Poly(ethylene terephtalate) Recycled from Post-Consumer Soft-Drinks Bottles

I.Poly(ethylene terephtalate) depolymerization by glycolysis process

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Poly(ethylene terephtalate) (PET), recycled from post-consumer bottles was depolymerized by glycolysis process using diethylene glycol (DEG) in the presence of zinc acetate catalyst. The glycolized products were mainly represented by monomer and dimer units. After a relatively long reaction time (over 2 h), an equilibrium was achieved between the two species. Considering the importance of the next steps, in attaining unsaturated polyesters with excellent mechanical properties, this study was concentrated on the identification and characterization of glycolysis reaction equilibrium phase. The evolution of the depolymerization reaction was investigated by the viscosity procedure, which was compared and found to be in good agreement with the functional analysis method.

Keywords: PET waste, glycolysis, oligomers, viscosity, equilibrium phase

Poly(ethylene terephtalate) (PET) is a semi-crystalline thermoplastic polyester [1-3] used on large scale in the manufacture of fibers, photographic films, packages or soft-drink bottles. Since 1980, the volume of consumed PET strictly in the beverages industry was estimated to over 320 million kilograms, corresponding to more than 1 billion bottles [4-7]. In order to avoid the increase of waste amount generation, different states of the world developed not only education programs to reduce consumption, but also engaged industrial branches to encourage the use of recycled materials from PET bottles [8-11].

Taking this into account, our investigation was focussed on certain nonfood applications of recycled PET. One of the most promising directions regarding this subject consisted in the depolymerization of PET flakes coming from soft-drink bottles into its monomer and oligomers. The resulted monomer can be used as raw material to synthesize polymers like unsaturated polyesters and polyols with higher economical importance.

Considering the importance of the next steps, in attaining unsaturated polyesters with excellent mechanical properties, this study was concentrated on highlighting the conditions of the equilibrium phase of the glycolysis reaction.

Therefore, the system PET-DEG described by a molar ratio PET/DEG = 1/1 was investigated. This ratio proved to be optimal taking into consideration the general characteristics of the entire process and the final properties of the resulted material. The experiments carried out in the presence of DEG in excess lead to final products with undesirable high flexibility. On the other hand, the compositions richer in PET afforded rigid unsaturated polyesters, weakly compatible with styrene. As a result, disadvantageous molar ratios drive the glycolysis process to products without significant economical value.

Experimental part

Materials and methods

PET flakes, as small, plane pieces with rectangular shape with a diagonal of around 10-12 mm, obtained by industrial recovering of post-consumer PET bottles were used as received. The intrinsic viscosity in 60:40 (w/w) phenol – 1,1,2,2 tetrachlorethane solution at 25°C, is about 0.65 dL/g corresponding to a number-average molecular weight of aproximatively $3 \cdot 10^4$ g/mol.

Diethylene glycol (DEG) was purified by vacuum distillation at 148°C/20 mmHg; the density of DEG was $\rho_{DEG}^{20} = 1.4472 g/cm^3$

The glycolysis reactions were carried out in a four-necked round bottom reactor mechanically stirred, fitted with a condenser, a thermometer and a nitrogen inset. PET and DEG are added in the reactor and the stirring is set to 200-300 rot/min. At the start of the reaction the amount of DEG seems insufficient to ensure a proper agitation, but this is quickly overcome as the temperature increases and the PET flakes are dissolved in DEG (about 0.5 h). The reaction is first heterogeneous, then homogeneous and continuously the viscosity of the system decreases as the glycolysis reaction proceeds.

The experiments involved 96 g of PET flakes, equivalent to 0.5 mol of repeating unit (molecular weight, 192 g/mol) in the PET chain. These were added to 53 g of DEG while keeping a molar ratio PET/DEG = 1/1. The mixture was charged with 0.48 g of zinc acetate as catalyst (0.5% by weight of PET).

The evolution of the depolymerization process was analyzed using viscosity measurements, respectively functional analysis.

The viscosity of the glycolized products was determined at temperatures ranging from 70 to 90°C with an Ubbelohde viscometer, size 3 with a constant k=4.2852.

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$$E + E \underset{k'}{\overset{k}{\rightleftharpoons}} Z + G \qquad \begin{array}{l} E{:}\ \text{—COOROH} \\ Z{:}\ \text{—COOROOC—} \\ G{:}\ \ \text{HOROH} \\ R{:}\ \text{—CH}_2\text{CH}_2\text{—} \\ \quad \text{—CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{—} \end{array}$$

$$v_g = \frac{d_{gl}}{dt} = ke^2 - 4k'z \cdot gl$$

$$\frac{4zgl}{e^2} = \frac{k}{k'} - \frac{v_g}{e^2k'} \qquad \frac{4zgl}{e^2} = C \qquad \frac{k}{k'} = K$$

$$C = K - \frac{v_g}{e^2k'} \qquad C_{ech.} = K \qquad K = \left(\frac{4z \cdot gl}{e^2}\right)_{ech.}$$

Fig. 1. Kinetic scheme used to study the evolution of the system to attain the glycolysis equilibrium state

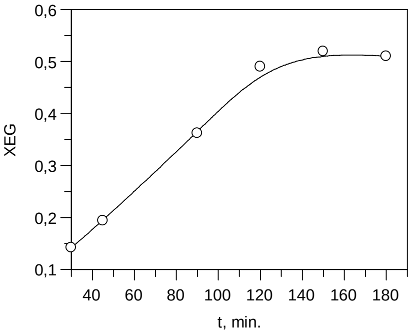

Fig. 2 Evolution of EG molar fraction (X_{EG}) with

Considering the functional analysis method, the progress of the glycolysis reaction with regard to the monomer-polymer equilibrium was studied using the kinetic scheme proposed in [12].

The samples taken from the reactor were purified by vacuum distillation of the glycols at 100°C and 1 mmHg. The mixture of ethylene glycol (EG) and DEG was recovered using liquid nitrogen in a collecting inset. EG was determined using the oxidation method with periodide [13] and DEG is thus determined gravimetrically. As a consequence, the molar fractions of the glycols and the global molar concentration of the glycols mixture (gl) were calculated. The residue resulted from the glycols separation was analyzed using the acetilation method (E 222-00, method A) in order to obtain the hydroxyl end groups. This allows the determination of the molar concentration of the end groups and the saponification index (SN)[13].

In order to investigate the parameters of the process, a reaction without the catalyst was also carried out. After 3 h, a high quantity of PET flakes was still unreacted, comparing to the reaction performed in the presence of the zinc acetate catalyst which leaded to a homogeneous aspect of the reaction after about 1 h. This justifies the use of a suitable catalyst for the depolymerization reaction in a reasonable period of time.

Results and discussions

In order to put into evidence the equilibrium state of this kind of systems, Challa proposed a kinetic model [12] that was adapted to our process. Keeping similar notations with Challa's system (fig. 1) presents the basic reactions that describe the chemical process. To characterize the systems evolution to equilibrium, parameter C was introduced explaining the global equilibrium constant of the depolymerization reaction. The variation of C during our experiment was the main criterion that made possible the approximation of the time needed for the system to be at equilibrium.

This method [12] was developed for reactions carried out on small reactants quantities (2÷5 g) at a temperature of 240°C, into a perfectly sealed system without stirring, to avoid errors related with heat transfer or glycol loss that are generally difficult to avoid in high volume reactors. Another important decisive factor involved in the same method is the molar fraction of ethylene glycol in relation with diethylene glycol. The hypothesis that considers both glycols in equimolar ratio at equilibrium seems reasonable. The experimental and theoretic results are presented in tabel 1, figures 2 and 3.

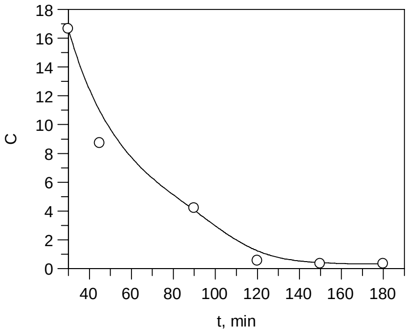

Fig. 3. Variation of parameter C during the reaction time

Table 1

Nr. crt.	Reaction time (min)	Global conc. of glycols (g/g)	Molar fraction of EG (X_{EG})	Conc. of glycols gl (mmol/g)	Conc. of end groups E (mmol/g)	Saponification index SN (mmol/g)	Conc. of structural units u_0 (mmol/g)	Molar conc. of ester groups Z (mmol/g)	C
1	30	0.169	0.142	1.698	1.185	8.020	4.010	3.417	16.66
2	45	0.164	0.194	1.678	1.486	7.942	3.971	3.228	8.72
3	90	0.082	0.362	0.911	2.375	7.360	3.680	2.498	4.21
4	120	0.049	0.490	0.587	2.921	6.810	3.405	1.944	0.547
5	150	0.038	0.519	0.460	3.112	6.670	3.335	1.779	0.339
6	180	0.038	0.510	0.458	3.103	6.605	3.302	1.751	0.335*

conc.=concentration, *$c_{ech.}$ = K

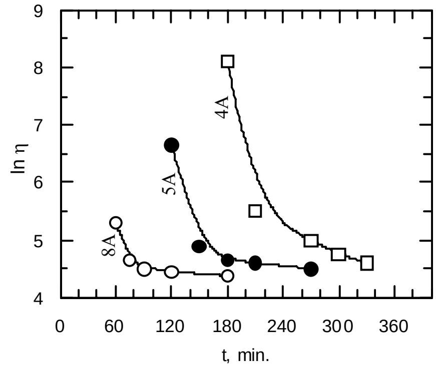

Fig. 4. Dynamic viscosity variation of the glycolysis products measured at 70°C versus reaction time for reactions performed at different temperatures: 8A (240°C); 5A (235°C), 4A (217°C)

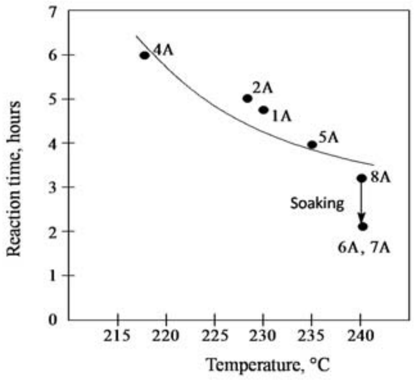

Fig.5. Dependency of time reaction with temperature emphasized by viscosity method

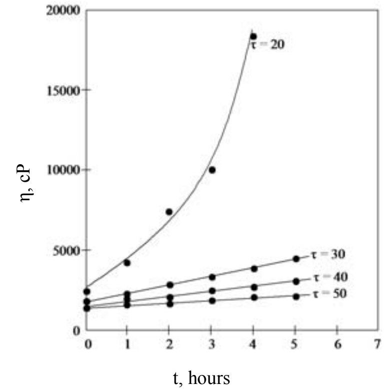

Fig. 6. Batch 1A (230°C), after a reaction time of 50 min - Viscosity modification at different shear stress (1 dyn/cm^2; 1 dyn=1 g·cm/s^2) at 70°C

As discussed before, both variables chosen to investigate the equilibrium evolution attain a constant value after about 180 min. At this point, the equilibrium constant of the system becomes K=0.33.

Although this method seems to be one of the most appropriate to follow the evolution of the whole process, some disadvantages should be taken into consideration:

- extensive series of tests that reduce efficiency in tracking process;
- inability to use functional analysis to achieve practical conditions with reference to the glycolysis reaction, especially at higher capacities, when a significant part of glycols is vaporized or condensed on top of the reactor segments;
- limited in scope to a relatively small number of systems; it is difficult to predict or adapt the method to systems with a large number of components and probably impossible with the use of higher molecular weight glycols (eg, polyethylene glycol).

There was thus necessary to conceive an easier operational progress to track the evolution and highlight the process conditions to achieve equilibrium in a relatively short reaction time. These criteria are met by measuring a physical property of the system, which must vary with the change of the chemical composition and must remain invariable with steady state. The property which was found to be well suited for this purpose is the dynamic viscosity of the reaction.

Without a theoretical basis sufficiently detailed viscosity method for tracking glycolysis progress reaction proved to be very sensitive and at the same time, the results are convergent with those suggested by functional analysis.

These issues are illustrated by figure 4 and describe the variation of dynamic viscosity. A very sharp decrease was registered in the first period; probably corresponding to the high reduction of the molecular weight of polyester and progressive achievement of physical homogeneity of the system and proper acceleration of the chemical attack. In the second part a slow variation of the dynamic viscosity with uniform tendency was observed, marking the steady state of the system and thus the end of the ester exchange process.

For the glycolysis carried out at 240°C (batch 8A), the time needed to achieve equilibrium was estimated at about 180 min. This value corresponds exactly with data obtained by the kinetic analysis. It also shows that the range of viscosity recorded based on glycolysis performed at different temperatures, is relatively narrow, highlighting the minimal difference in the composition of these systems.

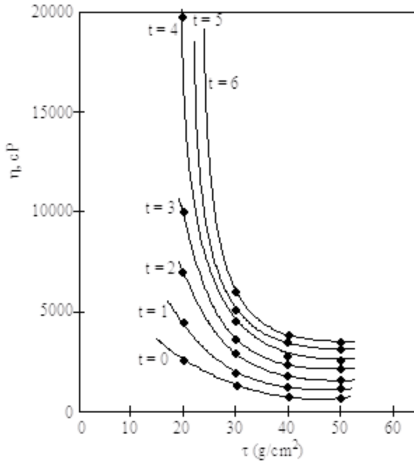

Fig. 7. Batch 1A (230°C), reaction time 50 min Viscosity modification depending on the shear stress measured after prolonged shearing; batch 1A (230°C), reaction time 50 min

This is consistent with the results of research conducted by Challa [12], who found a very slow variation of the equilibrium constant with temperature in the range 200-250°C.

However, we found large differences in the rate of reaching equilibrium. This is supported by the results presented in figure 5, revealing progressive reaction rate up to the equilibrium state with the increase of temperature. Experiments above 250°C were not used due to the danger of homolitic degradation and undesirable side effects, some of which were noted by Fontana [14]. Under these conditions, functional analysis emphasizes a certain inconsistency of the process, resulting mainly in hydroxyl functional groups loss. Temperatures below 200°C involve excessive reaction times and therefore represent no interest in the context of this paper.

Another interesting aspect revealed in figure 5 consists in the decrease with almost 1.5 h of the reaction time, which can be explained by the soaking with equivalent glycol of PET waste at ordinary temperature, for a period of 24 h prior to the start of the reaction (batches 6A, 7A). In conclusion, under normal conditions, part of the reaction time is represented by the glycol diffusion into polyester flakes, the actual basic reaction taking place much faster.

Although very sensitive, viscometry method remains a relative method; dynamic viscosity is strictly dependent on a particular set of experimental conditions. The non-Newtonian character of the specimens subject to measurements is the main reason for which a rigorous

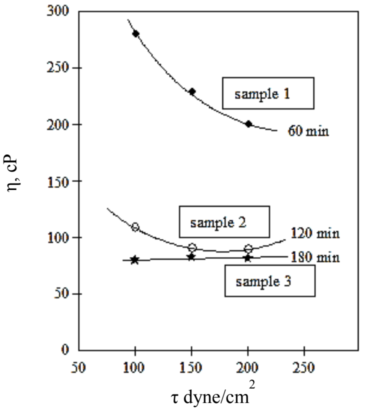

Fig. 8. Viscosity dependence with shear stress measured at 70°C for samples with different glycolysis degree (batch 8A)

control of the measuring conditions is necessary in order to keep the results at comparable values. From the rheological point of view, the glycolysis products present a viscosity highly dependent on the shear stress and time; this would require a more accurate characterization using the "apparent viscosity" or the "structural viscosity".

These characteristics are illustrated in figure 6, respectively figure 7. A strong dependence of viscosity on the shear stress and time suggests an aggregation phenomenon. This is facilitated by the weak prolonged shear stress and hindered by intense shearing, which breaks the underlying intermolecular aggregation. The same phenomenon of molecular rearrangement resulting in supramolecular aggregates was found even in the absence of shearing at temperatures ranging from 70-90°C that should ensure the mobility of higher molecular weight species.

One interesting note in this study is that the deviation from Newtonian behaviour is even more pronounced, as the specimen is extracted earlier from the reaction process, compared to the time required to achieve equilibrium. Samples that characterize the equilibrium phase of the system showed a normal behavior, viscosity is independent of shear stress intensity and shearing time.

This is not surprising if you consider responsible for the aggregation phenomenon the polyester chains still long enough in the early stages of glycolysis reaction and poorly solvated in the glycols mixture. Finally, the reaction products consist only in low-molecular weight species, mutually compatible, ensuring the disappearance of the aggregation character.

This effect is clear in figure 8, which may suggest an additional criterion to highlight the equilibrium reaction and the rheological behaviour of the reaction.

Conclusions

PET recycled from post-consumer soft-drink bottles was depolymerized by glycolysis process using (DEG) in the presence of zinc acetate catalyst. The resulted products mainly consist of PET monomer unit and dimer, and after long time reaction (over 2 h), it was demonstrated that equilibrium is attained between the two species. The evolution of the depolymerization reaction was investigated by the viscosity procedures, which were compared and found to be in good agreement with the functional analysis method. This procedure was able to determine and explain the conditions of the equilibrium phase of the system.

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