

Glycolysis of PET Waste and the Use of Glycolysis Products in the Synthesis of Degradable Co-polyesters

Abstract

We present the results of investigations into the utilisation of polymeric waste arising in the manufacture of polyester fibres. Polyethylene terephthalate waste of various molecular weights ($M_w \cong 13500$ and 18000) was glycolysed under different conditions including varying the PET/EG proportion, temperature and time. The glycolysis products (PGs) were estimated (the melting temperature, oligomer- and monomer content were assessed). The PGs, obtained under different conditions, with different contents of oligomers (about 50 and 70%), were used as raw materials in the synthesis of degradable polyesters of ethylene terephthalate (ET) and L-lactic acid (LA). The ET/LA polymers obtained were characterised by values above $65 \text{ cm}^3/\text{g}$ of the reduced viscosity, a melting temperature below 192°C and good melt stability at 260°C . In the study it was demonstrated that the PGs of clean PET wastes can be directly used in the synthesis of high-molecular degradable ET/LA co-polyesters with good processing properties.

Key words: PET waste, recycling, chemical recycling, biodegradable co-polyesters.

Introduction

The problem of utilising PET waste which arises in the production and processing of the polymer, as well as post-user waste, is presently being solved mainly by material or chemical recycling [1-4]. Depending upon the quality and purity of the waste and the current economic, technological and equipment conditions, the PET wastes are either regranulated, refined and reprocessed or degraded to obtain the starting materials for the synthesis of PET or copolymers or for other uses.

The chemical utilisation of PET can be accomplished by hydrolysis, methanolysis or glycolysis [1-3,5,6]. Hydrolysis, which may be carried out in a neutral, acid or alkaline medium [2,6-8], yields terephthalic acid (TA) and ethylene glycol (EG), which are raw materials in many chemical processes including polymer synthesis (polyesters, co-polyesters, co-polyamides and other copolymers). At our Institute, a PET hydrolysis process in a neutral medium [7-10] has been devised, which is run in a closed system with a large amount of water at $200\text{-}220^\circ\text{C}$ under a pressure of about 2 MPa.

DMT and EG, i.e. raw materials for the synthesis of PET, are obtained in the methanolysis of PET. The methanol-induced degradation of PET is performed under high pressure in the presence of catalysts. Many PET producers employ methanolysis to utilise the arising wastes [2,3,11,12]. Yang et al. have announced the possibility of conducting a very effec-

tive methanolysis without catalysts under supercritical conditions: $260\text{-}270^\circ\text{C}$ and a pressure of 9-11 MPa [6].

Glycolysis proceeding under the influence of EG is the true reverse reaction to the polycondensation of PET, reproducing the bis(hydroxyethylene) terephthalate (BHET) monomer. Usually a partial hydrolysis of the PET wastes with EG is applied to obtain a low molecular mixture of oligomers and BHET. The mixture is re-circulated to the PET synthesis process [2,3] or used in the synthesis of co-polyesters [13].

The PGs' properties and composition depend upon the initial PET/EG proportion and the glycolysis conditions, i.e. temperature and process time. According to earlier studies [14], the glycolysis process may be conducted at a relatively low temperature of 220°C for about 2 hours at the pressure of 0.15-0.5 MPa, with the molar EG/ET proportion equal to or higher than 2.5:1.

Under such conditions, the PGs obtained contain more than 50% of the BHET monomer, and resemble in their properties the partially polymerised product, which appears in a typical PET synthesis before vacuum polycondensation.

Partial PET glycolysis is also applied as a preliminary step in the degradation of PET to terephthalic acid, that is, before the hydrolysis step [5,15]. Such a combination of the two degradation processes is most advantageous when PET waste materials containing impurities and addi-

tives are processed. After the glycolysis step, the liquid and low-viscous PGs can be purified and filtered when still hot, allowing a terephthalic acid of high purity to be obtained.

In this study, the chemical utilisation of PET waste by glycolysis was employed to obtain a low-molecular ethylene terephthalate material suitable for the synthesis of biodegradable co-polyesters with L-LA. Up to now at the Institute, the ET/LA co-polyesters were synthesised with the use of pure starting materials, DMT, EG and L-LA [16-18]. Among other things, we determined the influence of their chemical (sequential) structure on the physico-chemical and thermal properties, and on the hydrolytic and compost degradability. It was defined that the statistical ET/LA copolymers, which have short ETx sequences (\bar{x} below 3.1-3.2) in their macromolecules, are characterised by a post-annealing melting temperature below $190\text{-}192^\circ\text{C}$ and a glass transition temperature $T_g > 57^\circ\text{C}$. Such co-polyesters easily hydrolyse at temperatures $\geq 55^\circ\text{C}$, hence their good degradability in moist compost [16,18]. In the present work, in the synthesis of copolymers based on PET glycolyzates and L-LA, advantage was taken of the experience gained hitherto with the ET/LA co-polyesters. The objective of this study was to explore the possibility of obtaining by this method such co-polyesters that would be degradable under hydrolytic- and compost conditions and characterised by a level of reduced viscosity (molecular weight) adequate for processing.

■ Materials and Methods

Glycolysis of PET waste

Two different pure PET waste materials were applied in the study without the dulling agent TiO_2 . The two polymers were characterised by molecular weights of $\bar{M}_v \approx 13,500$ and $18,000$. The glycolysis was conducted with EG in a stainless steel reactor equipped with an agitator and a drainage valve in the bottom. The reaction took place in a closed system with the mole proportion of EG/ET=2.48:1 and 1:1, and the total weight of reagents of 1.4 kg. Other process parameters were as follows: agitator speed 60 rpm, temperature 220-240°C, time 2-5 hours. The GPs were drained from the reactor into a metal vessel, cooled down, broken up and analysed.

Synthesis of the ET/LA co-polyesters

A 90% solution of L-LA made by Riedel de Haën and distributed by Aldrich, and the PGs from PET glycolysis prepared under selected conditions were used in the synthesis of ET/LA co-polyesters.

The synthesis was carried out in the presence of a catalyst and a thermostabilising agent, according to the method described in [16]. It is a method similar to the synthesis of PET from DMT and EG. The process was conducted in a stainless steel reactor with 0.9 dcm³ volume, equipped with electric heating, an anchor agitator, a drainage valve in the bottom and a vacuum system for the evacuation of the polycondensation by-products. The co-polyester obtained was extruded from the reactor by nitrogen pressure, solidified in water in band form, cut and dried.

A synthesis of ET/LA co-polyester was carried out for comparison, using the pure monomers DMT, EG and LA and applying the same conditions as in the synthesis of co-polyesters with the use of PGs.

Analytical methods

The melting temperature range of the PGs was measured using a Boetius apparatus. The PGs' fractional composition was defined by exploiting the diversified dissolving capacity of the mono- and oligomers in water, according to the method given in [14]. 50 g of the disintegrated PG was placed in a 1 dcm³ lab flask, 0.5 dcm³ of distilled water was added, and the flask content was heated at the boiling point under a reflux condenser for 30 minutes. The still hot beaker content was

then filtered at a temperature above 90°C separating the aqueous monomer solution from the undissolved oligomers. The filtrate was cooled to ambient temperature, then in a refrigerator at 6-8°C for 24 hours, and the crystallised monomer was separated by filtration. The filtrate was filled up to 600 dcm³ with water. From the solution a 20 cm³ sample was taken and evaporated, and the dry residue was estimated. All three fractions of the PG were dried to constant weight, weighed, and their melting temperature range was measured using the Boetius apparatus.

For the ET/LA co-polyesters obtained, the reduced viscosity (η_{red}), melting temperature T_m , softening temperature T_{sp} and melt flow index (MFI) were measured. The reduced viscosity was measured according to a method applied for PET. For this purpose the Ubbelohde viscometer with IIA capillary was used, together with a solution of 0.4 g co-polyester in 100 cm³ of a blend of phenol and tetrachloroethane (1:1). The measurement temperature was 25°C. The co-polyesters investigated were amorphous, and their T_m was characterised by a melting range using the Boetius apparatus. The penetrometric method was applied to measure the softening temperature. The co-polyester samples were first annealed at 95°C for 16 hours and at 140°C for 1 or 2 hours. The average value was calculated from parallel measurements using the six-point TS PA type 7-78 penetrometer made by Townsend Crowther Ltd USA. The Melt Flow Tester made by CEAST, Italy was used for measuring the MFI. The co-polyester samples were first dried in a vacuum dryer at 95°C for 16-20 hours. The MFI was measured after 6 and 30 minutes of annealing at 260°C, using a 0.5 mm capillary and a 2.16 kg piston load. The reduced viscosity of the extruded polyester monofilaments was measured. The change in the MFI and η_{red} , proceeding during the annealing at 260°C was estimated.

■ Results and Discussion

The properties and composition of the PGs of PET obtained under diversified conditions were investigated. The PGs made under selected conditions were used in the synthesis of degradable co-polyesters containing L-LA units.

In Tables 1 and 2, the results of PET glycolysis for waste polymers with

$\bar{M}_v \approx 13,500$ and $18,000$ are presented. The glycolysis process was investigated for the initial mole proportions of EG/ET=2.48:1 and 1:1 (weight proportion EG/PET=0.8:1 and 0.325:1) at temperatures of 220-230°C and 230-240°C respectively. After drainage and quenching of the reactor content, PGs were obtained with the yields of 86-94% at EG/ET=2.48:1 and 93-97% at EG/ET=1:1. The yields were calculated on the total amount of EG+PET used.

The glycolytic process in a closed system proceeds towards an equilibrium, which depends upon the process conditions such as the proportion of reagents and the temperature. The pressure in the reactor decreases with the decreasing amount of EG entering the reaction. Depending upon the proportion of reagents and temperature, the initial pressure amounted to 0.18-0.22 MPa. In the course of the process it decreased to the 0.14-0.18 MPa level. The PGs obtained undoubtedly contained EG, which was not quantitatively estimated when analysing the products. The presence of the free EG has an influence on the PGs' properties such as consistency (hardness) and melting temperature. From the data in Tables 1 and 2, it can be seen that (under given conditions) the oligomer content decreased to a certain level along with the glycolysis time. At the same time, the melting temperature of the oligomer fraction decreased and stabilised. The content level of oligomers in the PGs attained mainly depended upon the EG/ET proportion, though glycolysis temperature also had a certain influence.

With the EG/ET=2.48:1 proportion, PGs with an oligomer content of 47 and 50% were obtained at temperatures of 220°C and 230°C respectively. The reaction time of 120 minutes was sufficiently long. It can be seen that at the higher temperature (230°C, Table 1) and higher molecular weight of the PET (Table 2), the separated oligomer fractions were characterised by a higher melting temperature. It may be assumed that the glycolysis temperature of 220°C was advantageous at a higher EG/ET proportion, resulting in a more homogeneous run of the degradation. When using PET waste with diversified molecular weight, one must take account of certain quality differences in the PGs obtained, particularly the change in T_m of the oligomer fraction.

With the lowering of the mole EG/ET proportion to 1:1, it appeared necessary to increase the reaction temperature to 230°C and prolong the reaction time to 180 minutes. Under such conditions, PGs could be obtained without any content of gel-like particles as residues from the incomplete dissolution of the polymer

granules. At the temperature of 240°C, a homogeneous PET was attained as quickly as after 60 minutes.

At a low EG/ET proportion, the reaction run and the products' properties depended distinctly on the molecular weight of the PET used, though the attainable

level of oligomers in the PGs after an adequately long degradation time was diversified only within the narrow range of 70-74%. At 230°C, PGs containing 71% of oligomers were obtained after 240 and 300 minutes in the case of PET with $\bar{M}_v \sim 13500$ and $\bar{M}_v \sim 18000$ respectively. At 240°C,

Table 1. Results of glycolysis of PET waste with $\bar{M}_v \approx 13\ 500$.

*)**) Monomer and dry residue fractions showed melting in ranges 104-110°C and 95-107°C respectively. According to Aldrich, the pure monomer melts at 106-109°C. ***) Fragments of undigested polymer chips (gel-like particles) were seen in the molten product.

Trial, No	Glycolysis conditions					Characteristic of PGs				
	EG/ET mol. ratio	Temp.	Time	Pressure	Yield (to EG+PET)	Melting range	Oligomers		Monomer content*)	Residue content**)
							cont.	melting range		
-	°C	min	MPa	%	°C	wt%	°C	wt%	wt%	
2/F/03	2.48/1	220	60	0.18-0.15	96.5	108-120	48.5	130-140	44.9	6.6
3/F/03			120		93.8	105-120	46.9	128-139	47.0	6.1
4/F/03			180		92.7	106-118	47.5	131-142	46.8	5.7
5/F/03	(wt. ratio 0.8/1)	230	60	0.22-0.18	86.1	107-125	50.3	147-149	44.5	5.2
6/F/03			120		90.3	100-115	49.8	145-148	43.2	7.0
11/F/03	1/1	230	120	0.20-0.14	96.0***)	141-142	80.0	163-169	15.4	4.6
12/F/03			180		97.4	146-158	78.0	160-168	16.2	5.8
13/F/03			240		97.4	145-160	71.0	158-167	20.8	8.2
15/F/03	(wt. ratio 0.325/1)	240	60	0.20-0.16	95.3	152-165	73.9	172-177	21.5	4.6
16/F/03			120		95.0	150-163	72.9	171-176	21.9	5.2
17/F/03			180		95.3	150-160	70.4	160-174	25.1	4.5

Table 2. Results of glycolysis of PET waste with $\bar{M}_v \approx 18\ 000$.

*)**) Monomer and dry residue fractions showed melting in ranges 105-110°C and 95-105°C respectively. ***) Fragments of undigested polymer chips (gel-like particles) were seen in the molten product.

Trial, No	Glycolysis conditions					Characteristic of PGs				
	EG/ET mol. ratio	Temp.	Time	Pressure	Yield (to EG+PET)	Melting range	Oligomers		Monomer content*)	Residue content**)
							cont.	melting range		
-	°C	min.	MPa	%	°C	wt%	°C	wt%	wt%	
26/F/03	2.48/1	220	120	0.19-0.17	91.0	106-118	49.4	158-162	41.9	8.7
27/F/03					91.7	104-120	47.4	154-161	45.2	9.0
32/F/03	1/1	230	240	0.20-0.15	95.3***)	136-160	71.8	159-166	21.3	6.9
31/F/03			300		95.3	134-158	71.1	156-165	22.3	6.6
28/F/03			240	180	0.21-0.18	95.3	138-152	74.3	164-173	18.0
29/F/03	240	93.3		136-156		73.6	158-169	19.0	7.4	

Table 3. Results of co-polyester ET/LA syntheses using products of PET glycolysis (PGs). *) Comparative synthesis of co-polyester from pure DMT and EG; **) amorphous copolymers; slow fusion was observed in the broad temperature range.

Reactants	Co-polyester properties						
	η_{red}	T_m^{**}	T_{sp} : sampl. annealed		Melt flow testing (260°C, ϕ 0.5mm/2.16kg)		
			at 95°C	at 140°C	time at 260°C	MFI	η_{red}
	cm ³ /g	°C	°C		min.	g/10 min	cm ³ /g
DMT+EG/(+LA*)	68	138-200	187.1	190.5	6	2.22	64.5 (-5%)
					30	2.91 (+34%)	62 (-9%)
PG (~50% oligomers) + LA	73	125-155	174.0	177.4	6	2.00	60 (-18%)
					30	2.51 (+25%)	57 (-24%)
PG (~70% oligomers) + LA	66	135-155	171.6	178.4	6	1.84	61 (-7.5%)
					30	2.11 (+15%)	56.5 (-14%)

adequate PGs with 70 and 73.5% oligomer content could be attained after 180 and 240 minutes. Both the PGs and the oligomeric fractions contained showed a lower melting temperature range when the glycolysis temperature was 230°C. At that temperature, the process proceeded more homogeneously, but much more slowly than at 240°C.

It must be noted that the PGs fractions called 'monomer' were characterised by a melting temperature in the range of 104-110°C and in reality constituted the bis(hydroxyethylene) terephthalate (BHET). According to Aldrich's catalogue, the melting temperature of the substance with 98% purity reaches 106-109°C. The PGs fractions called 'residue' (dry residue isolated after the evaporation of the liquid from the solution which remained after the precipitation of the oligomer/monomer fraction) melted in the temperature range of 95-107°C. It can be assumed that these fractions were composed mainly of the monomer which still remained in solution after the crystallisation of the main monomer fraction.

To obtain PGs for the synthesis of ET/LA co-polyesters, a PET waste with $\bar{M}_v=18000$ was used. The following conditions were applied in the glycolysis of PET:

- mole proportion EG/ET=2.48:1, temperature 220°C, time 120 minutes,
- mole proportion EG/ET=1:1, temperature 230°C, time 300 minutes.

The PGs obtained under such conditions as raw materials for the synthesis of co-polyesters contained 47-50% and 71% of oligomers respectively. The synthesis was run in such a way that co-polyesters could be obtained with T_{sp} below 190-192°C. The results of the introductory syntheses of ET/LA co-polyesters from PGs of PET glycolysis and L-LA are presented in Table 3, in comparison with a co-polyester made from L-LA and pure DMT and EG.

According to earlier works [16-18], the introduction of easily hydrolysing aliphatic ester bonds along with LA mer units confers degradability (proneness to hydrolysis) on the ET/LA co-polyesters, which is especially clear in temperatures above 50°C. This is due to the high glass transition temperature of such polymers ($T_g>57^\circ\text{C}$). It was found that the random ET/LA co-polyesters with short (ET) $_x$ sequences (where \bar{x} is below 3.0-3.1),

characterised by good hydrolytic degradability in water and compost medium at 55°C and potential biodegradability, reveal T_{sp} below the range of 190-192°C. Good processibility in injection moulding and extrusion (film, fibres) can be attained when $\eta_{red} \geq 70 \text{ cm}^3/\text{g}$.

From the data in Table 3, it may be concluded that ET/LA co-polyesters can be obtained from PGs made of pure PET which will have properties similar to those made of pure starting materials (DMT, EG). Copolymers were made with T_{sp} within the range of 171-190°C, that is, at a level which assures proneness to hydrolysis and biodegradation. The copolymers obtained were amorphous, though revealing some hardening (crystallising) tendency during annealing at 95 and 140°C. The co-polyester granules annealed for 1 hour at 95°C or 2 hours at 140°C manifested turbidity typical for crystallised polymers. The crystallisation phenomenon of co-polyesters calls for further confirmation, for example by DSC investigations.

The co-polyesters obtained had η_{red} in the range of 66-83 cm^3/g indicating that ET/LA co-polyesters from pure PGs can be made with good processing and utility properties by selecting appropriate synthesis conditions, for example polycondensation time. As can be concluded from the data in Table 3, the PG-based co-polyesters were characterised by relatively good thermostability, only slightly lower than that of the co-polyesters made of pure raw materials DMT, EG and LA. Their η_{red} drop after 6 and 30 minutes annealing at 260°C amounted to 7.5-18% and 14-24% accordingly, MFI after 6 minutes of melting was in the range of 1.84-2.00 g/10 min, and dropped by 15-22% after 30 minutes of annealing at 260°C.

Summary

- Glycolysis of PET waste with the mole proportions of EG/ET=2.48:1 and 1:1 yielded GPs containing 47-50% and 70-74% oligomers, respectively. The following process parameters were adequate for the glycolysis of fibrous PET waste with the molecular weight of 18,000: temperature of 220°C, time of 120 minutes for the mole proportion of EG/ET=2.48:1 and temperature of 230°C, time of 300 minutes for the mole proportion of EG/ET=1.

- The PGs of PET hydrolysis obtained under the above conditions (pure, without TiO_2) appeared to be raw materials of full value for the synthesis of degradable ET/LA co-polyesters with $T_{sp}<192^\circ\text{C}$ and $\eta_{red} \approx 70 \text{ cm}^3/\text{g}$. This was confirmed in the introductory syntheses of co-polyesters in this study. According to earlier works [16-18], co-polyesters with such properties are characterised by very good susceptibility to hydrolysis, biodegradability and good processing behaviour. We envisage investigating the degradability of co-polyesters in further works.



Acknowledgement

This investigation was carried out within the scope of the research project SPUB-COST 628 of the Polish State Committee for Scientific Research.

References

1. F. Fourné, 'Synthetic fibres', ed. Hauser Verlag, Muenchen 1999.
2. U.K. Thiele; CFI Man-Made Fibres Year Book 2001, 71.
3. H. Meierkord; Chemiefas/Textilind. 1993, 43, 524.
4. L. Janzen; Chem. Fibres Int (CFI) 1998, 48, 390.
5. T. Rieckmann, J. Brown; Chem. Fibres Int. (CFI) 1995, 45, 182.
6. Y. Yang, Y. Lu, H. Xiang, Y. Xu, Y. Li; Polymer Degrad. Stabil., 2002, 75, 185.
7. A. Michalski; Fibres & Textiles in Eastern Europe 1993, 1(3), 38.
8. A. Michalski; Fibres & Textiles in Eastern Europe 2001, 9(1), 40.
9. Polish Pat. Appl. P-317 877.
10. Polish Pat. Appl. P-317 911.
11. Information; CFI Man-Made Fibres Year Book 2001, 21.
12. Polish Pat. Appl. P-126 009.
13. A. Michalski; Fibres & Textiles in Eastern Europe 2001, 9(1), 44.
14. A. Michalski; 'Utilising of polyester wastes'; I 'Glycolysis of polyester wastes', Research report, Institute of Chemical Fibres, Łódź, 1978.
15. Polish Pat. Appl. P-342 144.
16. K. Grzebieniak; 'Studies on the synthesis process of biodegradable co-polyesters of ethylene terephthalate and lactic acid'; research project (granted), 2001.
17. K. Grzebieniak; Fibres & Textiles in Eastern Europe 1996, 4(1), 34.
18. K. Grzebieniak, M. Ratajska, G. Strobin; Fibres & Textiles in Eastern Europe 2001, 9(2), 61.

Received 09.02.2004 Reviewed 04.05.2004