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*D.O. Chervakov, V.V. Ved, V.V. Fedan, K.M. Sukhyy, O.V. Chervakov***INFLUENCE OF SOLID-STATE POLYCONDENSATION CONDITIONS ON THE INTRINSIC VISCOSITY OF RECYCLED POLY(ETHYLENE TEREPHTHALATE)****Ukrainian State University of Science and Technologies, Dnipro, Ukraine**

The study investigates the influence of solid-state polycondensation (SSP) conditions on the change in intrinsic viscosity (IV) of recycled poly(ethylene terephthalate) (PET) processed via a bottle-to-bottle technology. Experimental work was carried out within the temperature range of 110–160°C while varying the duration of SSP. It was found that during SSP at 110–130°C, the intrinsic viscosity of PET-BTB increased by 23–34%, whereas the melt flow index (MFI) decreased by up to 54%, indicating a nonlinear relationship between IV and MFI. A mathematical model was proposed to predict IV as a function of temperature, SSP duration, and MFI value. Validation of the model revealed a deviation not exceeding 6%, which confirms its high practical reliability. The proposed approach enables a reduction in the scope of experimental work required for optimizing SSP conditions of recycled PET and assessing its recyclability toward products with the desired level of physical and mechanical properties.

Keywords: poly(ethylene terephthalate), solid-state polycondensation, hydrolytic degradation, intrinsic viscosity, melt flow index.

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Introduction

A series of studies focuses on examining the effect of solid-state polycondensation (SSP) on the rheological properties [1] and molecular weight of recycled poly(ethylene terephthalate) (PET). It is well known that increasing the molecular weight of recycled PET during SSP is a prerequisite for its effective reprocessing into finished products, as it reduces brittleness and improves melt processability. The growth in molecular weight of PET occurs through transesterification and esterification reactions involving polymeric and/or oligomeric PET fragments with terminal hydroxyl and carboxyl groups, which are formed during the hydrolytic degradation of PET at

elevated (processing) temperatures. The mechanisms of these reactions have been described in detail in refs. [2–4].

It has also been reported [5–7] that transesterification reactions proceed at a higher rate than esterification, while the efficiency of the SSP process depends on several additional factors, such as PET particle size, the presence of chain extenders, temperature, duration, and reaction medium [3,8,9].

However, there is still a lack of sufficiently substantiated studies evaluating the relationship between molecular weight (intrinsic viscosity, IV) and melt flow index (MFI) for recycled PET. Therefore,

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the aim of this work is to assess the correlation between these parameters for recycled PET depending on the SSP processing conditions.

Experimental

Materials

The recycled natural-color PET, washed and prepared according to the bottle-to-bottle (BTB) recycling technology (PET-BTB, General Plastic, Slovenia), had an initial IV=0.68 dl/g.

Sample preparation

Conditioning of the PET samples was carried out in a vacuum drying oven at 21°C for 48 hours.

Drying of the samples prior to SSP was performed in a thermal oven within the temperature range of 110–160°C.

The melt flow index (MFI) of PET was determined in accordance with ISO 11334.

The intrinsic viscosity (IV) of PET was measured in its phenol solutions in compliance with ISO 11443.

Results and discussion

According to the literature sources [2–4] and previous studies [1,5], it has been established that SSP proceeds more intensively in the crystalline phase of PET [2–5]. It was further determined that conducting SSP within the temperature range of 110–160°C, corresponding to the onset and completion of cold crystallization, is the most effective for promoting chain growth [5].

Figure 1 presents the results of IV determination for the initial PET-BTB. As can be seen, the characteristic viscosity of PET-BTB at zero concentration is IV=0.69 dl/g, which is in good agreement with the nominal passport value of

IV=0.68 dl/g.

For the SSP of PET-BTB, and in line with the approach adopted in the present study series [1], but differing from earlier works [5], the drying of PET-BTB was performed in a conventional thermal oven without vacuum application, which is more economically feasible.

The results of IV determination for PET-BTB in phenol at SSP temperatures of 110°C, 120°C, and 130°C as a function of process duration are presented in Figs. 2–4.

As can be seen from the obtained results, during the SSP of recycled PET-BTB at temperatures of 120°C and 130°C for 4 hours, IV increased from 0.73 to 0.96 and 0.98 dl/g, corresponding to a 31.5% and 34.2% rise, respectively. The initial data used for developing the mathematical model describing the influence of SSP conditions on the intrinsic viscosity and melt flow index of recycled PET-BTB are summarized in Table.

When determining the intrinsic viscosity of PET in a phenol solution, the following interpretation of the Mark–Kuhn–Houwink equation¹ is applied:

$$IV = 2.1 \cdot 10^{-4} \cdot M_w^{0.77} \quad (1)$$

Analyzing the results reported in ref. [10], the obtained values of IV, MFI, and M_w show some differences. In the referenced study, the reported values were IV=0.67 dl/g, MFI=26 g/10 min, and M_w =35,500, whereas in our work, the corresponding parameters were IV=0.68 dl/g, MFI=35 g/10 min, and M_w =36,209. Such a discrepancy in the MFI

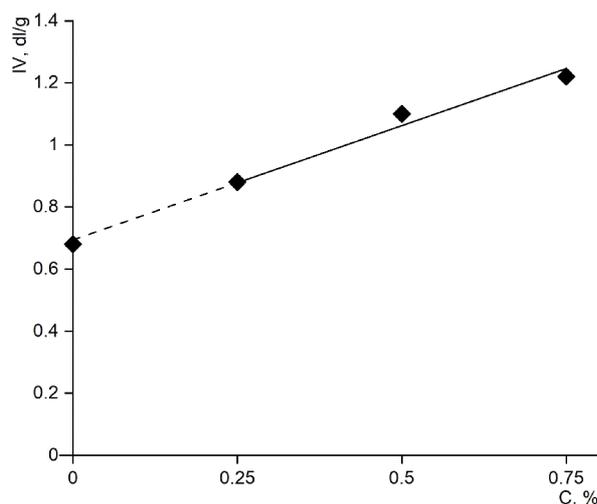


Fig. 1. Dependence of the reduced viscosity of the initial recycled PET-BTB on its concentration in phenol

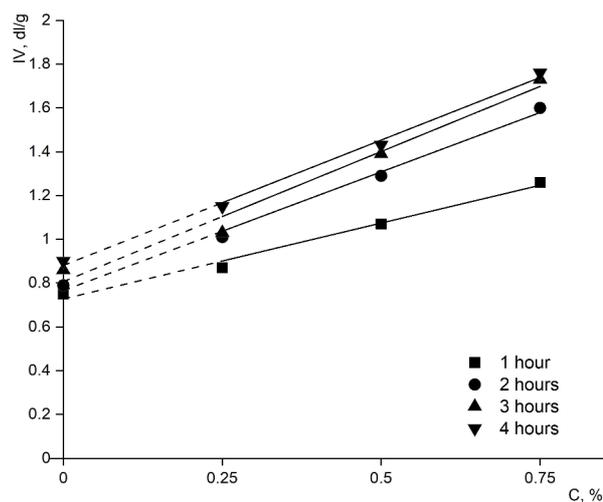


Fig. 2. Dependence of the reduced viscosity of recycled PET-BTB, subjected to SSP at 110°C for different process durations, on its concentration in phenol

¹ IUPAC Compendium of Chemical Terminology (the «Gold Book»). Mark–Houwink equation. Term M03706, 2nd ed. 2019.

values may be attributed to the following:

– differences in testing conditions, particularly the temperature, applied load, and capillary diameter during melt flow measurements;

– variations in sample preparation, including the duration and temperature of drying, initial moisture content, and degree of crystallinity of the material.

The low efficiency of the solid-state polycondensation (SSP) process for recycled PET-BTB at 110°C, as well as the nonlinear dependence of intrinsic viscosity (IV) on the melt flow index [1], complicate the use of these technological parameters for constructing an adequate mathematical model. For this reason, only the data obtained at

SSP temperatures of 120°C and 130°C were considered when analyzing the relationship between IV and MFI. The absence of noticeable polymer chain growth at 110°C can be attributed to conformational restrictions within the polymer matrix and the limited removal of absorbed moisture under these conditions, which hinder the progression of polycondensation reactions.

Figure 5 shows the dependence of intrinsic viscosity on the melt flow index, illustrating the relationship between these parameters for PET-BTB samples subjected to SSP at different temperatures and process durations.

The obtained experimental dependencies reveal a clear trend of increasing intrinsic viscosity with

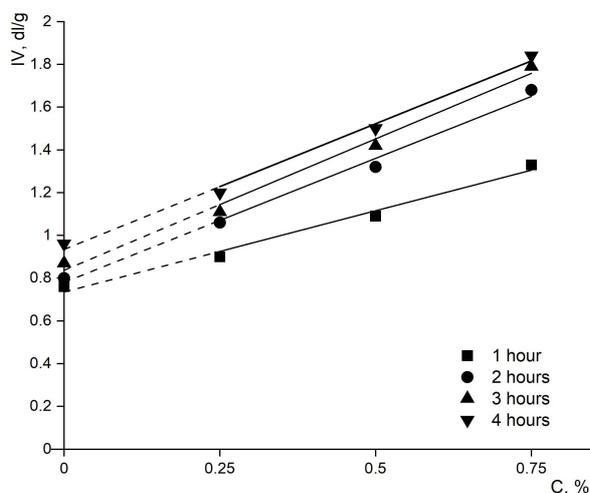


Fig. 3. Dependence of the reduced viscosity of recycled PET-BTB, subjected to SSP at 120°C for different process durations, on its concentration in phenol

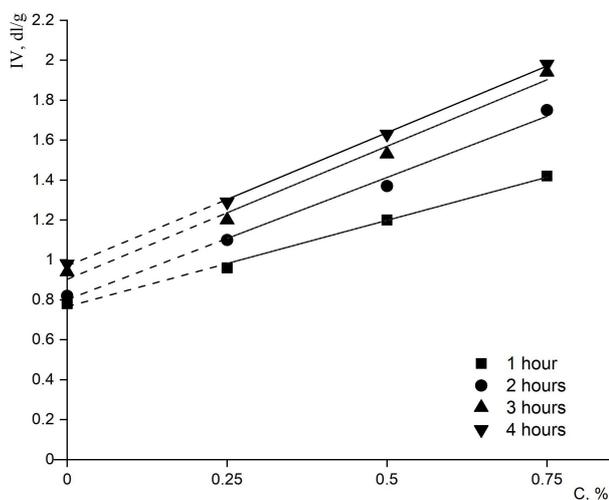


Fig. 4. Dependence of the reduced viscosity of recycled PET-BTB, subjected to SSP at 130°C for different process durations, on its concentration in phenol

Influence of SSP conditions on the relative molecular mass (M_m), intrinsic viscosity (IV), and melt flow index (MFI) of recycled PET-BTB

Temperature, °C	Duration of SSP, h	MFI, g/10 min	IV, dl/g	M_m
0	0	35.0	0.68	36209
110	1	33.0	0.75	41123
	2	31.5	0.79	43993
	3	28.0	0.86	49122
	4	25.0	0.90	52109
120	1	29.0	0.76	41836
	2	30.0	0.80	44718
	3	19.0	0.87	49865
	4	19.0	0.96	56665
130	1	28.0	0.78	43271
	2	29.0	0.82	46175
	3	17.5	0.94	55137
	4	18.0	0.98	58203
150	2	12.0	0.93	54376
160	2	11.5	0.97	57433

decreasing melt flow index. This behavior indicates a consistent increase in the molecular weight of the polymer as a result of SSP process. The approximation curves constructed after data processing accurately reproduce the general behavior of the system, confirming the presence of a stable correlation between the rheological parameters and the feasibility of mathematical modeling of the process.

Based on the obtained results, the following equations were proposed for predicting intrinsic viscosity, melt flow index, and relative molecular weight:

$$IV = 0.6538 + 0.0015 \cdot T - 0.00388 \cdot MFI + 0.04737 \cdot \tau, \quad (2)$$

$$MFI = \frac{0.6538 + 0.0015 \cdot T + 0.04737 \cdot \tau - IV}{0.0038}, \quad (3)$$

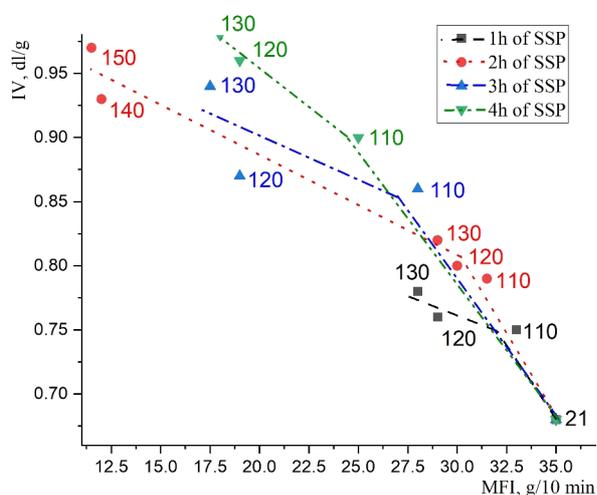


Fig. 5. Dependence of IV on MF for PET-BTB after SSP at different temperatures (°C) and process durations

$$MFI = 376.19 \exp(-3.273 \cdot IV), \quad (4)$$

$$M_w(T, \tau, MFI) = \left(\frac{0.6538 + 0.0015 \cdot T - 0.0038 \cdot MFI + 0.04737 \cdot \tau}{2.1 \cdot 10^{-4}} \right)^{1/0.77}, \quad (5)$$

where IV is the intrinsic viscosity, dl/g; MFI is the melt flow index, g/10 min; M_w is the average molecular weight; T is the temperature of solid-state polycondensation, °C; and τ is the duration of the SSP process, h.

Equation (3) describes the dependence of intrinsic viscosity on the technological parameters of the SSP process and the melt flow index. On its basis, expressions (3)–(5) were derived, allowing the prediction of the melt flow index or molecular weight from the known values of temperature and process duration.

The obtained equations reproduce the experimental data with a high degree of correlation ($R^2 \approx 0.98$), confirming the adequacy of the models in describing the structural evolution processes of poly(ethylene terephthalate) during SSP.

The accuracy of the model correlations was evaluated by comparing the calculated values with the experimental data. The results are presented in Fig. 6. The maximum deviation did not exceed 6%, which, at the current stage of the study, can be considered satisfactory.

To verify the applicability of the proposed model (2) at SSP temperatures above 130°C, additional experiments were conducted to determine the intrinsic viscosity at 150°C and 160°C under identical processing conditions for a duration of 2 hours.

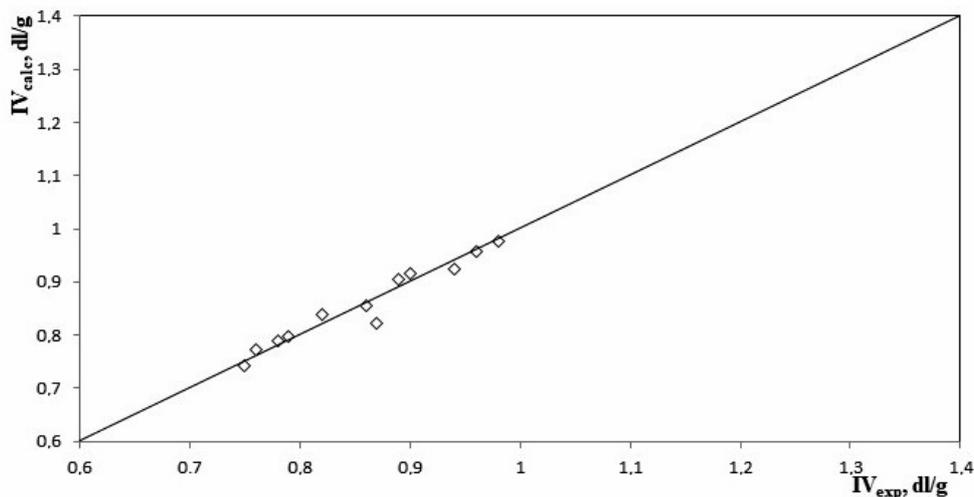


Fig. 6. Comparison of experimental and calculated data

It was found that during SSP at 150°C for 2 hours, the experimentally obtained IV value was 0.93 dl/g, while the theoretically calculated value according to equation (2) was $IV_i=0.9295$ dl/g, resulting in a deviation of only 0.04%. In the case of SSP at 160°C for 2 hours, the experimentally obtained IV was 0.97 dl/g, and the theoretically calculated value $IV=0.9485$ dl/g, corresponding to a deviation of 2.2%.

Based on the obtained results, it can be concluded that the proposed model and the applied approach are capable of predicting changes in intrinsic viscosity for PET-BTB with an error margin below 5%. This confirms the adequacy of the model and demonstrates that it can significantly reduce the time and cost required for forecasting IV variations depending on SSP processing conditions.

Conclusions

During the SSP of recycled PET within the temperature range of 110–160°C, an increase in intrinsic viscosity by 23–34% was observed, indicating an effective rise in the molecular weight of the material. The reduction of MFI during SSP was found to be nonlinearly correlated with the increase in intrinsic viscosity, suggesting a complex interdependence between these rheological parameters. The developed empirical model describes the relationship between intrinsic viscosity, process temperature, duration, and melt flow index; the deviation of the calculated values from the experimental data does not exceed 6%, confirming the model's satisfactory predictive accuracy. The proposed approach can be applied to reduce the experimental effort required for optimizing SSP conditions, thereby demonstrating its practical significance for industrial recycling technologies of poly(ethylene terephthalate).

It should be noted that the mathematical model presented in this work represents only one possible approximation derived from experimental data within the investigated temperature and time ranges. To improve the predictive accuracy of rheological parameters for PET, further studies should expand the statistical dataset to include a broader range of SSP conditions. An important direction for future development lies in minimizing human influence through automation of measurements, standardization of intrinsic viscosity and melt flow index testing procedures, and the implementation of machine learning algorithms for developing more universal predictive models.

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**ВПЛИВ УМОВ ТВЕРДОФАЗНОЇ
ПОЛІКОНДЕНСАЦІЇ ВТОРИННОГО
ПОЛІЕТИЛЕНТЕРЕФТАЛАТУ НА ЙОГО
ХАРАКТЕРИСТИЧНУ В'ЯЗКІСТЬ**

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Черваков О.В.*

У роботі досліджено вплив умов твердофазної поліконденсації (SSP) на зміну характеристичної в'язкості вторинного поліетилентерефталату (PET), який проходить технологічні стадії підготовки за схемою bottle-to-bottle. Експериментальні дослідження охоплювали температурний діапазон 110–160°C при варіації часу проведення SSP. Встановлено, що в ході SSP при 110–130°C в'язкість PET-ВТВ зростає на 23–34%, тоді як показник текучості розплаву знижується до 54%, що вказує на нелінійну залежність між в'язкістю та показником текучості розплаву. Запропоновано математичну модель прогнозування в'язкості залежно від температури, тривалості SSP та значення показника текучості розплаву. Перевірка моделі показала відхилення не більше 6%, що свідчить про її високу практичну придатність. Представлений підхід дозволяє зменшити витрати на експериментальні дослідження при оптимізації процесу SSP вторинного PET та оцінки його здатності до переробки і отримання виробів з необхідним рівнем фізико-механічних властивостей.

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

**INFLUENCE OF SOLID-STATE POLYCONDENSATION
CONDITIONS ON THE INTRINSIC VISCOSITY OF
RECYCLED POLY(ETHYLENE TEREPHTHALATE)**

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The study investigates the influence of solid-state polycondensation (SSP) conditions on the change in intrinsic viscosity (IV) of recycled poly(ethylene terephthalate) (PET) processed via a bottle-to-bottle technology. Experimental work was carried out within the temperature range of 110–160°C while varying the duration of SSP. It was found that during SSP at 110–130°C, the intrinsic viscosity of PET-BTB increased by 23–34%, whereas the melt flow index (MFI) decreased by up to 54%, indicating a nonlinear relationship between IV and MFI. A mathematical model was proposed to predict IV as a function of temperature, SSP duration, and MFI value. Validation of the model revealed a deviation not exceeding 6%, which confirms its high practical reliability. The proposed approach enables a reduction in the scope of experimental work required for optimizing SSP conditions of recycled PET and assessing its recyclability toward products with the desired level of physical and mechanical properties.

Keywords: poly(ethylene terephthalate); solid-state polycondensation; hydrolytic degradation; intrinsic viscosity; melt flow index.

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