SOLID-PHASE POLYCONDENSATION OF POLYETHYLENE TEREPHTHALATE WITH TECHNOLOGIES OF ITS REACTIVE EXTRUSION

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It has been experimentally confirmed that polyethylene terephthalate during its processing into products destruct without carrying out the process of solid-phase polycondensation. The conditions for both primary and secondary polyethylene terephthalate have been determined for carrying out the process of solid-phase polycondensation for its effective reaction extrusion with chain extenders. To confirm the effectiveness of the parameters of the solid-phase polycondensation process of polyethylene terephthalate, its reaction extrusion was carried out with commercially available chain extenders of the diepoxide class. The optimal content of chain extenders of the diepoxide class for changing the complex of physical, mechanical and rheological properties of polyethylene terephthalate modified by them was determined. It allows obtaining materials with an increased by 2.2 times characteristic viscosity.

KEYWORDS

polyethylenetrephatlate, solid state polycondensation, hydrolytic dedtruction, interistic viscosity, chain extender
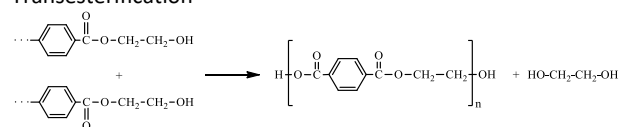
1 INTRODUCTION

The process of solid-phase polycondensation (SSP) of polyethylene terephthalate (PET) is sufficiently studied and is necessary to increase the molecular weight of secondary raw materials. An increase of molecular weight allows PET to be reprocessed into finished products and to reduce the amount of products formed during hydrolytic, thermo-, thermo-oxidative and thermo-mechanical destruction [Chen 1969, Chang 1970, Chang 1983, Molnar 2019, Sukhyy 2022].

SSP begins immediately after the transition of the polymer from the glass-like state to the highly elastic state and continues until the transition of PET to the viscous-flow state [Papaspyrides 2009, Rimar 2022, Sukhyy 2023]. The higher temperature and duration of SSP, the better it occurs [Chen 1969, Chang 1970, Chang 1983, Molnar 2019, Rimar 2022, Sukhyy 2022].
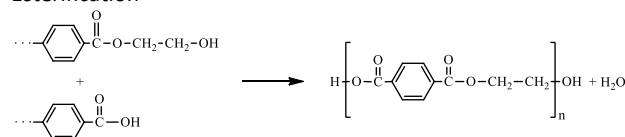
It is widely known that in the course of SSP, transesterification and esterification of polymeric and/or oligomeric derivatives of PET with hydroxyl and carboxyl groups occurs according to the following mechanisms [Duh 2002, Kim 2003, Culbert 2004]:

Transesterification

Esterification

The reaction of transesterification occurs much faster than esterification.

It is noted that the size (granules/flakes), chain growth catalyst, presence of acetaldehyde, temperature, time and environment of SSP and significantly affect the speed of this process [Dias 2000, Duh 2002, Kim 2003, Culbert 2004].

However, it should be noted that the parameters of conducting SSP of polyethylene terephthalate for its processing by the reactive extrusion method are almost not studied, the authors approached this empirically [Karayannidis 2000, Incarnato 2000, Harth 2021].

Reactive extrusion (REX) is a highly productive method of obtaining new and/or modified polymer materials in a single technological process by the extrusion method [Dhavalikar 2003, Di Maio 2001, Chervakov 2015, Anisimov 2019]. REX combines the traditionally separated processes - polymer synthesis/modification and the granulation/formation process in two or more worm extruders.

Currently, it is widely known [Hopmann 2017, Cassagnau 2007, Machado 2000, Sukhyy 2021, Sukhyy 2021a, Zhao 2020] that the formation of unsaturated bonds, oligomeric derivatives with hydroxyl, carboxyl, and vinyl ester groups during the destruction and processing of polymers provides the possibility of carrying out polycondensation, polyaddition, etc. reactions on them with so-called chain extenders (CE, chain extenders).

The most suitable compounds that can participate in chain elongation for PET are: di-, tri-, and tetraepoxides; carbodiimides; di- and triisocyanates; oxazolines; dianhydrides and caprolactams [Dias 2000, Karayannidis 2000, Dhavalikar 2003, Sukhyy 2021a, Pluta 2001].

Based on the above, the selection of technological parameters for conducting SSP PET for a more effective course of reaction extrusion is relevant. The amount of polymeric and/or oligomeric PET derivatives with hydroxyl and carboxyl groups will affect the quality of REX.

2 MATERIALS AND METHODS

2.1 Materials

The next materials were used:

- Primary PET brand BC 210 (Sabic, Saudi Arabia) with a characteristic viscosity (IV) of 0.8 dl/g (PET-V)
- Secondary PET flexa of natural color is washed and prepared according to the bottle to bottle technology (General Plastic, Slovenia) with a characteristic viscosity of 0.71 dl/g (PET-BTB).
- Granules from secondary crystalline PET (InterPET, Ukraine) with a characteristic viscosity of 0.63 dl/g (PET-C).
- Epon 1009 (WestLake epoxy, USA) diepoxide was chosen as the chain extender (CE).

2.2 Extrusion and Sample Preparation

The following equipment was used:

- Regranulation and compounding of PET with chain extender was performed on a TSE-35 series twin-screw extruder with L/d = 40 (Haisi, China).
- Die-casting of standard samples was carried out on a Kuasy 25x32/1 casting machine.
- Determination of the level of properties and standard samples were produced in accordance with the current ISO standards.

3 RESULTS AND DISCUSSION

Differential scanning calorimetry of primary polyethylene terephthalate (PET-V) before and after extrusion was used to determine the parameters of SSP (Figs. 1, 2). Before extrusion, PET-V did not go through the SSP process but was only dried at a temperature of 120 °C for 60 minutes.
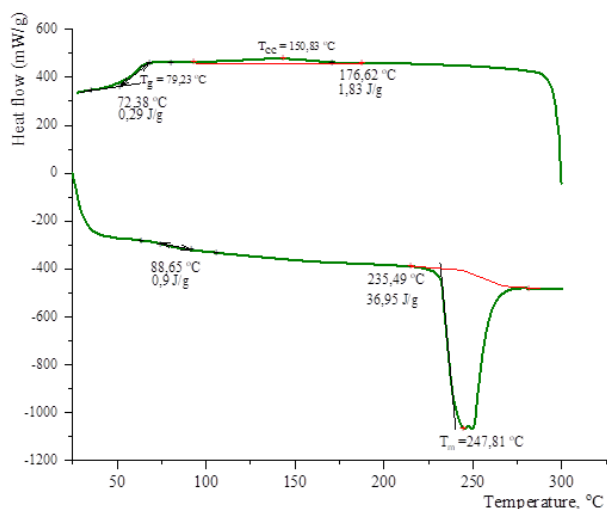

Figure 1. DSC data analysis of virgin polyethylene terephthalate PET-V before extrusion

As can be seen from the results of the DSC analysis of PET-V:

- the glass transition temperature (Tg) is 79 °C;
- cold crystallization temperature (Tcc) is 151 °C;
- melting point (Tm) is 248 °C;
- degree of crystallinity is 20%.

The degree of crystallinity was calculated according to the equation [25]:

$$\%_C = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{m0}} * 100$$

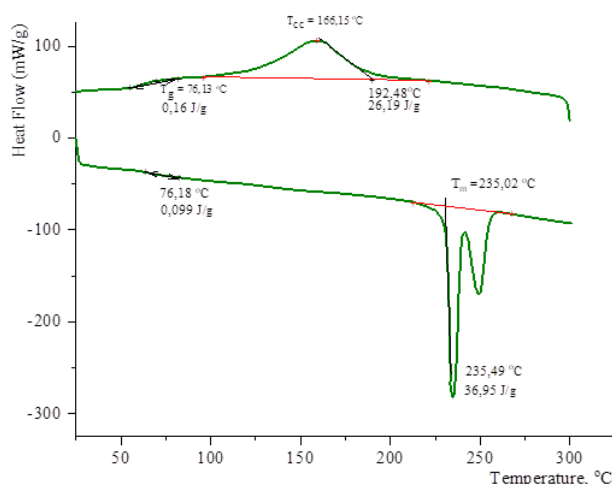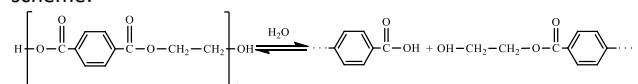ΔH_{m0} for PET-V =119,8 J/g

Figure 2. DSC analysis data of primary polyethylene terephthalate PET-V after extrusion

Based on the results of the DSC analysis of PET-V after extrusion, the glass transition, cold crystallization and melting temperatures, together with the degree of crystallinity, change slightly:

- the glass transition temperature (Tg) is 76 °C;
- cold crystallization temperature (Tcc) is 166 °C;
- the melting point (Tm) is 235 °C;
- degree of crystallinity is 11% (calculated according to formula (1)).

The obtained results and the analysis of literature data prove that without conducting the SSP process during the processing of PET, the processes of its hydrolytic destruction may occur [Chen 1969], which makes it impossible to effectively process it into products. Hydrolytic destruction leads to a loss of PET molecular weight, while a decrease in the glass transition and melting temperature and an increase in the cold crystallization temperature are observed.

This can also be observed when comparing the DSC results of PET-V before and after extrusion (Figs. 1 and 2), after PET-V extrusion, significantly less energy is needed to melt it. According to literature sources [Pluta 2001, Austin 2018], the hydrolytic destruction of PET occurs according to the following scheme:

It should be noted that this work is not devoted to the study of hydrolytic destruction of PET.

According to literature sources, SSP occurs more intensively in the crystalline phase of PET [Chang 1970, Chang 1983, Molnar 2019, Sukhyy 2022]. In our opinion, it is precisely at the temperatures of the beginning and end of cold crystallization that SSP for REX will be most effective. Based on the results of DSC analysis, the optimal temperature for conducting SSP will be from 110 to 160 °C.

It is widely known that the melt flow index (MFI) is a characteristic that not only qualitatively indicates the ability of polymers to flow under load but can also characterize materials by the average molecular weight distribution. Generally, the higher the MFI, the lower the molecular weight and vice versa.

We studied the change in MFI depending on the temperature and time of SSP (Fig. 3). Determination of MFI for PET was carried out under standard conditions (temperature 250 °C, load 2.16 kg).
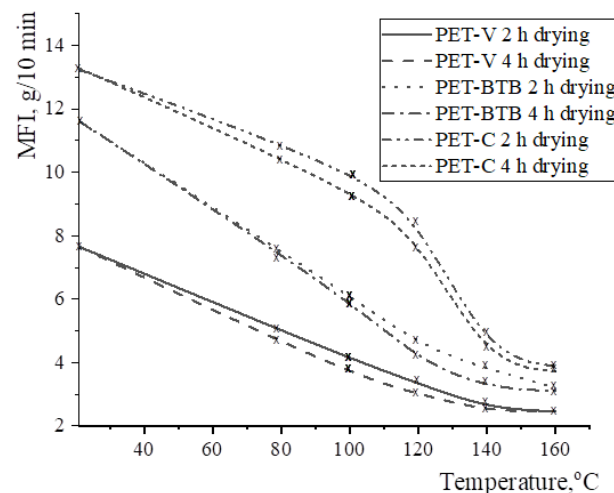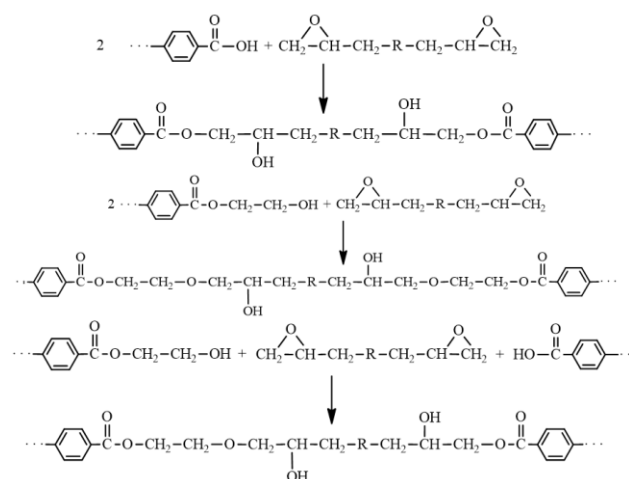

Figure 3. Change in the MFI indicator of polyethylene terephthalate depending on the conditions of SSP

As can be seen from Figure 3, the decrease in the flow rate of the melt is most likely a consequence of the increase in molecular weight during the course of the solid-phase

polycondensation process. Classically, the SSP process for secondary PET takes place within 12-20 hours at temperatures of 200-240 °C [Chen 1969, Chang 1970, Chang 1983, Molnar 2019, Sukhyy 2022 and 2023]. As noted earlier, the SSP stage is a very important technological component that allows secondary PET to be recycled with almost no loss of basic properties. However, for reaction extrusion, this duration of SSP is not optimal, because there is a decrease in the number of potentially reactive groups required for reaction extrusion (REX).

Based on the data of Fig. 4 in our opinion, the SSP process for REX should take place at temperatures in the range of 140-160 °C for 2 hours. Increasing the time of the SSP process from 2 to 4 hours is not appropriate, because the melt flow index for all samples is almost within the same limits.

To confirm this opinion, we conducted REX with a known chain extender (CE) based on Epon 1009 diepoxide [Haralabakopoulos 1999]. The authors of this work proposed the following schemes of interaction of CE with hydroxyl and carboxyl groups of polymeric and/or oligomeric derivatives of PET:

To confirm the possibility of interaction processes, we studied the change in MFI (Table 1) depending on the CE content in PET after the SSP process (at a temperature of 140-160 °C for 2 hours).

In order to effectively evaluate the selected parameters, we chose the polymer with the lowest characteristic viscosity, namely PET-C. The SSP process took place in dryers equipped with a hot air circulation system and a stirring device. The introduction of liquid components onto the surface of the PET-C granule took place in a high-speed two-blade mixer. The combination of PET with a chain extender was carried out in a twin-worm extruder at temperatures in the zones from 220 °C to 260 °C.

Table 1. Change in the melt flow index (MFI) depending on the conditions of the solid phase polycondensation process (140 °C/160 °C for 2 hours) and the chain extender content.

Property indicator	Epon 1009 chain extender content, mass %					
	0	0,2	0,4	0,6	0,8	1,0
MFI, g/10 min	4.5/3.7	4.3/3.3	3.1/3.1	2.7/2.6	2.1/1.9	1.9/1.9

As can be seen from the results shown in Table 1, the optimal temperature for the SSP process for REX is 160 °C. The MFI indicator decreases by 2.2 times when using the optimal CE content - 0.8 wt.%. Such a phenomenon is probably a consequence of the interaction of CE with hydroxyl and carboxyl groups of polymeric and/or oligomeric PET derivatives. To confirm the effectiveness of the SSP process for REX and to determine the basic level of physical, mechanical and rheological characteristics at the optimal CE content (0.8 wt.

%), we produced standard samples from compound PET. The test results of standard samples are shown in Table 2.

Table 2. Test results of compositions based on PET (the SSP process took place for 2 hours at a temperature of 160 °C) before/and after their combination with a chain extender (0.8 wt. %).

Property indicator	Material type			
	PET-V	PET-BTB	PET-C	[23]
Intrinsic viscosity, dl/g	0.80/0.91	0.71/0.92	0.63/0.83	0.74/0.67
Melt flow index, g/10 min	2.5/2.2	3.1/2.4	4.5/2.6	n/d
Tensile strength, MPa	47.0/51.0	45.0/52.6	48.6/54.3	n/d
Elongation at break, %	165/190	134/210	51/73	n/d
Impact elasticity by Charpy, KJ/m²	10/8	6/4	5/4	n/d

As can be seen from the results shown in Table 2, the results of the increase in the characteristic viscosity of PET obtained by us, in comparison with the data of work [Pluta 2001], are slightly different. The authors of the work [Haralabakopoulos 1999] stated that before combining PET with CE, the SSP process took place for 24 hours at a temperature of 120 °C. At the same time, chain growth was explained by the decrease in the number of carboxyl groups from 42 to 20 eq/106 g. The low value of the characteristic viscosity of the modified PET may be related either to a small number of functional (hydroxyl or carboxyl) groups in the studied PET or to the passage of specific, unstudied processes that occur under the conditions of REX.

As a result of our work, it was established that in the process of conducting REX in the presence of a chain extender (diepoxide Epon 1009) in the optimal amount of 0.8 wt.%, an increase in IV of all materials is observed. At the same time, the largest difference (Δ) between the characteristic viscosity indicators among the original PET materials and reactively modified ones is observed for crystalline PET-C, which has the smallest IV value. Thus, the IV difference for the entire range of modified materials studied was: ΔPET-V = 13%; ΔPET-BTB = 30%; ΔPET-C = 32%.

4 CONCLUSIONS

Based on the above presented results, the original PET was not proven as suitable for REX, probably due to the insufficient number of hydroxyl and carboxyl groups of polymeric and/or oligomeric derivatives.

The increase in tensile strength and relative elongation at break is most likely due to a change in the structure of the modified PET.

The drop in Charpy impact strength is probably a consequence of the change in the degree of crystallinity, regularity and architecture of the supramolecular structures of PET and its derivatives.

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