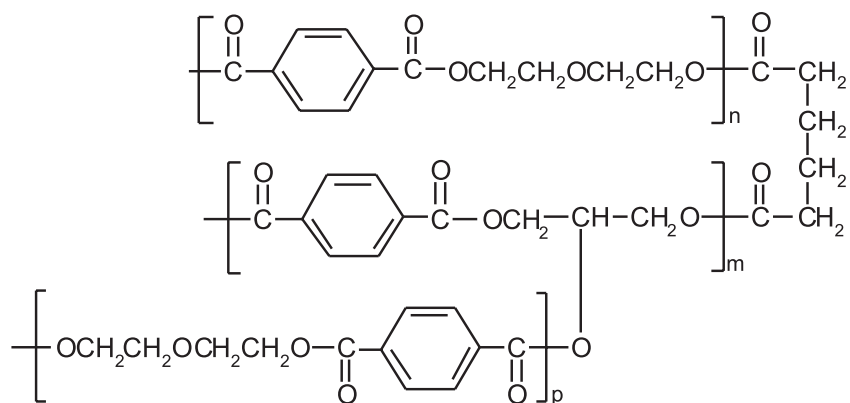
a tendency to solidification when stored at room temperature, the reproducibility of the characteristics of the resulting polyester polyols is insufficient, and the products of transesterification are not compatible with blowing agents. These problems can be partly solved by adding flexible aliphatic acids such as adipic, sebacic or glutaric, which take part in polycondensation with diols present in the reaction system [6, 7]. Polyester polyols containing segments of adipic acid (ADA) are used in applications where flexibility is essential, e. g., in flexible foams and elastomers [13].

In order to obtain amorphous and more viscous APP, the effect of GI and ADA additives to transesterification formulations on the properties of APP was evaluated in this study. The possible structure of slightly branched APP containing segments of ADA and GI is shown in Scheme 2.

The synthesis of APP from industrial PET waste and DEG resulted in transesterification products which, when cooled down, appeared as viscous transparent oils. The polyester polyol, which was synthesized from PET and DEG without any additive, after 28 days of storage at room temperature turned into a white crystalline paste. The melting point of this APP was 41.3 °C. In order to decrease the crystallinity of the polyester polyols, different amounts of GI and a fixed amount of ADA were added to the reaction mixture. Two series of APP were synthesized. The series APP1 was prepared by the use of 6.5% of ADA and up to 7.5% of GI, while the series APP2 was synthesized using 2–12% of GI without ADA. Glycolyses using the new recipes resulted in APPs which even after a long storage had no melting point. The absence of melting as well as the different visual appearance suggested that APP1 from the recipes containing ADA and GI were more stable against crystallization than APP2, and the stability increased with increasing glycerol content (Fig. 1). A viscosity of the transesterification products increased with increasing glycerol concentration which suggested noticeable increase in molecular weight and slight branching of APP.

b) Effect of amount and type of catalyst on APP properties

Despite the evident effect, catalysts in transesterification of PET waste are used reluctantly since they cannot be removed from the products and can exert an undesirable effect on the production of polyurethane (PU). Usually, inorganic substances present even in small quantities favour or retard PU formation. It is known that the synthesis of polyester polyols can be done



Scheme 2. Fragment of the structure of slightly branched APP containing segments of ADA and GI

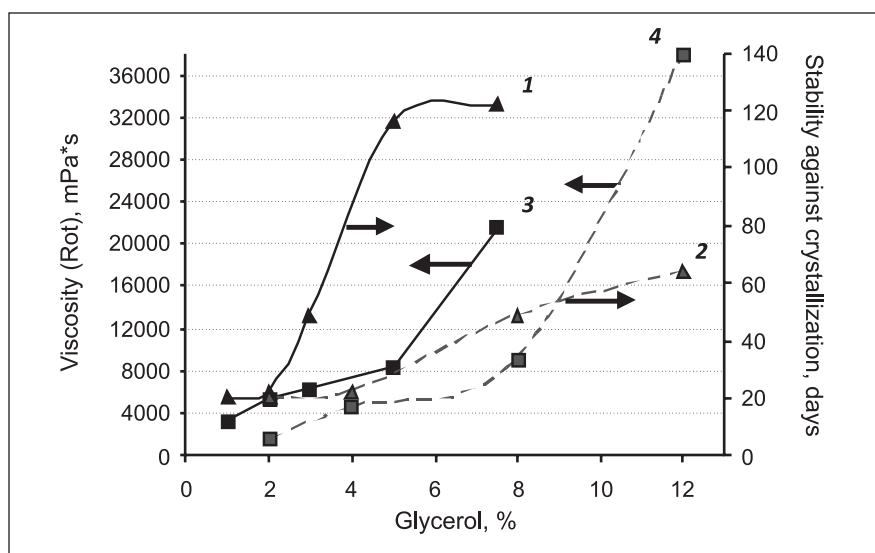


Fig. 1. Effect of glycerol concentration on stability against crystallization (1, 2) and viscosity (3, 4) of APP. APP1 (1, 3) was prepared using 6.5% ADA and APP2 (2, 4) without ADA

without an external catalyst since this reaction is self-catalyzed by carboxyl groups of precursors. Nevertheless, the best results (short reaction time, low acidity of final products) are obtained in the presence of specific catalysts, such as tin compounds (tin 2-ethylhexanoate, dibutyltin dilaurate), titanium (tetrabutyltitanate), antimony or lead compounds, p-toluene sulfonic acid. Acidity is an important characteristic of polyols. It was found studying the polyester polyol with a very low acidity that the resistance against hydrolysis of the resulting polyurethane was very high. Organometallic catalysts proved to be especially effective since they promoted the reaction between isocyanate and hydroxyl groups [7, 13].

APP3 were obtained by transesterification of PET waste with DEG in the presence of fixed amounts of Gl (1%) and ADA (16%) and using different amounts and types of organometallic catalyst. APP3 with the hydroxyl values 250 to 260 mg KOH/g and low acid values (about 0.4 mg KOH/g) were synthesized. The viscosity of APP3 was in the range 6000 to 6500 mPa · s and slightly depended on the type of the catalyst used (Fig. 2a).

Nevertheless, all catalysts promoted transesterification of PET waste; APP3 synthesized in the presence of DBTL were the most stable against crystallization. An excess of the catalyst was not suitable because it promoted formation of the products with a lower stability against crystallization (Fig. 2b). The origin of the effect of catalysts on the stability of APP against crystallization was not evidenced, but possibly it was determined by differences in the interaction of the residual catalyst with the functional groups of the polyols.

CONCLUSIONS

The products of recycling of industrial PET waste obtained by glycolysis with EG contained mainly bis(hydroxyethyl) terephthalate (BHET). High quality BHET obtained from industrial PET waste can be used without further purification to produce PET suitable for food applications.

Glycolysis of PET waste with DEG yielded aromatic polyester polyols (APP) with the hydroxyl number in the range 290 to

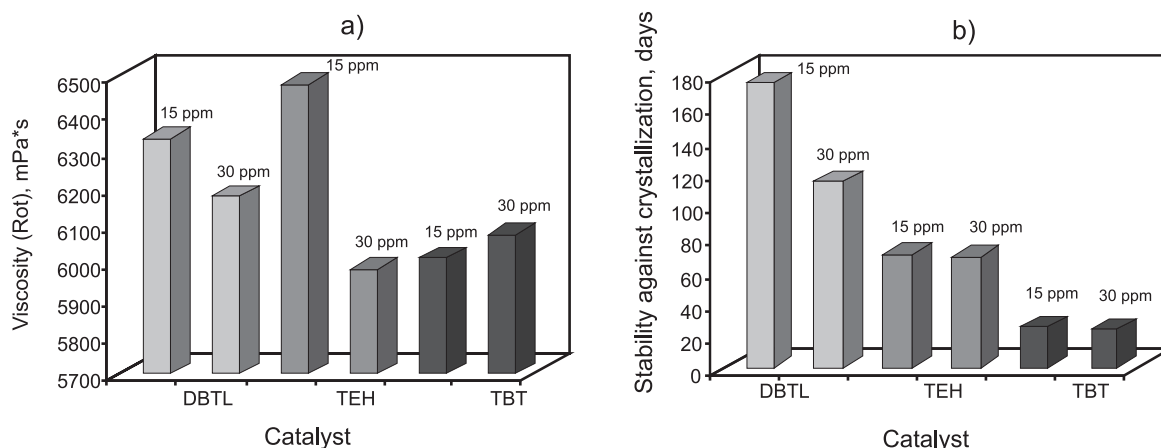


Fig. 2. The effect of catalyst on viscosity (a) and stability against crystallization (b) of APP3 obtained by transesterification of PET waste with DEG in the presence of 1% Gl and 16% ADA

430 mg KOH/g and viscosity in the range 3000 to 38000 mPa · s. APP synthesized without any additives after 28 days of storage turned into a white crystalline paste. APPs synthesized in the presence of functional additives glycerol and adipic acid were amorphous, more viscous and much more stable against crystallization. The viscosity of APP slightly depended on the catalyst type and its concentration, and the excess of the catalyst promoted formation of the products with a lower stability against crystallization.

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PRAMONINIŲ POLIETILENTEREFTALATO ATLIEKŲ GLIKOLIZĖ, SIEKIANT GAUTI BIS(HIDROKSJETILEN) TEREFTALATĄ IR AROMATINIUS POLIESTERPOLIOLIUS

Santrauka

Ištirtas grįžtamasis gamybinių polietilentereftalato (PET) atliekų perdirbimas glikolizės būdu. PET atliekas veikiant 1,2-etandioliu (etilen-glikoliu, EG), gautas bis(hidroksietilen)tereftalato (BHET) ir jo oligo-merų mišinys. Reakciją vykdant 3 val. 190°C temperatūroje pasiekta didelė (apie 82%) aukštos kokybės BHET išeiga. PET atliekas veikiant 2,2'-oksidietanoliu (dietilenglikoliu, DEG), susintetinti aromatiniai poliesterpolioliai (APP), kurių hidroksilo skaičius kinta nuo 290 iki 430 mg KOH/g, o dinaminė klampa nuo 3000 iki 38000 mPa · s. APP, kurių sintezei buvo naudojami funkciniai priedai glicerolis ir / ar adipo rūgštis, buvo amorfiniai, klampesni ir mažai linkę kristalizuotis juos laikant gana ilgą laiką. APP klampa mažai priklauso nuo metaloorganinio katalizatoriaus prigimties ir jo koncentracijos, tačiau didesnę polinkį kristalizuotis turi APP, gautieji esant didesnėms katalizatoriaus koncentracijoms.