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*Research Article*

# Effect of Reprocessing on the Crystallization of Different Polyesters

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Abstract: The changes in crystallization characteristics of four polyesters were investigated during multiple processing. Two of these were petroleum-based materials: poly (ethylene terephthalate) (PET) and poly (butylene terephthalate) (PBT), and two were bio-based materials: poly (lactic acid) (PLA) and poly (butylene succinate) (PBS). We found that during non-isothermal crystallization the different type of polyesters shown different behaviour: the PET and PLA materials were more sensitive to the cooling rate than the PBT and PBS. Interestingly, at low cooling rates, the number of reprocessing steps had no significant effect on the crystallinity of PBT and PBS, but reduced it for PET, but increased it for PBT.

*Keywords: polyesters, bio-based polymer, petroleum-based polymer, crystallization, recycling*

## I. INTRODUCTION

Modern industries need materials that have properties which are not found among the traditional materials used, so the manufacture of materials with special specifications has raised the interest of researchers in recent years [1,2,3,4]. Different types of polyester materials have started to be widely used, since these polymers are commonly used in most applications due to their low cost, adaptability and high mechanical properties such as strength and moisture resistance. They are used as the main component in different industries and daily products such as textiles, clothes, backpacks, home furniture, pillows, napkins, air and water filters, packaging materials, computers and recording tapes, building and construction materials and electrical insulation as well as in the medical field. Also, biodegradable polyester materials are used in environmentally friendly products like compostable bags and food containers [1,2,3,5,6].

Polyester can be classified into two main types depending on the raw materials used in their production. One of them is bio polyester, which is extracted from renewable resources such as microorganisms and plants like sugarcane and corn, the most important of which are polylactic acid (PLA) and polybutylene succinate (PBS) [7,8]. The other type is called petroleum-based polyesters, which can be obtained from petrochemical raw materials, including polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) [9,10]. In addition, bio-based polyesters are considered more environmentally friendly than their petroleum-based counterparts because they reduce dependence on fossil fuels [7,8,9,10]. However, both types of polyesters have their advantages and disadvantages, and the selection of the most suitable option depends on the specific needs of a particular application [7,8,9,10].

Polyester recycling has received great attention in recent years because it helps reduce the amount of waste, energy consuming and environmental impacts and conserve resources [7,9,11]. Also, the recycling process can have an effect on the structure of the polymer, including its crystallinity, thus affect the mechanical properties of polymer [11,12].

The present work was undertaken to study the effect of reprocessing on the non-isothermal crystallization behaviour of PET, PBT, PLA and PBS. This work is intended to provide a better insight into the crystallization kinetics of petroleum-based and bio-based polyesters.

***Table 1.*** *Tested polyesters*

| *Name* | *Origin* | *Type (Producer)* | *MFI parameters* | *MFI value* |
|---|---|---|---|---|
| PET | Petroleum-based | Neopet 80 (Neogroup) | 260°C / 1.2 kg | 21 g / 10 min |
| PBT | Petroleum-based | Pocan B1305 (Lanxess) | 250°C / 2.16 kg | 47 $cm^3$ / 10 min |
| PLA | Bio-based | Ingeo 3100HP (Natureworks) | 210°C / 2.16 kg | 24 g / 10 min |
| PBS | Bio-based | BioPBS FZ91PM (PTT MCC Biochem) | 190°C / 2.16 kg | 6 g / 10 min |

## II. Materials and Methods

### 1. Materials

The type and main properties of the two petroleum-based and two bio-based polyesters tested are presented in **Table 1**.

For reprocessing the materials Labtech 26-44 (Labtech Engineering, Thailand) twin screw extruder with a screw diameter of 26 mm and an L/D ratio of 48 was used. The main parameters of extrusion processing are summarized in **Table 2**. This step was repeated twice for the reprocessed samples.

***Table 2.*** *Processing parameters*

| *Name* | *Drying* | *Temperature zones* | *Screw speed* |
|---|---|---|---|
| PET | 160 °C / 4 h | 270 - 280 °C | 34 rpm |
| PBT | 120 °C / 4 h | 250 - 260 °C | 65 rpm |
| PLA | 90 °C / 5 h | 195 - 205 °C | 52 rpm |
| PBS | 80 °C / 5 h | 160 - 170 °C | 85 rpm |

### 2. Methods

Intrinsic viscosity (IV) measurements were done by RPV-1 (PSL Rheotek, USA) automatic solution viscometer according to ASTM D4603 standard. The IV values were measured at 30 °C in a 60/40 weight mixture of phenol/tetrachloroethane solvent with a concentration of 0.5 g/dl.

Crystallization characteristics were investigated using a non-isothermal DSC program using a DSC131 EVO (Setaram, France) device. The measurements were performed in nitrogen atmosphere with a flow rate of 50 ml/min. Samples were heated from room temperature to melting temperature ($T_m$)+30 °C at a rate of 20 °C/min, held for 4 min to erase thermal history, and then cooled back to 0 °C temperature at different rates (40, 20, 10, 5, and 2.5 °C/min). From the exothermic crystallization peak shown on the cooling curve the peak crystallization temperature was determined. Crystallinity ($X_c$) was calculated by Eq. (1) from the DSC heating scans at a heating rate of 20 °C/min, after specimens crystallized from a molten state to room temperature with different cooling rates. The area of each peak has been considered as the crystallization and melting enthalpy, $\Delta H_{cc}$ and $\Delta H_m$, respectively.

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \qquad (1)$$

The term $\Delta H_m^0$ is a reference value corresponding to the heat of melting of a 100% crystalline polymer, the value of which is 140 J/g for PET [13]; 145 J/g for PBT [14]; 195 J/g for PBS [15] and 93 J/g for PLA [16].

## III. Results and Discussion

The degradation of the polyesters during reprocessing was characterised by IV measurements. It was found that reprocessing had no remarkable effect on IV of PBS and PBT, while it led to a decrease in the viscosity of the rest of the types of polyesters used, especially PET as shown in **Table 3**.

***Table 3.*** *Effect of reprocessing on the intrinsic viscosity of PET, PBS, PBT and PLA*

| *Name* | *0x* | *1x* | *2x* |
|---|---|---|---|
| PET | 0.79 ± 0.01 | 0.69 ± 0.01 | 0.67 ± 0.01 |
| PBT | 1.49 ± 0.01 | 1.49 ± 0.01 | 1.48 ± 0.01 |
| PLA | 0.84 ± 0.01 | 0.83 ± 0.02 | 0.82 ± 0.01 |
| PBS | 1.26 ± 0.02 | 1.20 ± 0.01 | 1.17 ± 0.02 |

Non-isothermal crystallization was used to investigate how the crystallization of different polyesters changes during multiple processing. Typical DSC curves are shown in **Fig. 1**. It can be seen that as the cooling rate increases, the degree of undercooling increases and the crystallization peak shifts to a lower temperature.

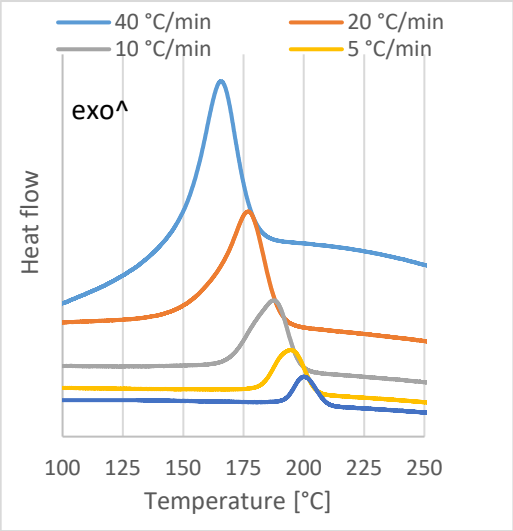
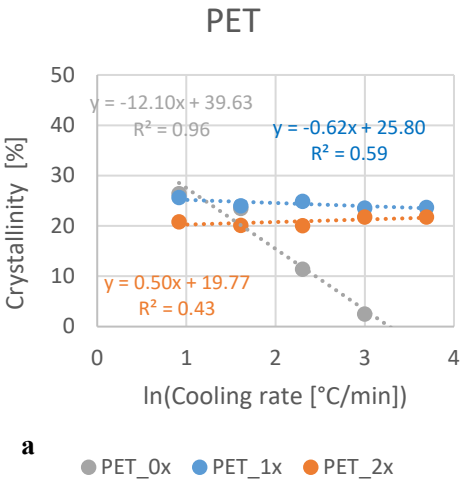


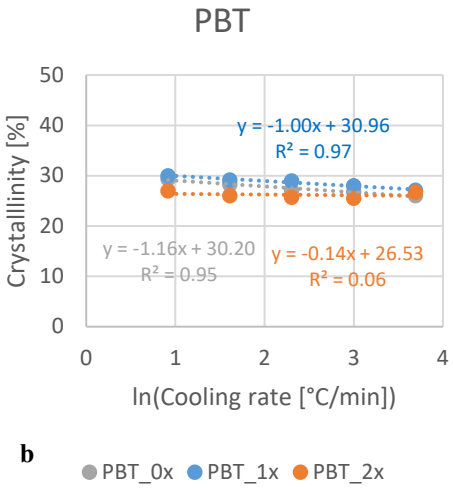

***Figure 1.*** *DSC cooling curves with crystallization exotherm (Once-processed PET sample)*

The evaluations of the measurements are summarised in **Fig. 2** and **3**. The change in crystallinity as a function of the natural logarithm of the cooling rate is shown in Figure 2. For all samples, a logarithmic relationship between the crystallinity formed and the cooling rate is observed. It can be seen that the cooling rate has a marginal effect on crystallinity in PBS and PBT polymers. For the original PET, as well as for the original and recycled PLA materials, a significant change in crystallinity is observed for different cooling rates: faster cooling reduces the proportion of crystalline phase. The resulting crystallinity is generally in the range of 20-30%, except for original PET, where crystallinity is lower at high cooling rates; for once and twice-processed PLA, where the crystallinity is higher than this range at low cooling rates and for all PLA material lower at high cooling rates.

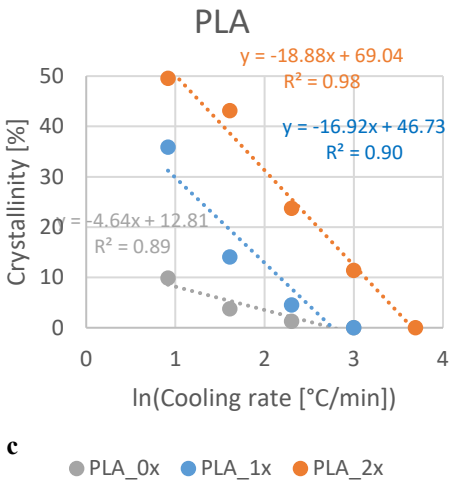
In the case of PLA, the crystallinity increases with the number of processing steps as expected because a decrease in molecular weight results in less restricted chain mobility [17]. However, in the case of PET the reprocessed sample has lower crystallinity than the once-processed sample in the whole cooling rate range. This can be explained by the fact that in PET, the smaller the molecular weight of the fraction, the shorter the chain, which makes it more difficult to fold the chains, the activation energy increases and therefore the crystallization rate is lower [18].




**a**




**b**




**c**

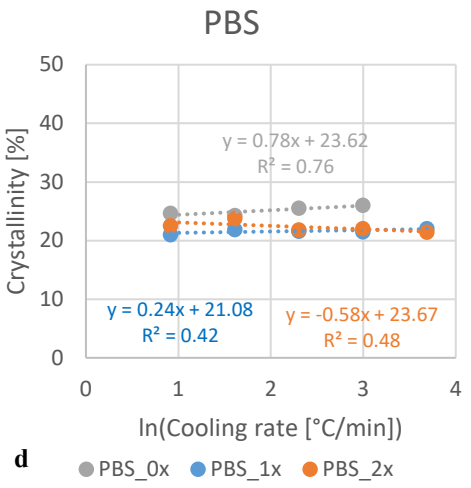
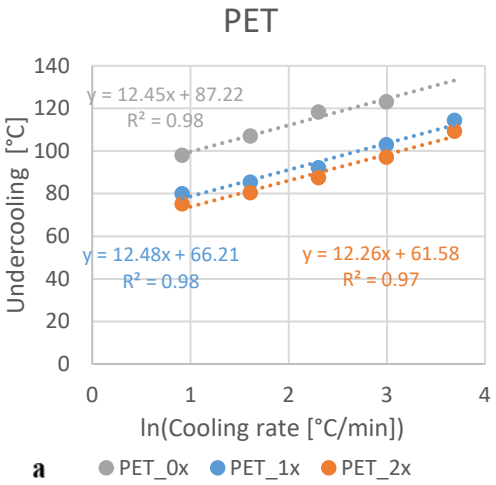
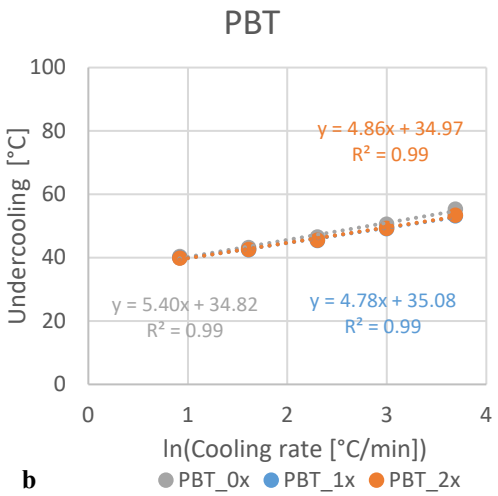
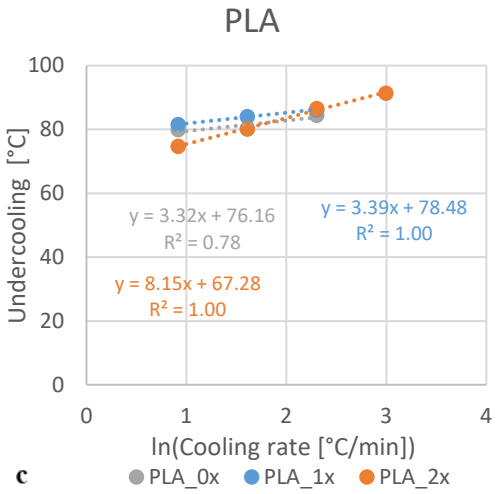



**Figure 2.** Effect of cooling rate on the crystallinity (a: PET; b: PBT; c: PLA; d: PBS; 0x: original material; 1x: once-processed materials; 2x: twice-processed (reprocessed) materials).

Non-isothermal crystallization data can be analyzed in terms of the degree of undercooling ($\Delta T_c$) defined as the temperature difference between the equilibrium melting temperature ($T_{m0}$) and the peak temperature of crystallization ($T_{c,p}$) in the cooling scan [19]. The equilibrium melting temperatures used for calculation of the level of undercooling were: 280°C for PET [19], 245°C for PBT [20], 130°C for PBS [21] and 184°C for PLA [22]. It can be established that the degree of undercooling is in each case linearly related to the natural logarithm of the cooling rate (**Fig. 3**). It can be observed that for PET and PBS the original material crystallizes at significantly higher level of undercooling than the once and twice reprocessed variants, while no such big differences are seen for PBT and PLA.



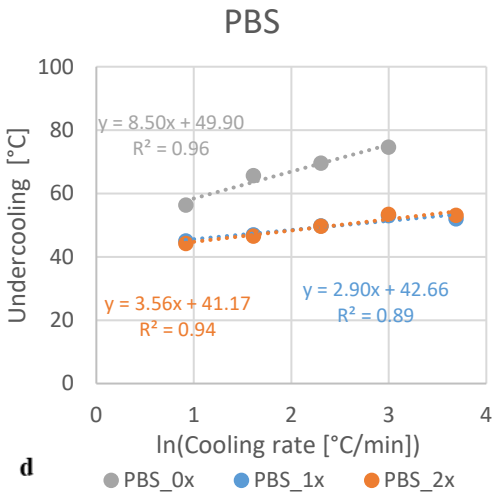




**Figure 3.** Effect of cooling rate on the degree of undercooling (a: PET; b: PBT; c: PLA; d: PBS; 0x: original material; 1x: once-processed materials; 2x: twice-processed (reprocessed) materials)

Based on Nadkarni et al. [23] the ΔTc with cooling rate can be fitted to a linear equation, however in the polyesters tested in our case these functions show logarithmic trends. Based on the function parameters on **Fig. 2** and **3** we defined the $\Delta T_{c,1}$ as the degree of undercooling required in the 1 °C/min cooling rate which is related to the thermodynamic driving force for nucleation, and ΔXm,1 indicating crystallinity at a cooling rate of 1 °C/min. **Fig. 4** shows the change of $\Delta T_{c,1}$ and $\Delta X_{m,1}$ after the processing steps in the case of the different polyester materials. It can be observed that reprocessing typically reduces the value of $\Delta T_{c,1}$, but the value of $\Delta X_{m,1}$ can vary in several ways during recycling, depending on the type of polyester.

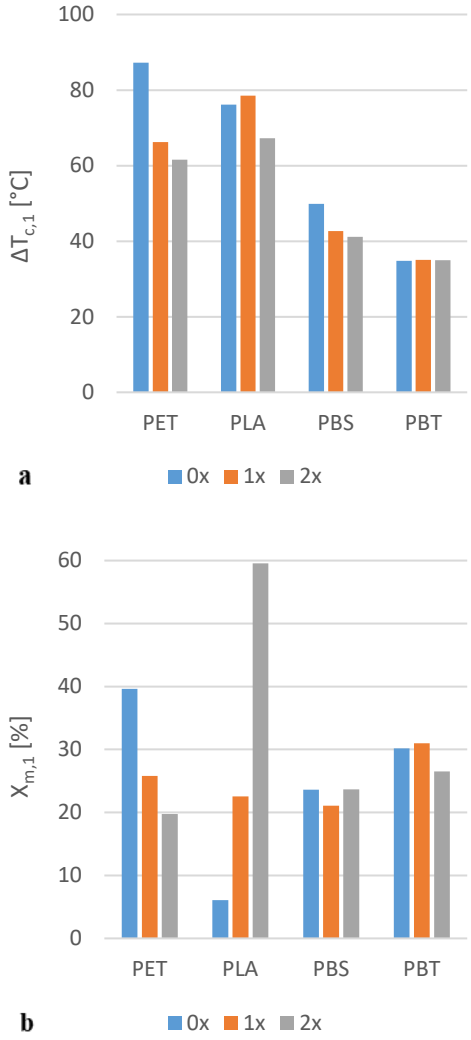



**Figure 4**. The change of the degree of undercooling (a) and the crystallinity (b) after the processing steps at a cooling rate of 1 °C/min; 0x: original material; 1x: once-processed materials; 2x: twice-processed (reprocessed) materials)

## IV. Conclusions

Experiments were carried out to investigate the crystallization of different types of bio-based and petroleum-based polyesters at different cooling rates. Based on the measurement results the degree of undercooling and the crystalline fraction formed were determinate and compared between different polyester types and processing steps.

Our experimental results reveal that the both overcooling and crystallinity are logarithmically related to the cooling rate. By extrapolating the fitted functions, we determined the $\Delta T_{c,1}$ and $\Delta X_{m,1}$ value corresponding to a cooling rate of 1 °C/min. $\Delta T_{c,1}$ is related to the thermodynamic driving force for nucleation and its value depends mainly on the type of polyester: the highest for PET and the lowest for PBT. $\Delta X_{m,1}$ is primarily influenced by the crystal growth rate, which is connected to the that mobility or diffusion of molecular chains. For PET and PLA. for which reprocessing has caused significant degradation, this value varies greatly during the recycling steps: While in the case of PET, degradation during reprocessing reduces the crystallinity formed, PLA, on the contrary, increases the crystalline fraction. For PBS and PBT, no significant change in crystallinity is observed at low cooling rates.

### AUTHOR CONTRIBUTIONS

**Z. Taha Taha**: Experiments.

**A. Ádámné Major**: Supervision, Review and editing.

**F. Ronkay**: Conceptualization, Analysis of the results.

### Disclosure Statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## REFERENCES


[1] J. D. Reehard, Understanding Solids, the Science of Materials, Wiley Sons ltd, England, 2004.

[2] R. M. Wang, S. R. Zheng,Y. P. Zheng, Polymer matrix composites and technology, Woodhead Publishing and Science Press, 2011. https://doi.org/10.1533/9780857092229

[3] D. B. Harris, Engineering composite materials, The Institute of Materials, London, 1999. https://doi.org/10.1007/978-1-84882-831-5

[4] D. L. Chung, Composite Materials -Science and Applications, Engineering Materials and Processes, London, 2010. https://doi.org/10.1007/978-1- 84882-831-5

[5] W. D. Callister, Materials science and engineering, John Wiley & Sons, Inc, USA, 2006, https://doi.org/10.1007/BF01184995

[6] J. Scheirs, T. E. Long, Modern polyesters chemistry and technology of polyesters and copolyesters, Wiley series in Polymer Science, 2003.

[7] Q. Zhang, M. Song, Y. Xu, W. Wang, Z. Wang, L. Zhang, Bio-based polyesters: Recent progress and future prospects, Progress in Polymer Science 120 (2021) 101430. https://doi.org/10.1016/j.progpolymsci.2021.101430

[8] P. B. Yang, M. G. Davidson, K. J. Edler, S. Brown, Synthesis, Properties, and Applications of Bio-Based Cyclic Aliphatic Polyesters, Biomacromolecules, 2021. https://doi.org/10.1021/acs.biomac.1c00638

[9] M. Rabnawaz, I. Wyman, R. Auras, S. Cheng, A roadmap towards green packaging: current status and future outlook for polyesters in the packaging industry, Green Chemistry, 2017. https://doi.org/10.1039/x0xx00000x

[10] A. Larrañaga, E. Lizundia,, A review on the thermomechanical properties and biodegradation behaviour of polyesters, European Polymer Journal, Volume 121, December 2019, 109-296. https://doi.org/10.1016/j.eurpolymj.2019.109296

[11] R. Franz, F. Welle, Recycling of Post-Consumer Packaging Materials into New Food Packaging Applications—Critical Review of the European Approach and Future Perspectives, Sustainability 2022, 14, 824. https://doi.org/10.3390/su14020824

[12] V. Shanmugam, O. Das, R. E. Neisiany, K. Babu, S. Singh, M. S. Hedenqvist, F. Berto, S. Ramakrishna, Polymer Recycling in Additive Manufacturing: An Opportunity for the Circular Economy, Materials Circular Economy, 2020. https://doi.org/10.1007/s42824-020-00012-0

[13] B. Molnar, F. Ronkay, Effect of solid-state polycondensation on crystalline structure and mechanical properties of recycled polyethylene-terephthalate, Polymer Bulletin, 76, 2387–2398, 2019. https://doi.org/10.1007/s00289-018-2504-x

[14] D. Heidrich, M. Gehde, The 3-Phase Structure of Polyesters (PBT, PET) after Isothermal and Non-Isothermal Crystallization, Polymers, 14(4), 793, 2022. https://doi.org/10.3390/polym14040793

[15] M. C. Righetti, M. L. di Lorenzo, P. Cinelli, M. Gazzano, Temperature dependence of the rigid amorphous fraction of poly (butylene succinate). RSC Adv. 11, 25731–25737, 2021. https://doi.org/10.1039/D1RA03775G

[16] O. Mysiukiewicz, M. Barczewski, Crystallization of polylactide-based green composites filled with oil-rich waste fillers, Journal of Polymer Research 27: 374, 2020. https://doi.org/10.1007/s10965-020-02337-5

[17] S. Saeidlou, M. A uneault, C. B. Li H.,Park, Poly(lactic acid) crystallization, Progress in Polymer Science, Volume 37, Issue 12, Pa 1657-1677,2012. https://doi.org/10.1016/j.progpolymsci.2012.07.005

[18] P. C. Zilanova, S. M. Ribas, G. M. Guzman, Isothermal crystallization of poly(ethylene-terephthalate) of low molecular weight by differential scanning calorimetry: 1. Crystallization kinetics, Polymer, volume 26, Issue3, Pages 423-428, 1985. https://doi.org/10.1016/0032-3861(85)90205-8

[19] M. L. Di Lorenzo, C. Silvestre, Non-isothermal crystallization of polymers, Progress in Polymer Science, 1999, Vol. 24, No. 6, pp. 917–950. https://doi.org/10.1016/S0079-6700(99)00019-2

[20] A. Mehta, U. Gaur, B. Wunderlich, Equilibrium melting parameters of poly (ethylene terephthalate), Journal of Polymer Science: Polymer Physics Edition, Vol. 16, 289-296,1978. https://doi.org/10.1002/pol.1978.180160209

[21] D. Heidrich, M. Gehde, Calorimetric analysis of the crystallization of PBT considering the dynamic cooling condition of real processing, Polymer Testing, Volume 85, May 2020, 106459. https://doi.org/10.1016/j.polymertesting.2020.106459

[22] R. Androsch, K. Jariyavidyanont, A. Janke, C. Schick, Poly (butylene succinate): Low-temperature nucleation and crystallization, complex morphology and absence of lamellar thickening, Polymer, Volume 285, 126311, 2023. https://doi.org/10.1016/j.polymer.2023.126311

[23] V. M. Nadkarni, N. N. Bulakh, J. P. Jog, Assessing polymer crystallizability from nonisothermal crystallization behavior, Advances in Polymer Technology, Vol. 12, No. 1, 73-79, 1993. https://doi.org/10.1002/adv.1993.060120107