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THE INFLUENCE OF SOLID-STATE POLYCONDENSATION OF POLYETHYLENE TEREPHTHALATE ON ITS RHEOLOGICAL PROPERTIES

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The influence of solid-state polycondensation conditions on the rheological properties of polyethylene terephthalate was determined. Mathematical models describing the dependence of the melt flow rate of both virgin and recycled polyethylene terephthalate on the time and temperature of the solid-state polycondensation process were developed. A correlation between the melt flow rate and the average molecular weight of polyethylene terephthalate was demonstrated. Experimental studies showed that conducting solid-state polycondensation of recycled polyethylene terephthalate at temperatures ranging from 130^0C to 160^0C for 3 hours produces polymeric materials with higher molecular weight and, consequently, improved performance properties.

Keywords: polyethylene terephthalate, solid-state polycondensation, hydrolytic degradation, melt flow rate, intrinsic viscosity.
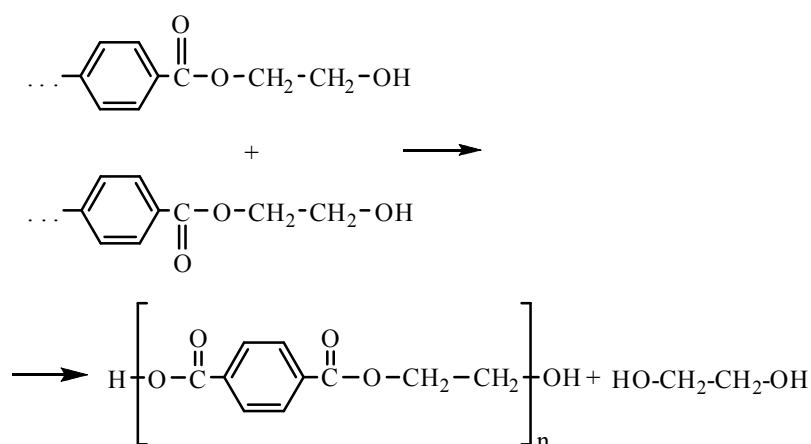
Introduction

The solid-state polycondensation (SSP) process for both virgin and recycled polyethylene terephthalate (PET) is well established and essential for increasing its molecular weight.

An increase in the molecular weight of recycled PET allows it to be reprocessed into finished products by reducing the number of unwanted products that can be formed during hydrolytic (HD), thermo-oxidative (TOD) and thermomechanical destruction [1−5] in the recycling process.

SSP begins immediately after the transition of the polymer from a glassy to a highly elastic state and lasts until PET enters the viscous state [6]. It is widely known that during SSP, transesterification and esterification of polymeric and/or oligomeric PET derivatives with hydroxyl and carboxyl groups by the following mechanisms [7−10]:
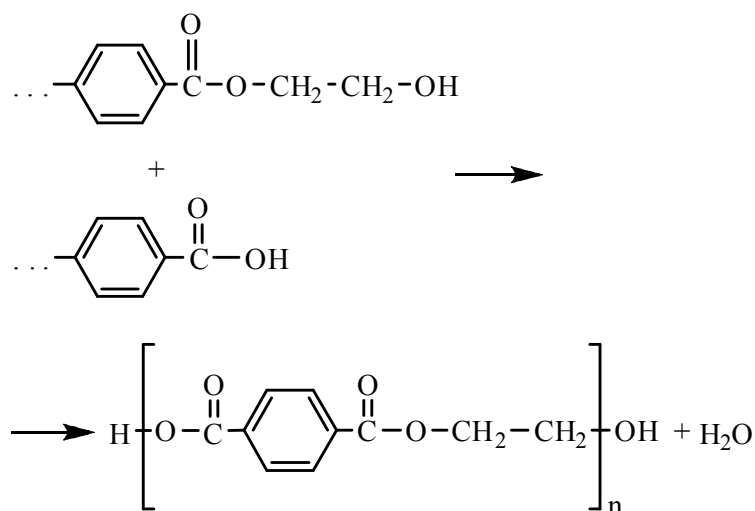
− transesterification:

− esterification:

$$\text{...}-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$$

$$+$$

$$\text{...}-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{OH}$$

$$\longrightarrow \text{H} \left[\text{O}-\underset{\text{O}}{\underset{\|}{\text{C}}}-\underset{\text{O}}{\underset{\|}{\text{C}}}-\text{O}-\text{CH}_2-\text{CH}_2 \right]_n \text{OH} + \text{H}_2\text{O}$$

It should be noted that transesterification reactions occur at a higher rate than esterification.

It has been noted that the efficiency of SSP process is influenced by a number of factors: the size of PET particles, the presence of chain extender, temperature, time, environment of SSP, etc. [7−10].

However, the parameters of carrying out the solid-state polycondensation of polyethylene terephthalate for it processing by reactive extrusion are almost not studied, and the authors approached their study empirically [11−14].

Experimental

The following materials were used in this study:

− virgin PET brand BC 210 (PET-V, Sabic, Saudi Arabia) with the intrinsic viscosity (IV) of 0.80 l/g;

− recycled PET of natural color, washed and prepared according to bottle to bottle technology (PET-BTB, General Plastic, Slovenia) with IV=0.71 l/g;

− granules from secondary crystalline PET (PET-C, InterPET, Ukraine) with IV=0.63 l/g.

Sample preparation: drying of the examined PET samples was carried out in a thermal chamber in the temperature range of 110−160⁰C.

The determination of the melt flow index was carried out in accordance with the current ISO 1133 standards.

Results and discussion

According to literature sources [2−4] and our previous studies [5], it has been determined that SSP occurs more intensely in the crystalline state of PET [2−5]. We have previously established that SSP will be the most effective temperatures of 110 to 160⁰C (beginning and end of cold crystallization, respectively) [5].

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 their average molecular mass. Generally, the higher the MFI the lower the molecular weight. For SSP, from an economic point of view, in contrast to previous studies [5], PET drying was carried out in a conventional thermal chamber without vacuum rather than in a vacuum chamber.

MFI for PET-V was determined under standard conditions (temperature of 250⁰C and load of 2.16 kg). Change of MFI over time at different temperatures of the SSP process for PET-V is shown in Fig. 1.

Analyzing the results of the above studies, it can be concluded that the change of MFI for primary PET-V occurs more efficiently in the temperature
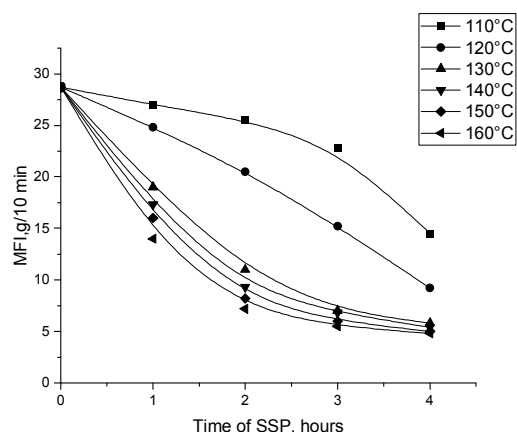

Fig. 1. Change in flow index of MFI primary melt of polyethylene terephthalate (PET-V) depending on the conditions of solid state polycondensation

range of 130−160⁰C, which corresponds to the temperature range of the beginning of PET «hot crystallization» [5].

After 3 hours of the SSP process in the above temperature range, the MFI index is almost unchanged and achieves a conditional «plateau».

Based on analysis of the obtained results on solid-state polycondensation of virgin PET (PET-V), the following conclusions can be drawn:

− the change of MFI during the SSP without the use of vacuum is not extreme;

− effective SSP temperatures are 130−160⁰C;

− the duration of the SSP process should be at least 3 hours.

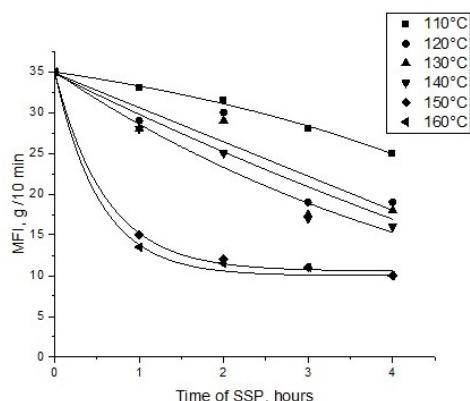The MFI change over time at various temperatures for SSP of PET-BTB is presented in Fig. 2.

Fig. 2. Variation of the melt flow index of recycled polyethylene terephthalate (PET-BTB) depending on the conditions of solid-state polycondensation

Analysis of the results shown in Fig. 2 shows that the temperature range of effective SSP process for PET-BTB is 150−160⁰C.

It should be noted that the MFI for PET-BTB is slightly higher than for primary PET-V. This difference is probably due to the different ways of HD, TOD and thermal prehistory of recycled material processing.

The change in MFI for PET-BTB samples during the SSP, as well as for PET-V, is not extreme. Effective temperatures for SSP are 150−160⁰C with drying process over 2 hours.

Similar to virgin PET and PET-BTB, we investigated the change of MFI depending on temperature and time of SSP for re-granulated PET. Determination of MFI for PET-BTB was carried out under standard conditions (temperature of 250⁰C and weight of 2.16 kg).

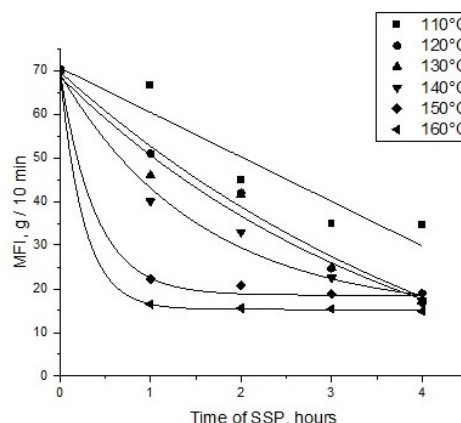The PET-C MFI changes are shown in Fig. 3 depending on the SSP conditions.

Fig. 3. Variation of the melt flow index of secondary polyethylene terephthalate (PET-C) depending on the conditions of solid-state polycondensation

Based on the above studies, it can be concluded that for PET-C, the change in MFI occurs similarly to virgin PET and PET-BTB. However, it should be noted that the MFI of PET-C without drying is significantly larger than for virgin PET and PET-BTB, which is probably due to the significant flow of HD, TOD and the much larger thermal prehistory of the re-granulated material. The effective temperatures for conducting SSP are 150−160⁰C when drying for more than 1 hour.

Based on the experiments and empirically obtained data, we propose the following mathematical model for determining MFI depending on SSP conditions (time and temperature). Experimental data analysis was performed by regression analysis [6] using the following type regression equation:

$$y = b_0 + b_1 x_1 + b_2 x_2. \tag{1}$$

In equation (1), we assumed the following: $x_1 = \ln(\exp(\tau))$; $x_2 = \ln(t)$; $y = \ln(MFI)$; τ is the time of SSP (hours); and t is the temperature of SSP (⁰C).

The parameters are given in logarithmic mode for next transforming the regression equitation with exponentiation operation. Statistical model takes the following form:

$$MFI = \alpha \cdot e^{\tau \cdot B} \cdot t^C. \tag{2}$$

Considering on transformation, the b_0, b_1, b_2 values are given in Table 1 according to the following operation: $A = e^{b0}$, $B = b_1$, and $C = b_2$.

The model parameters were obtained according to each material and temperature ranges 150−160⁰C and 110−140⁰C. The adequacy of the models was assessed by Fisher's test ($F > F_t$).

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Parameters of statistical model (2) (A, B, and C are the model coefficients; F is the calculated Fisher's criterion; and F_t is the tabulated value of Fisher's criterion)

Material	Temperature, ^{0}C	A	B	C	$F > F_t$
PET-V	110–140	$3.5 \cdot 10^8$	−0.323	−3.379	58.46>4.35
PET-V	150–160	445.516	−0.454	−0.57	61.04>4.96
PET-BTB	110–140	1383.89	−0.201	−0.734	21.63>4.35
PET-BTB	150–160	10391.5	−0.336	−1.187	16.93>4.96
PET-C	110–140	13046.2	−0.314	−1.077	79.76>4.35
PET-C	150–160	$2.8 \cdot 10^8$	−0.347	−3.116	7.42>4.96

As can be seen from Table 1, the model coefficients for the given temperature intervals for each material are adequately described by equation (2).

The model calculations (Table) were evaluated by comparison with experimental data. The results are shown in Fig. 4. The maximum deviation was 15% at this stage of research. It can be accepted as satisfactory.
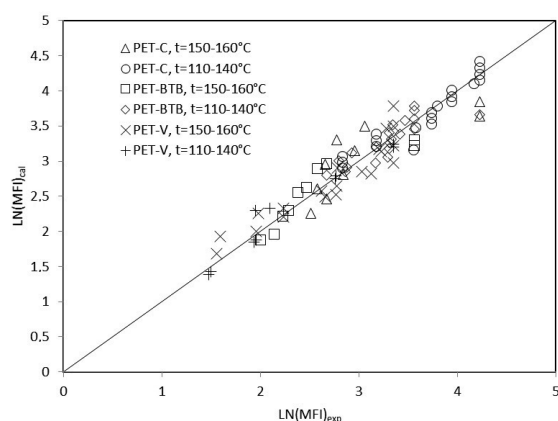

Fig. 4. Comparison of experimental and calculated data

As mentioned above, melt flow index is a characteristic that not only qualitatively indicates the ability of polymers to flow under loads, but can also characterize materials by their average molecular mass distribution. In turn, using the IV, the molecular weight can be determined using the classical Mark-Kuhn-Houwink equation [7−14].

In determining the intrinsic viscosity of the PET in a solution of phenol and 1,2-dichlorobenzene (50:50), the following interpretation of the Mark-Kuhn-Houwink equation is used [15]:

$$IV = 2.1 \cdot 10^{-4} \cdot M_w^{0.82}. \qquad (3)$$

We carried out study to determine the intrinsic viscosity and calculated the molecular weight of PET-V, PET-BTB, and PET-C samples.

The intrinsic viscosity was determined according to ISO 1628-1. The results of the intrinsic viscosity determination are shown in Fig. 5.

As can be seen, IV is 0.79 l/g, 0.73 l/g and 0.37 l/g for PET-V, PET-BTB and PET-C, respectively. The molecular weight (MW) for the experimental PET samples was calculated according to the equation (3); it is equal to 22922, 20817 and 9088 for PET-V, PET-BTB and PET-C, respectively.

For these samples, the MFI was determined to be 28.5 g/10 min (for PET-V with MW=22922); 35.4 g/10 min (for PET-BTB with MW=20817); 68.4 g/10 (for PET-C with MW=9088). A correlation was found between MW and MFI indices. Thus, the correlation for the MW is as follows: 22922:20817:9088=1.0:1.1:2.5, and the correlation for the MFI is as follows: 1.0:1.2:2.4, which is very close.

Conclusions

As a result of this research, the optimal conditions (temperature and process duration) for conducting solid-state polycondensation of virgin and recycled polyethylene terephthalate were found to be 130−160^{0}C for more than 1−3 hours. SSP conditions were selected depending on the history of PET production or processing. The necessity of SSP for PET is dictated by the need to obtain polymeric materials based on PET with a higher molecular weight and, accordingly, with an enhanced performance properties.
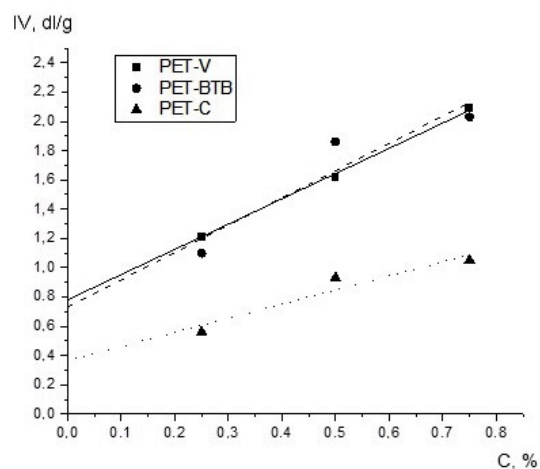

Fig. 5. Intrinsic viscosity of PET in phenol solution and 1,2-dichlorobenzene (50:50) determined at 25^{0}C

The SSP conditions for both virgin PET-V and recycled PET-BTB and PET-C polymers are very similar. Mathematical models of MFI change as a function of drying time and temperature (PET of different prehistory) for each of the cases have been developed. These models are effective in the range of SSP temperatures (130−160⁰C) and have a standard error of no more than 15%.

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ВПЛИВ ТВЕРДОФАЗНОЇ ПОЛІКОНДЕНСАЦІЇ ПОЛІЕТИЛЕНТЕРЕФТАЛАТУ НА ЙОГО РЕОЛОГІЧНІ ВЛАСТИВОСТІ

Д.О. Черваков, В.В. Ведь, В.В. Федан, К.М. Сухий, О.В. Черваков

Встановлено вплив умов перебігу процесів твердофазної поліконденсації поліетилентерефталату на його реологічні властивості. Розроблено математичні моделі залежностей показника текучості розплаву первинного та вторинного поліетилентерефталату від часу та температури проведення його твердофазної поліконденсації. Показана кореляція між показником текучості розплаву та показником середньої молекулярної маси поліетилентерефталату. На підставі здійснених експериментальних досліджень встановлено, що проведення твердофазної поліконденсації вторинного поліетилентерефталату (при температурі 130−160⁰C протягом 3 годин) дозволяє одержувати полімерні матеріали з більш високою молекулярною масою, і, відповідно, з підвищеним рівнем експлуатаційних властивостей.

Ключові слова: поліетилентерефталат, твердофазна поліконденсація, гідролітична деструкція, показник текучості розплаву, характеристична в'язкість.

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