RESEARCH ARTICLE

Applied Polymer SCIENCE **WILEY**

Non-isothermal crystallization kinetic of recycled PET and its blends with PBT modified with epoxy-based multifunctional chain extender

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Abstract

A fundamental understanding of crystallization behavior is essential for the processing of both virgin and recycled polymers. This research delves into the crystallization characteristics and non-isothermal crystallization kinetics of recycled polyethylene terephthalate (rPET) and its blends with poly butylene terephthalate (PBT), which have been modified using epoxy-based multifunctional chain extenders (CE). The preparation of rPET/PBT blends involved a twin-screw extruder, with varying weight ratios and different CE concentrations. Differential scanning calorimetry was employed to perform crystallization analysis on the samples. The results underscore the profound impact of blend composition on the thermal characteristics of the system, with CE exerting only a marginal influence. The glass transition temperatures (T_g) of the two polymers were measured at 49 and 79°C. During blending, the T_g values demonstrated variations relative to the proportions but did not adhere to the Fox equation. Furthermore, PBT was found to enhance the crystallization tendencies of rPET, resulting in an increase in relative crystallinity from 11% to 36%. Notably, the crystallization rate of PBT at 0.40 min^{-1} exceeded that of rPET at 0.36 min^{-1}. PBT minimally affected the crystallization rate constant of rPET-dominant blends, while rPET significantly reduced the crystallization rate in PBT-dominant blends.

KEYWORDS
chemical modification, non-isothermal crystallization kinetic, recycling, thermal properties

1 | INTRODUCTION

Polyethylene terephthalate (PET) is a commonly used fossil-based polyester with a low melt viscosity and slow crystallization kinetics and is one of the most commonly used plastics.[1,2] Because of its mechanical, thermal, optical, and barrier properties, PET is mainly used in the packaging industry as plastic bottle for water and soft drinks. Because of the large volume and purity of the material stream, a market for mechanical recycling of

PET has developed, where it is usually reused in the packaging industry, as films or bottles for detergents, as well as in the textile industry.[1] Currently, recycled PET (rPET) is here mainly used for short-life applications,[3] whereas an increase in product life cycle of components made from rPET can have positive effect on the CO_2 footprint and less environmental impact. Therefore, the use of the rPET as foams for insulation and lightweight construction applications is promising. However, the foaming process imposes certain requirements on the polymer in terms of viscosity,[4,5] melt strength,[6,7] and crystallization behavior.[8,9]

The crystallization behavior of certain types of PET was studied by Fann et al.[10] They showed that the crystallization rate of PET at 200°C is significantly reduced from 1.16 to 0.02 and 0.08 min^{-1} for rPET and extruded PET (ePET), respectively. This reduction becomes even more pronounced when the isothermal crystallization temperature is lowered to 190 and 180°C, respectively. Furthermore, it was shown that blending rPET with ePET allows to adjust the crystallization rate in the rPET-dominant blends (rPET80ePET20). In contrast, there was no significant change in the crystallization rate in the ePET-dominant blends (rPET20ePET80).[10] Another study by Papageorgiou et al.[11] investigated the effects of branching and crosslinking on the crystallization kinetics of PET. For this purpose, they synthesized several PETs with varying proportions of branched repeating units. They found that at a small amount of branching, less than 0.25 wt.%, effected neither the crystallization rate nor the induction time. They attributed these results to the increase in viscosity of the melt, which promotes the formation of crystallization nuclei. Above 0.25 wt.% branched content in the backbone, a significant reduction of the crystallization rate constant from 0.084 to 0.009 min^{-1} was observed. Additionally, the Avrami parameter decreased from 2.5 to 2.0 when the branching of the polymer chain was increased up to 0.875 wt.%. This decrease could be due to the lower chain mobility caused by branching.[11] Awaja et al.[12] investigated the effects of branching induced by chemical modification with pyromellitic dianhydride on the crystallization behavior of rPET. It was found that with the addition of 0.25 wt.% chain extender (CE), the melting temperature decreases by 3 K, while the crystallization temperature increases by 2 K, and thus decreases the total crystallization.[12] The induced branching acts as defect in the chain morphology, which also decreases the prepatterning of the crystals.[8,11–13] Nofar et al.[14] studied the crystallization behavior of rPET modified with 0.4 and 0.8 wt.% multifunctional epoxy resin CE. They observed a slight increase in the crystallization rate and crystallinity of rPET when it was modified with 0.4 wt.% CE. Further

increase in CE content leads to a significant decrease in the crystallization rate of the modified rPET. They explained these results by the increased nucleation rate, as the branches could act as nucleating agents. Above a certain amount of CE, the decreased chain mobility overcomes the nucleation effect, so the crystallization rate decreases.[14] A similar reduction in the crystallization rate of rPET after modification with 1.0 wt.% CE was published by Candal et al.[15] In our previous work with poly butylene terephthalate (PBT)[6,16,17] and polylactic acid,[8,18] we have also demonstrated comparable effects on the crystallization behavior of linear thermoplastics.

In addition to chemical modification, mixing with suitable partners also alters the thermal properties of the polymer system. In terms of thermodynamics, polymer blends are divided into miscible, immiscible, or partially miscible systems. In miscible blends, where both components are crystallizable, crystallization from a homogeneous melt can lead to the formation of cocrystals.[19] In addition to the requirement of miscibility in the melt, similar molecular structures and crystal lattice structures as well as similar crystallization rates are also required.[20] Instead of cocrystallization, crystalline/crystalline-mixed systems usually crystallize simultaneously with the formation of finely dispersed crystals.[21] Dangseeyun et al.[22] investigated the crystallization behavior of crystalline/crystalline poly trimethylene terephthalate (PTT)/PBT blends. They found a melting point depression, with both polymers crystallizing simultaneously at the so-called pseudo-eutectic crystallization point. The crystallization temperature of PBT at a cooling rate of 10 K/min was lowered from 192 to 174°C by increasing the PTT content up to 60 wt.%. On the other hand, crystallization temperature of PTT slightly increased from 180 to 182°C when a smaller amount of PBT up to 30 wt.% was added.[22] This phenomenon can be explained by the fact that the polymer chains are entangled with each other, and therefore, phase separation occurred first.[20,22] These entanglements hinder chain mobility and thus crystal formation and growth, as also shown by Stocco et al.[23] The thermal behavior of PTT/PET blends was studied by Liang et al.[24] who obtained similar results. Both studies showed a change in T_g as a function of blend ratio according to the Fox equation. According to this model, the relative crystallinity of the polymer with the higher melting point increases slightly upon mixing. This can be correlated with the shift in T_g to lower temperatures where decrease in T_g is associated with increased chain mobility near the melting range and can improve crystallization properties. In turn, the readiness to crystallize decreases with an increase in T_g.[22,24] Mishra and Deopura[25] studied the crystallization kinetics of PET and PBT blends by adding a small amount of PBT to a PET matrix. They found a

decrease in melting temperature up to 4 wt.% PBT. In addition, the small amount of PBT was found to increase the chain mobility of PET, thereby increasing the crystallization rate above 200°C. In non-isothermal crystallization, a significant decrease in crystallization rate was observed for blends containing more than 6 wt.% PBT.[25] In our previous work, we investigated the thermal behavior of rPET/PBT blends over a wide range of blend variations. It was found that with increasing rPET content, the overall crystallization decreased, which was attributed to the increase in T_g. In addition, it was found that the crystallization behavior of rPET could be improved by mixing with PBT, while the crystallization of PBT was not affected by the rPET content. The change in cocrystallization increased when the cooling rate was decreased. At a slow cooling rate, cocrystallizations with less packed crystals and less perfect structures could be formed.[14] The noni-sothermal crystallization behavior of PET/PBT mixtures was studied by Wang et al.[26] for the 30/70 ratio. They found that the crystallization halflife of the blend increases at a cooling rate of 20 K/min or slower compared with pure PBT. On the other hand, the crystallization rate increases when the mixture is cooled at 40 K/min. They explained this phenomenon by an increase in the degree of supercooling. This would also increase the movement of the polymer chains and thus the crystallization rate.[26]

The aim of this paper is the investigation of the crystallization behavior of rPET and its blends with PBT, both in their unmodified and CE-modified states, with a particular focus on understanding how various factors, such as composition, chemical modification, and blending, influence their crystallization kinetics and thermal properties.

2 | EXPERIMENTAL

2.1 | Materials and sample preparation

PBT Pocan B1300 was purchased from Lanxess AG (Cologne, Germany). PBT has a T_g of 48°C, a melting peak ranging from 216 to 227°C at a molecular weight of 66,000 g/mol. PET recycled from soft drink bottles was provided by Arcelik A.S. (Istanbul, Turkey). This grade has a M_w of 44,000 g/mol, a T_g of 77°C, and is semicrystalline as received. The chain modifier used was a multifunctional epoxy-based Joncryl ADR 4468, referred to as Joncryl or CE, from BASF (Ludwigshafen, Germany). This modifier has a molecular weight of 7250 g/mol and an epoxy equivalent weight of 310 g/mol. The glass transition temperature is at 59°C.
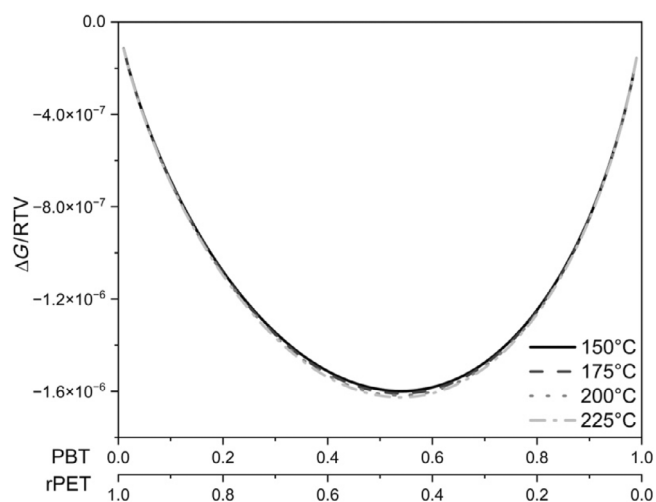

FIGURE 1 Free energy of mixing of recycled polyethylene terephthalate (rPET) and poly butylene terephthalate (PBT).

From literature, blends of PET and PBT are often reported as miscible blend.[27,28] However the miscibility is strongly affected by the molecular weight and thermodynamic interactions. To predict the miscibility behavior of the blend, we used the well-known Flory and Huggins Equation (1):

$$\frac{\Delta G}{RTV} = \left(\frac{\phi_1}{V_{1m}} \times \ln\phi_1 + \frac{\phi_2}{V_{2m}} \times \ln\phi_2 + \frac{\phi_1\phi_2}{RT}(\delta_1 - \delta_2) \right), \quad (1)$$

where ΔG represents the free energy of mixing, R the universal gas constant, T the temperature, V the volume element, ϕ the volume fraction, V_m the molar mass, and δ the solubility parameter, respectively.

The miscibility depends on the blend ratio, the temperature, and the molecular weight of each component. These factors can be described by the so-called solubility parameter.[29] Using a difference in the solubility parameter of $0.05 \, J^{0.5} cm^{-1.5}$[30] a term representing the free Gibbs energy for mixing can be calculated. The relation between the blend ratio and the free Gibbs enthalpy of mixing is displayed in Figure 1. The equation shows that the two polymers used should be miscible over the entire mixing range.

2.2 | Processing

Compounding of rPET, PBT, and CEs is carried out using a laboratory scale twin screw extruder (Gülnar Makina Ltd., Turkey) with 16 mm screw diameter and L/D ratio of 30. The rotation speed for processing was set at 100 rpm and the temperature profile was set at

50-220-260-260-260-260°C (from hopper to the die). All formulations were weighed, mixed, and dried at least 16 h under vacuum at 50°C before processing and processed immediately after removal from the vacuum oven to minimize moisture absorption before processing. The extrudate was cooled in a water bath, granulated and dried in a vacuum oven. Possible reactions between polyesters and the CE used have already been listed in a previous publication.[31] Please note that depending on the concentration of the CE, branching and cross-linking may occur in addition to chain elongation, which may have different effects on the thermal behavior.[11–14]

2.3 | Thermal behavior of rPET/PBT blends

The crystallization behavior of unmodified rPET/PBT blends and modified rPET/PBT blends was studied using a differential scanning calorimeter (DSC 1) from Mettler Toledo (Columbus, OH, USA). All experiments were performed under a nitrogen atmosphere. To ensure comparability of the measurement signals obtained, 5–10 mg samples were weighed in each case. The dried samples were heated from 25 to 280°C at a heating rate of 10 K/min, held for 2 min, and cooled to 25°C at 10 K/min. T_g was determined from the second heating curve, which was processed similarly to the first.

Non-isothermal crystallization studies were performed by heating samples in a nitrogen atmosphere. The temperature range was set from 25 to 280°C, with a heating rate of 10 K/min and cooling rates of 2.5, 5, 10, and 20 K/min, respectively. To ensure reproducibility of results, all measurements were performed three times. The degree of crystallinity was determined by comparing the experimental heat of fusion with the theoretical value of 100% crystalline PBT ($\Delta H_{0m} = 140$ J/g)[33] and rPET ($\Delta H_{0m} = 140$ J/g).[33] The evaluation was performed using STARe software (Mettler-Toledo AG, Schwerzenbach, Switzerland) following the approach of Saidi et al[34] with a straight baseline. Non-isothermal crystallization kinetics were analyzed based on the Jeziorny-modified Avrami theory[35] using a Python script.

Thermogravimetric analysis was conducted using a TG 209 F1 Libra instrument from Netzsch (Selb, Germany). About 10 mg of the sample was carefully weighed and placed in an 85 μL Al_2O_3 crucible. The analysis spanned the temperature range of 25–600°C at a heating rate of 10 K/min, employing a nitrogen or synthetic air at a flow rate of 50 mL/min. Data processing was carried out using Proteus analysis version 8.0.

2.4 | Polarized optical microscopy

The spherulitic morphology of unmodified rPET/PBT blends was observed using the AXIOSkOP 2 optical microscope MAT (Carl Zeiss, Oberkochen, Germany). The extruded samples were sandwiched between two slides and melted in an oven at 270°C. They were then held at this temperature for 1 min to ensure complete melting and then cooled down to 240°C at a cooling rate of 20 K/min. The images were collected between 240°C and the respective final crystallization temperature at a cooling rate of 1 K/min.

3 | RESULTS AND DISCUSSION

3.1 | Thermal stability of rPET-PBT blends

The thermal stability of the unmodified rPET-PBT blends under nitrogen (N_2) and oxygen (O_2) atmospheres is shown in Figure 2. Depending on the blend composition, the decomposition temperature decreases from 403°C for pure rPET to 376°C for pure PBT under N_2 conditions (Figure 2a).

In contrast, rPET75PBT25 and rPET50PBT50 show significant changes in the decomposition temperature of the pure polymers. rPET25PBT75 shows no significant difference in decomposition temperature compared with PBT. In addition, the residual mass, which can be attributed to the aromatic components,[32] increases with a higher rPET content. This is since the repeat unit of rPET has a higher aromatic content. In an oxygen atmosphere (Figure 2b), decomposition takes place at lower temperatures for all the blend variations. The decomposition temperature of rPET decreases from 403 to 334°C. The decomposition temperature of PBT also decreases by about 70 K to 309°C. In contrast to N_2, a two-stage decomposition takes place in O_2. The presence of O_2 also allows the aromatic components to be completely oxidized, leaving no residual mass.[32] Since the modification does not influence the $T_{D(95\%)}$, the results are only given in the Supporting information. Based on these results, analysis conditions have been selected to avoid degradation.

3.1.1 | Crystallization behavior of rPET-PBT blends

The first and second DSC heating curves of the unmodified blends are shown in Figure 3, the measured values are summarized in Table 1. The two polymers were found
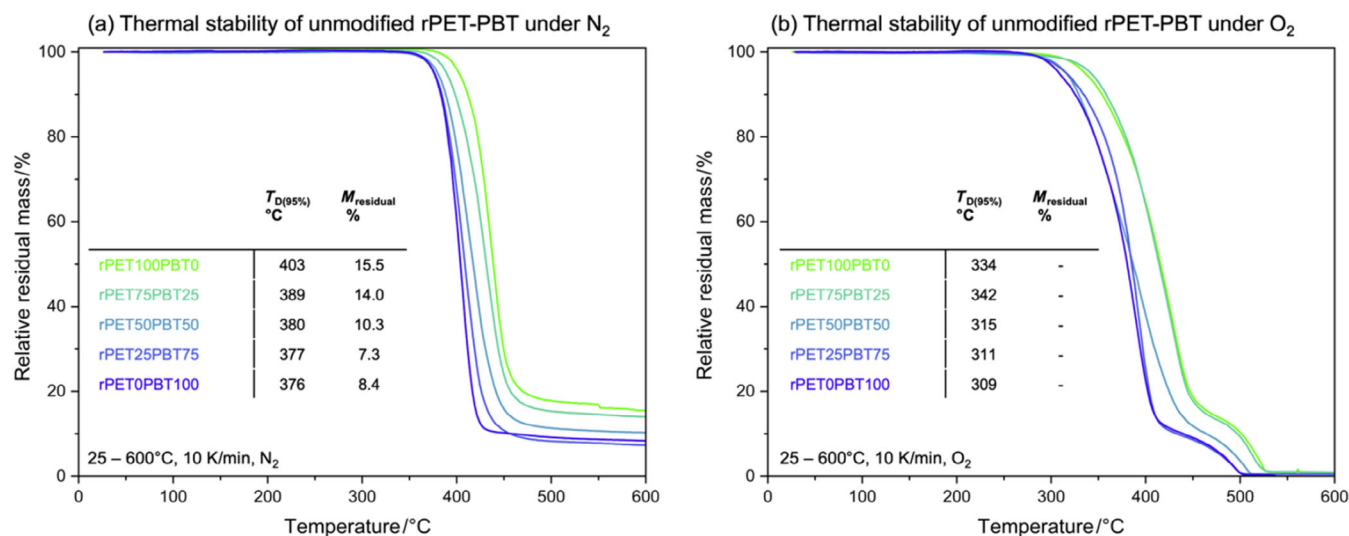
FIGURE 2 Thermal stability of the unmodified rPET-PBT blends with varied blend ratio under (a) N_2 and (b) O_2 atmosphere. PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate. [Color figure can be viewed at wileyonlinelibrary.com]
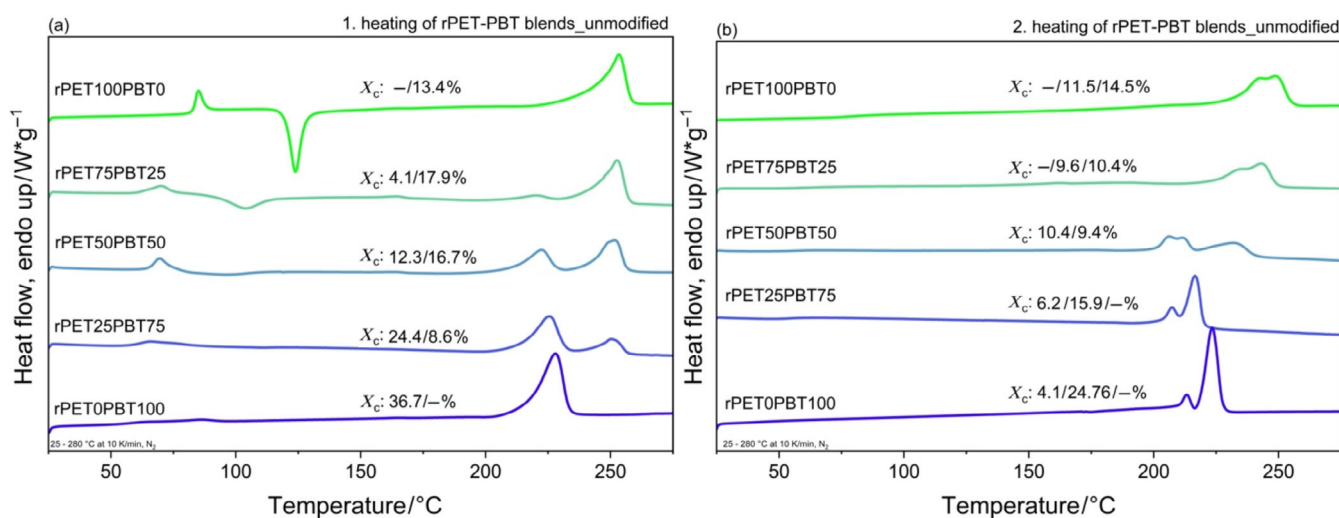

FIGURE 3 Thermogram of unmodified rPET-PBT blends (a) first heating curve and (b) second heating curves 25–280°C with 10 K/min, N_2. PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Values of T_g, T_{cc}, and T_m from the unmodified rPET/PBT.

	First heating			Second heating		
	T_{cc} (°C)	$T_{m,PBT}$ (°C)	$T_{m,rPET}$ (°C)	T_g (°C)	$T_{m,PBT}$ (°C)	$T_{m,rPET}$ (°C)
rPET100PBT0	124	-	253	79	-	242/249
rPET75PBT25	104	221	253	58	-	238/243
rPET50PBT50	99	222	252	56	206	232
rPET25PBT75	-	226	251	52	207/216	-
rPET0PBT100	-	227	-	49	212/216	-

Abbreviations: PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate.

to be miscible in the amorphous state, which was evident from a single T_g value (Figure 3b).[28,33] The T_g of pure and unmodified PBT and rPET was at 49 and 79°C, respectively. The resulting T_g of the polymer blend depends on the blend ratio. The T_g-shift of miscible polymer blends can be evaluated and described by the Fox Equation (2) and the Gordon-Taylor Equation (3) considering the polymer interaction parameter, in the case of PET and PBT, 0.995,[33] 1.01,[34] and 1.16[28] were determined.

$$\frac{1}{T_{g,blend}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}, \tag{2}$$

$$T_{g,blend} = \frac{w_1 T_{g,1} + k(1-w_1)T_{g,2}}{w_1 + k(1-w_1)}, \tag{3}$$

where w_i is the weight fraction of the component i, k is the interaction parameter between the two components and the indices 1 and 2 representing PBT and rPET, respectively.

The measured and calculated T_g of the blends is shown in Figure 4. For rPET25-PBT75, rPET50-PBT50 and rPET75-PBT25, a T_g of 52, 56, and 58°C, respectively, was determined.

The T_g of the blends with a higher rPET content is significantly lower than the values calculated using both equations. The difference between the measured and calculated T_g increases with increasing rPET content, while rPET25-PBT75 and rPET50-PBT50 show a small deviation of 3 and 6 K from the Gordon-Taylor equation. The difference to the calculated value for rPET75-PBT25 increases significantly to 22 K. One reason for this
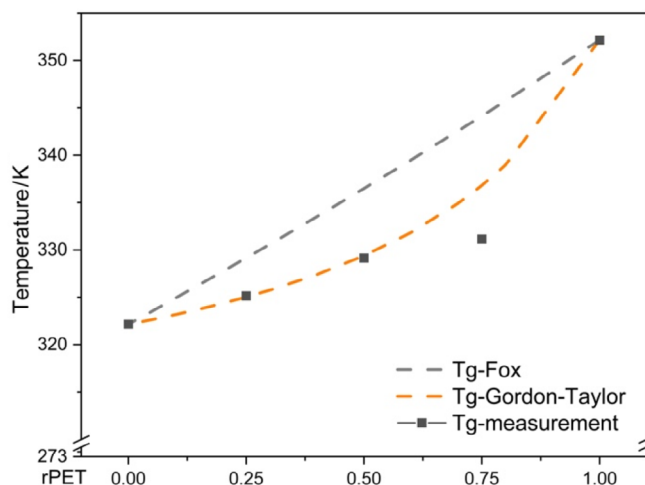
phenomenon could be a transesterification that occurs during processing of the two polymers, as it was shown previously.[35,36] In addition, rPET contains impurities such as PVC, which can act as a catalyst for degradation.[1] Therefore, the probability of the transesterification reaction increases with the proportion of rPET. The pattern of measured T_g is similar to the results published by Avramova et al.[33] for annealed PET/PBT mixtures. The closer the blend is to the 50:50 composition, the smaller the change in T_g for different blend compositions. The reported Gordon-Taylor parameter values of 3.14 and 3.02 through the annealed series of measurements by Avramona et al.[33] and Stein et al.[37] respectively, describes relatively accurately the T_g change given in Figure 4.

A significant decrease in the cold crystallization temperature can also indicate miscibility in the amorphous state.[22,38,39] As can be seen in Figure 3a, cold crystallization occurs during the initial heating of rPET. It is known from literature that PET has a slow crystallization rate,[10,23] which is due to its relatively rigid backbone.[40] The PET melt passing through the extruder is quenched in water and thus the polymer chain has less time to orientate and crystallize. The cold crystallization was only detected in unmodified rPET up to a blend containing up to 50% of PBT. The cold crystallization temperature of rPET decreased from 123 to 101°C and the cold crystallization reduced from 17% to 2% considering the rPET50PBT50 blend. The decrease in cold crystallization could be due to the shift of T_g from 79 to 58°C, resulting in higher chain mobility of PBT-rich blends.[22,39]

The results demonstrate that rPET and PBT are miscible in the amorphous state. On the other side, two separate melting peaks were observed (Figure 3a), which are attributed to an immiscibility of the crystalline phase. The main reasons for this separate crystallization stems from the difference in crystallization rate, chemical and crystal structure between PET and PBT.[21,41] Furthermore, from Figure 3a a melting point depression in the blend was observed. It is well known that the melting point of a polymer is affected not only by thermodynamic factors but also by morphological parameters such as the crystal thickness.[42] The melting temperature deflection increases with increasing volume fraction of rPET. Therefore, the greatest deflection of the melting temperature of PBT was found in rPET75-PBT25 at 220°C with correspond to a shift of 8 K.

Furthermore, a decrease in the total crystallinity of the PBT phase was found. Since both polymers show less or no cocrystallization at high cooling rates,[9] the possibility to generate a separated and ordered PBT phase diminishes, with increasing PET content. In our case, the relative crystallinity of PBT reduces from 37% to 16%, while PET shows the quite opposite behavior. The
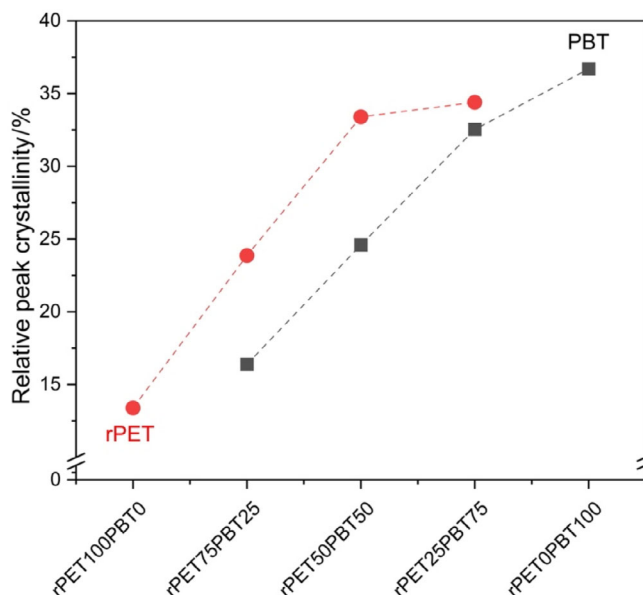

FIGURE 4 Calculated and determined T_g of rPET-PBT with varied ratios. PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate. [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 5 Variation of relative peak crystallinity of recycled polyethylene terephthalate (rPET) and poly butylene terephthalate (PBT) phase with their blend composition. [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 6 Thermogram of the unmodified rPET-PBT blends, first cooling curves. PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate. [Color figure can be viewed at wileyonlinelibrary.com]

relative crystallinity of the rPET-phase increases with PBT content, as shown in Figure 5. This corresponds to the reduction in T_g and the increased chain mobility due to the mixing.[22,39]

From the second heating curve of rPET50-PBT50 (Figure 3b), it can be seen that the melting point of both polymers become closer and interpenetrate each other. The melting points are in general lower compared with the one shown during the first heating (Figure 3a) which denotes that the crystals are less perfect. Since transesterification takes place at higher temperatures, the chemical structure of both polymers becomes more inhomogeneous and this phenomena leads to a reduced crystallization rate.[35,36] From the second heating curve (Figure 3b), it is clear that only the dominant phase crystallizes in both the rPET25-PBT75 and rPET75-PBT25 blends. This phenomenon has also been described by Stein et al.[37] in PET/PBT blends, and verified by WAXS, FTIR, and DSC.

Since both polymers are miscible in the melt state, the chain segments interpenetrate each other.[27,43] As discussed before, the polymers must separate before crystallization can take place. Therefore, a significant decrease of the crystallization temperature from 205°C for pure rPET to 178°C for rPET50PBT50 is detected (see Figure 6). For blend containing 50% rPET and 50% of PBT, the most pronounced melting point deflection was found. When the PBT content increases further, the crystallization temperature increases to 185 and 192°C for rPET25PBT75 and PBT, respectively. Furthermore,
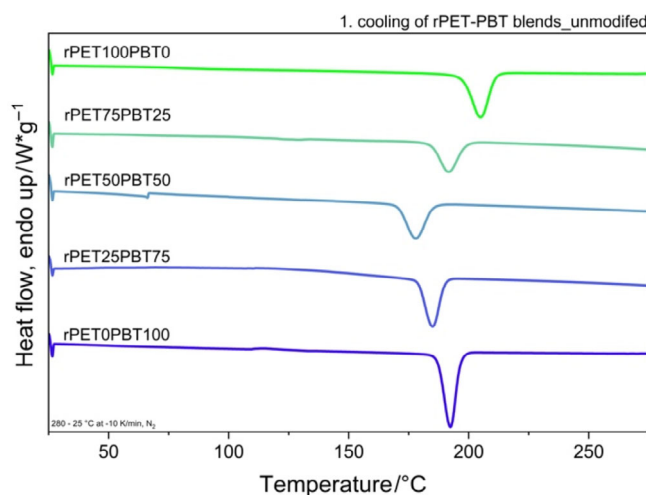
Figure 6 shows that both polymers crystallize simultaneously indicating a pseudo-eutectic crystallization behavior,[43] which results in finely dispersed crystals of both components (Figure 9). The polarized optical microscope (POM) measurement reveals that neither PBT nor rPET act as nucleating agent. The crystallization temperature deflection found in the DSC was proven by the POM measurements.

3.1.2 | Crystallization behavior of CE-modified rPET-PBT blends

The effects of chain modification on the first heating of rPET50-PBT50 and rPET75-PBT25 are shown in Figure 7. Since the modification does not influence the T_g the focus will be set on the crystallization behavior. Increasing the concentration of CE lowers the peak temperature of rPET from 253°C for the unmodified rPET50-PBT50 blend to 248°C for the blend with 1.0 wt.% CE. Similar behavior was also observed for rPET75-PBT25 and rPET25-PBT75. In contrast, the melting peak temperature of PBT appears to be constant except for the modification with 1.0 wt.% CE. Furthermore, a broadening of the initial melting temperature of rPET was observed. Because of long chain branching (Scheme shown in[31]), the mobility of the chain segments and the possibility of self-assembly reduces, resulting in less perfect crystals.[6] The total crystallinity of rPET50-PBT50 increases from 29.5% to 33.5% by the addition of 0.50 wt.% CE. The total crystallinity of rPET-dominant blends increases from 22.0% to 24.6% upon addition of 0.25 wt.% CE. In both cases, the
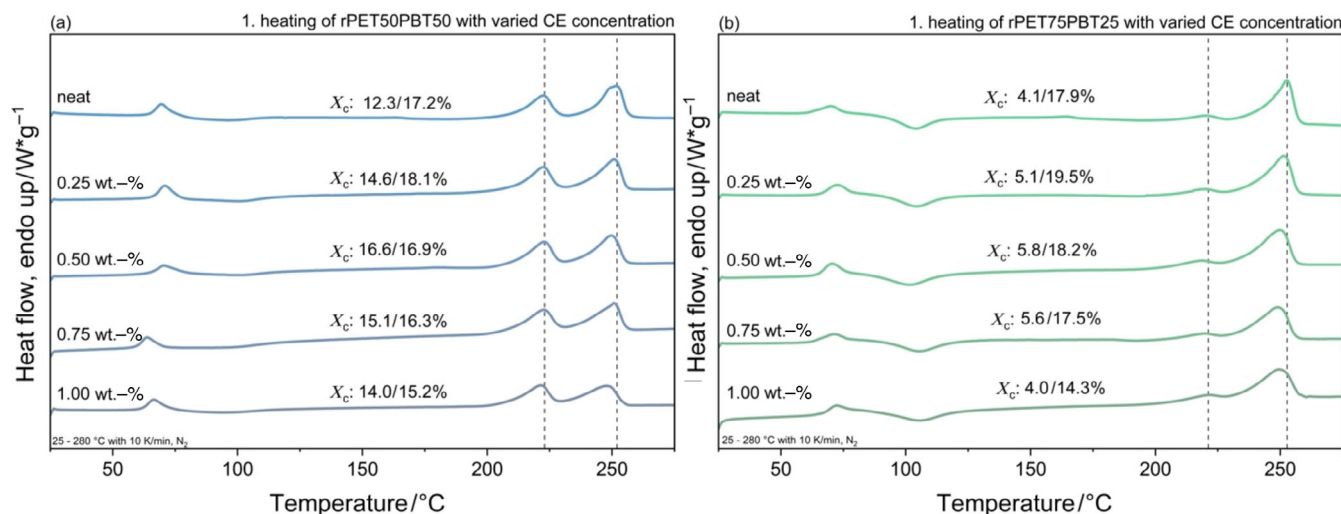
FIGURE 7 1. Heating curves of (a) rPET50-PBT50 and (b) rPET75-PBT25 with varied concentration chain extender (CE). PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate. [Color figure can be viewed at wileyonlinelibrary.com]

increase in total crystallinity was associated with the crystallinity of the PBT phase. It is assumed that the branched chains act as nucleation sites,[8,11] so that the crystallization of the PBT phase is promoted. If the content of CE is further increased, the increasing viscosity hinders crystal growth,[11] resulting in lower overall crystallinity. In order to gain a deeper insight into the influence of blend composition on the crystallization behavior, the non-isothermal crystallization kinetics is diccused below.

3.1.3 | Non-isothermal crystallization kinetics

The non-isothermal crystallization kinetics of unmodified and modified blend systems was determined using the Avrami equation modified according to Jeziorny.[13,22,24,44] For this purpose, the thermograms of the blends at different cooling rates were evaluated using a Python script. The procedure of the script is listed in the Supporting information. The relative crystallization of the unmodified blends at a cooling rate of -2.5 K/min is shown in Figure 8.

It can be seen from Figure 8 that the PBT rich blend shows a faster increase in relative crystallinity at the initial stage of the crystallization. This initial stage represents the nucleation and shows that PBT is more favorable than that of rPET. This can be inferred from the time required to reach 5% relative crystallinity. It is also obvious that neither PBT nor rPET nucleate each other in the blended systemes, as both pure polymers exhibit faster initial crystallization behavior. This can also be deduced from the images taken with a polarizing microscope (see Figure 9). As can be seen in the images,
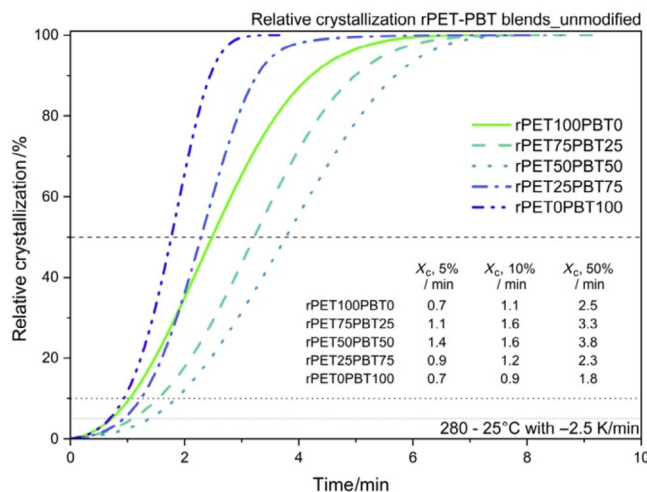

FIGURE 8 Relative crystallization of the unmodified rPET-PBT blends at cooling rate of -2.5 K/min. PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate. [Color figure can be viewed at wileyonlinelibrary.com]

crystallization begins simultaneously, resulting in the sputtered crystal image described in the literature.[20,27,43] It is noticeable that at a cooling rate of 1 K/min, the initial crystallization temperature does not correlate according to the blend ratio of the two pure materials. For rPET25-PBT75, a crystallization range very similar to that of pure PBT was found, which, as mentioned above, is related with the little to nonexistent crystallization of rPET phase. It is also noticeable that the crystallization area of the rPET-dominant blend approaches that of PBT. This behavior is attributed to the necessary phase separation and the eutectic crystallization point described in the literature.[21,24,43]
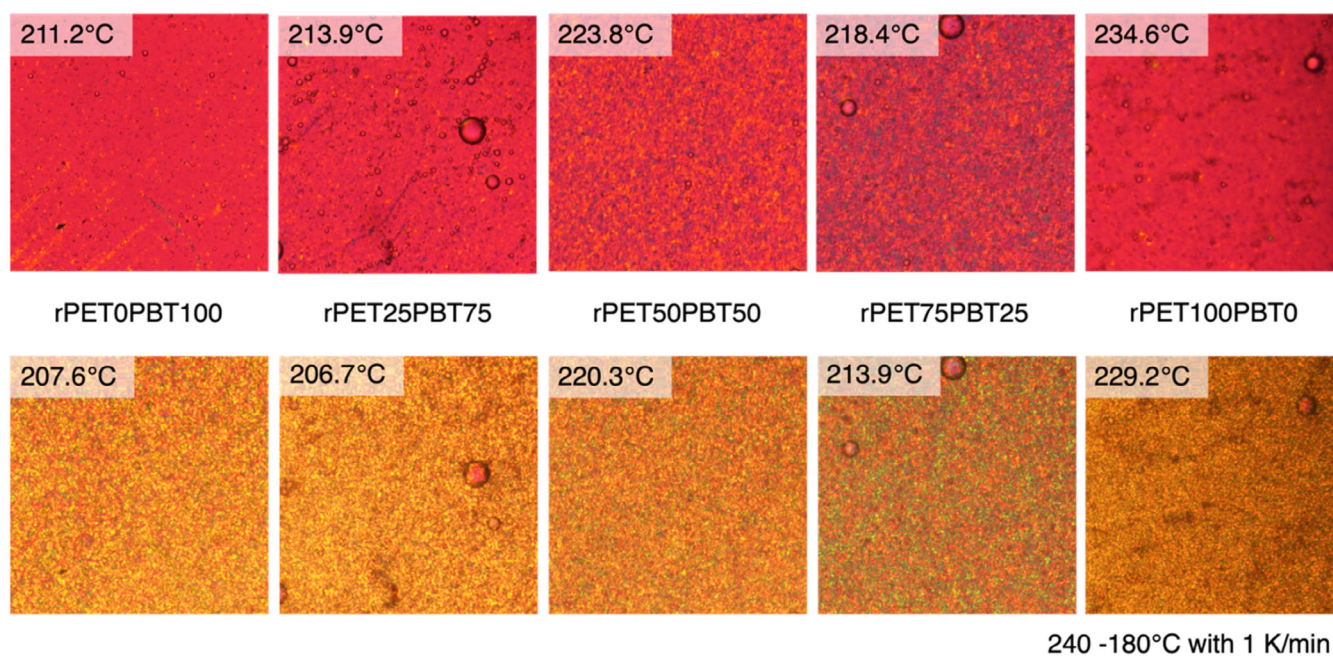
FIGURE 9 Polarized optical micrographs of the unmodified blends. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Crystallization halftime of unmodified and modified rPET-PBT blends (cooling rate: −2.5 K/min).

	Unmodified (min)	0.25 wt.% (min)	0.50 wt.% (min)	1.00 wt.% (min)
rPET0PBT100	1.8	2.0	2.0	2.0
rPET25PBT75	2.3	2.3	2.3	2.4
rPET50PBT50	3.8	3.0	3.2	3.4
rPET75PBT25	3.3	3.0	3.0	2.2
rPET100PBT0	2.5	3.1	3.0	3.5

Abbreviations: PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate.

Additionally, it can be seen from Figure 8 that the slope of the curve is higher for PBT-rich blends. This can be attributed to the higher chain mobility of the more flexible chain structure of PBT.[45] In addition, PBT is known to have an energetically favorable crystal structure compared than PET, and thus a lower activation energy of crystallization.[41,45]

In general, it can be seen that PBT has a higher crystallization rate than rPET, as described in literature.[27,28,41,46,47] The relative crystallization of both unmodified polymers rPET and PBT are similar up to a relative crystallinity of 10%. Additionally, the crystallization halftime is strongly dependent on the blend composition. Under the measurement conditions, rPET50-PBT50 has the longest crystallization halftime with 3.8 min, followed by rPET75-PBT25 with 3.3 min and rPET25-PBT75 with 2.3 min. This series can be explained by the fact that crystallization in rPET50-PBT50 is significantly more inhibited due to the

phase separation, which is essential for crystal formation.[22,43]

The crystallization halftimes at a cooling rate of −2.5 K/min for the blend systems and CE concentrations are listed in Table 2. When modified with CE, the crystallization rate of PBT slightly decreases due to the long chain branches formed, which is reflected in the longer crystallization halftime.[8,13] However, no significant difference was found between 0.25 and 1.00 wt.% of CE. The measured crystallization halftimes are comparable with the values of Kuhnigk et al.[13] who measured 2.0 min for unmodified PBT and 2.3 min for PBT modified with 1 wt.%. The addition of rPET increases the crystallization halftime with the most significant occurring at rPET50-PBT50. In general, the crystallization halftime increases with rPET and CE content.

This trend was previously demonstrated by Wang et al.[26] and by Dangseeyun et al.[22] for PTT/PBT mixtures. This behavior is induced by the phase separation that the

blend must undergo prior to crystallization.[43] More closer the proportion of the two polymers in the blend, more time is need for separation. With increasing CE content and the resulting higher viscosity, the crystallization rate decreases continuously.[11,12,48]

Figure 10 shows the relative crystallization of rPET50-PBT50 as a function of CE concentration at a cooling rate of −2.5 K/min (Figure 10a) and − 10 K/min (Figure 10b). It can be seen from the cooling rate of −10 K/min that the initial stage (nucleation) is similar for all samples except the unmodified sample. This difference was not prevailing at a cooling rate of −10 K/min. During the crystallization, a reducing speed can be detected with increasing CE content for a cooling rate of −2.5 K/min. The measurements at −10 K/min did not show any significant trend. The influence of the CE and thus the influence of the chain structure on crystallization can be deduced from lower cooling rate measurements. Long chain branching decreases chain mobility, which inhibits crystallization, as previously noted, and discussed in the literature.[11,12] Most importantly, nucleation is retarded with a high content of CE compared with the pure material. However, at higher cooling rates, the influence of the measurement method outweighs the effect of long chain branching or the changes in chain structure (Figure 10b). At a cooling rate of −10 K/min, no significant influence of the CE was detected. Therefore, when considering the Avrami parameters and crystallization rate constants, the values at low cooling rates are discussed below.

The non-isothermal crystallization constants of the rPET-PBT blends calculated via Jeziorny-modified Avrami-like equation are shown in Figure 11 for a cooling rate of −2.5 K/min (a) and −10 K/min (b) versus the blend ratios. The blue line indicates the level of crystallization constants of unmodified PBT and the green line that of rPET.

As expected, PBT has in general a higher crystallization rate constant than rPET (see Tables 3 and 4). The difference in crystallization constants of the two polymers becomes more apparent as the cooling rate increases. At a cooling rate of −2.5 K/min, crystallization constants of 0.40 and 0.36 min^{-1} were obtained for PBT and rPET, respectively. The difference between the two pure polymers increases from 0.04 to 0.08 min^{-1} at −10 K/min. At −10 K/min, PBT has a crystallization constant of 1.11 min^{-1} and rPET of 1.03 min^{-1}. At low cooling rates, the crystallization behavior of the blend is dominated by diffusion processes to separate the polymers.[19,49] Therefore, all blends show significantly lower crystallization rates compared with the unmodified polymers. rPET75-PBT25 and rPET50-PBT50 exhibit a crystallization constant of 0.19 and 0.22 min^{-1}, respectively. With a crystallization constant of 0.30 min^{-1}, rPET25-PBT75 exhibits the highest crystallization rate of the investigated blends. It can be deduced that miscible polymer blends interfere with each other during crystallization.

Modification by CE increases the crystallization rate, especially for the blends rPET50-PBT50 and rPET75-PBT25. This is due to the branching points formed, which can serve as nucleation centers.[11,18] This could be shown on the relative crystallization of rPET50-PBT50 with different modifications (see Figure 10). However, on the other hand, a slight decrease in the crystallization rate was observed for PBT and rPET when increasing CE content, whereas no significant
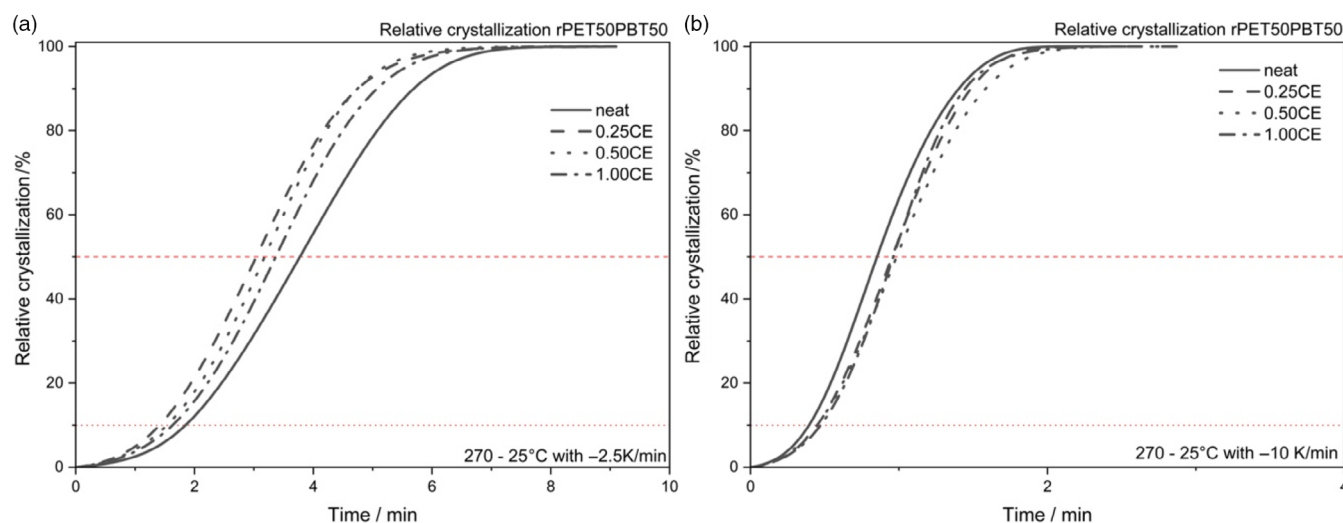

FIGURE 10 Effect of the cooling rate on the crystallization time of rPET50PBT50; (a) −2.5 K/min and (b) −10 K/min. PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate. [Color figure can be viewed at wileyonlinelibrary.com]

change was observed for rPET25-PBT75 (see Table 2). This can be attributed to the fact that PET has a lower diffusion rate due to its lower flexibility, which inhibits crystallization but also the previous reaction with the CE.[45] As the cooling rate increases (Figure 11b), the difference between the two polymers becomes more apparent. While PBT hardly effects the crystallization rate constant of the rPET-dominant blends, a significant reduction of the crystallization rate in the PBT-dominant blends by rPET was observed (see Table 4). The CE modification of rPET, rPET75-PBT25, and rPET50-PBT50 leads to a decrease in the crystallization rate, as described in the literature.[12,50] In contrast, for rPET25-PBT75, the

modification leads to a slight increase in the crystallization rate, except modification with 1.0 wt.% CE. As the cooling rate increases, the chain mobility decreases and thus the diffusion rate of the chain segments to the crystal edges is reduced. If this diffusion is reduced by steric hindrances due to long-chain branching or transesterification in the polymer chain, the crystallization rate also decreases accordingly.[11,12,47,50–52]

The increase in T_g compared with pure PBT (Figure 4) decreases both the potential crystallization time and the chain mobility.[22,24] This could be the reason why the crystallization rate constant of PBT to rPET50PBT50 decreases significantly (Figure 11b). For
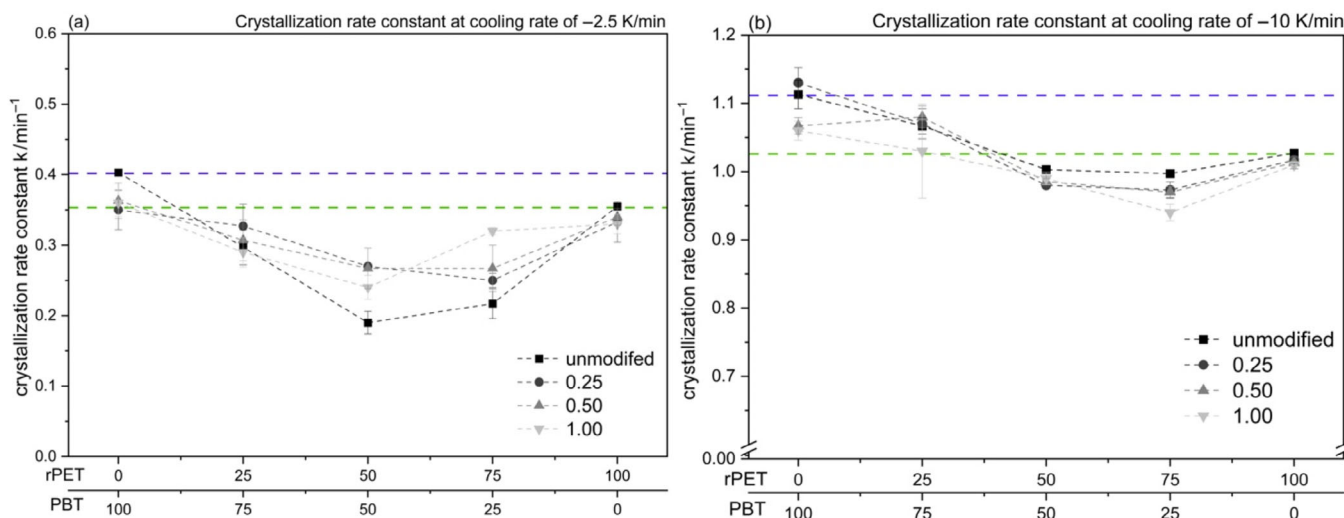

FIGURE 11 Crystallization rate constant of chain extender modified rPET-PBT blends at a cooling rate of −2.5 K/min (a) and − 10 K/min (b). PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Crystallization rate constants of the unmodified and modified rPET-PBT blends cooling with −2.5 K/min.

	Unmodified	0.25 wt.%	0.50 wt.%	1.00 wt.%
rPET0PBT100	0.40 ± 0.005	0.35 ± 0.028	0.36 ± 0.025	0.36 ± 0.019
rPET25PBT75	0.30 ± 0.025	0.33 ± 0.031	0.31 ± 0.029	0.29 ± 0.021
rPET50PBT50	0.19 ± 0.021	0.27 ± 0.000	0.27 ± 0.029	0.24 ± 0.017
rPET75PBT25	0.22 ± 0.021	0.25 ± 0.010	0.27 ± 0.033	0.32 ± 0.005
rPET100PBT0	0.36 ± 0.005	0.33 ± 0.029	0.24 ± 0.012	0.33 ± 0.014

Abbreviations: PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate.

TABLE 4 Crystallization rate constants of the unmodified and modified rPET-PBT blends cooling with −10 K/min.

	Unmodified	0.25 wt.%	0.50 wt.%	1.00 wt.%
rPET0PBT100	1.11 ± 0.021	1.13 ± 0.022	1.07 ± 0.012	1.02 ± 0.02
rPET25PBT75	1.07 ± 0.012	1.07 ± 0.022	1.08 ± 0.016	1.06 ± 0.02
rPET50PBT50	1.00 ± 0.005	0.98 ± 0.000	0.99 ± 0.005	0.98 ± 0.02
rPET75PBT25	1.00 ± 0.005	0.97 ± 0.012	0.97 ± 0.009	0.93 ± 0.02
rPET100PBT0	1.03 ± 0.005	1.02 ± 0.025	1.01 ± 0.009	0.97 ± 0.00

Abbreviations: PBT, poly butylene terephthalate; rPET, recycled polyethylene terephthalate.

rPET, on the other hand, the reduction in T_g does not outweigh the relatively low diffusion due to the stiff backbone. For this reason, there is no significant difference between the rPET-dominant blend and the unmodified material.

4 | CONCLUSION

In conclusion, the thermal behavior of rPET-PBT blends has been thoroughly investigated through a series of DSC measurements. The key findings and conclusions drawn from this study are as follows:

Miscibility in the amorphous state: the DSC measurements revealed that rPET and PBT are miscible in the amorphous state, as evidenced by a single T_g for the blends. The T_g values of the pure PBT and rPET were 49 and 79°C, respectively.

Effect of blend ratio: the T_g of the polymer blend was found to depend on the blend ratio, and this behavior was described using the Fox equation and the Gordon-Taylor equation. The measured T_g values of the blends deviated from the calculated values, with larger discrepancies observed at higher rPET contents. This deviation may be attributed to transesterification and the presence of impurities like PVC in rPET.

Cold crystallization: cold crystallization was observed during the initial heating of rPET, with the crystallization temperature decreasing as the rPET content increased. This reduction in cold crystallization temperature is attributed to the shift in T_g and increased chain mobility in PBT-rich blends.

Phase separation in crystalline state: in contrast to the miscibility in the amorphous state, two separate melting peaks were observed in the blends, indicating immiscibility in the crystalline phase. The melting points of both polymers were affected by blend composition, with the most significant deflection observed in rPET75-PBT25.

Total crystallinity: the total crystallinity of the PBT phase decreased as the rPET content increased, while the relative crystallinity of the rPET phase increased due to improved chain mobility during mixing.

CE modification: the addition of a CE did not significantly affect T_g but had notable effects on crystallization behavior. It increased the crystallization rate in rPET50-PBT50 and rPET75-PBT25 blends due to the formation of branching points that act as nucleation sites.

Crystallization kinetics: the non-isothermal crystallization kinetics revealed that the PBT-rich blend exhibited faster nucleation, while the rPET-rich blend approached the behavior of pure PBT. The presence of a CE influenced crystallization rates, with higher content leading to longer crystallization halftimes.

Influence of cooling rate: cooling rate affected crystallization behavior, with slower rates resulting in greater differentiation between the two polymers. PBT exhibited a higher crystallization rate constant compared with rPET.

In summary, this study provides valuable insights into the thermal behavior of rPET-PBT blends, shedding light on their miscibility in the amorphous state, phase separation in the crystalline state, and the impact of CE modification. These findings contribute to a better understanding of the properties and potential applications of these blends in various industries. Further research may explore the practical implications of these observations in materials engineering and manufacturing processes.

AUTHOR CONTRIBUTIONS
Andreas Himmelsbach: Conceptualization (lead); data curation (lead); formal analysis (lead); funding acquisition (lead); investigation (lead); methodology (lead); software (supporting); validation (lead); visualization (lead); writing – original draft (lead); writing – review and editing (lead). **Christian Brütting:** Writing – original draft (equal). **Yavuz Akdevelioglu:** Writing – original draft (supporting). **Rodrigo Q. Albuquerque:** Software (lead); writing – original draft (supporting). **Mohammadreza Nofar:** Supervision (supporting); writing – original draft (supporting). **Holger Ruckdäschel:** Conceptualization (supporting); project administration (lead); resources (lead); supervision (lead); writing – original draft (supporting); writing – review and editing (equal).

CONFLICT OF INTEREST STATEMENT
The authors declare no competing financial interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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