

ISOTHERMAL AND NON-ISOTHERMAL CRYSTALLISATION KINETICS OF pCBT AND PBT Polymers as studied by DSC

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The crystallisation behaviour of in situ polymerised cyclic butylene terephthalates (pCBT) and poly(butylene terephthalate)s (PBT) were studied by differential scanning calorimetry (DSC) both under isothermal and non-isothermal conditions. The crystallisation was analysed by adopting the Avrami, Ozawa and Kissinger methods for the isothermal and non-isothermal crystallisations, respectively. An Avrami exponent n between 2 and 3 was found for the pCBTs whereas the exponent ranged between 3 and 4 for the PBTs. The Ozawa exponent m varied for all materials between 2 and 3. Differences in the crystallisation kinetics were also reflected in the related activation energy data.

Keywords: Avrami, cyclic butylene terephthalate (CBT, pCBT), isothermal crystallisation, Kissinger, non-isothermal crystallisation, Ozawa, poly(butylene terephthalate) (PBT)

Introduction

Traditional semicrystalline engineering thermoplastics, such as poly(butylene terephthalate) (PBT), are potential candidates to replace thermosetting resins in various composite applications due to their competitive thermal stability. Key aspect of the targeted replacement is whether the melt viscosity of the related thermoplastics can be substantially reduced. The required viscosity reduction can be achieved by using macrocyclic oligomers which undergo ring-opening polymerisation yielding linear thermoplastic polymers (e.g. [1]). This strategy is now followed even for high-temperature resistant thermoplastics [2].

Cyclic butylene terephthalate oligomers (CBT) became commercially available recently. Prior to polymerisation the melt viscosity of the CBT at temperatures $T=140^{\circ}\text{C}$ may be as low as 20 mPa s [3] matching the viscosity of usual thermosetting resins well. The polymerisation time of the CBT can be tailored upon request by the type and amount of the catalysts [4]. A further advantage of CBT is that polymerisation can be performed also below the melting temperature of the resulting PBT. In industrial practice an isothermal treatment at $T=190^{\circ}\text{C}$ is preferred because the polymerisation is accompanied with crystallisation due to which the solidified product can be removed from the mould without cooling of the latter [5, 6]. The polymerisation and crystallisation of the in situ polymerising CBT show several peculiarities.

Though the ring-opening polymerisation should be athermic [1], modulated differential scanning calorimetric (MDSC) investigations demonstrated the onset of some exothermic processes [7, 8]. This was attributed to recrystallisation phenomena among the various oligomers [7], and even to the polymerisation [8], nonetheless, without further proofs. Wide angle X-ray scattering (WAXS) works evidenced that PBT from CBT (denoted as pCBT hereafter) has higher crystallinity and far more perfect crystals than PBTs produced by the usual polycondensation techniques [9, 10]. Numerous papers underlined this difference in the crystallinity based on DSC results (e.g. [6, 9, 10]).

The crystallisation kinetics of pCBT were not yet addressed in the scientific literature. Accordingly, aims of the present work were to study the crystallisation behaviour of pCBTs both under isothermal and non-isothermal conditions and compare the related results with those of selected traditional PBTs. A further goal of this work was to study whether the CBT type (i.e. compositional change of the oligomers) affects the crystallisation behaviour.

Experimental

Four materials have been investigated in this study: CBT 160, CBT XB3-CA4, PBT B4520 and PBT B6550.

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The one-component CBTs were produced by Cyclics Co. and marketed under CBT-XB3-CA4 and CBT-160, respectively. They differ from one another in the composition of the constituent macrocyclic oligomers, namely CBT-160 contained more tetramer than CBT-XB3-CA4. This is well reflected by their melt viscosities: at $T=150^{\circ}\text{C}$ the melt viscosity of the CBT-XB3 is 160 mPa s, whereas that of CBT 160 is 10 Pa s.

PBT B6550 and PBT B4520 were analysed as reference materials. They are commercially available and were used as kindly supplied by the BASF AG.

The measurements have been executed on a Diamond DSC from PerkinElmer, taking always around 3–4 mg for the measurements. Both CBT materials have been dried in an oven for 2 h at 80°C before DSC measurements.

The CBT160 and CBT-XB3-CA4 have been polymerised in situ during the 1st heating step with a heating rate of $20^{\circ}\text{C min}^{-1}$ up to 250°C . The influence of additional time on the polymerisation has been investigated, too, as previous DSC results indicated that the holding time in the melt may affect the crystallisation behaviour [7, 8]. For this purpose, the crystallisation properties have been compared with and without a 15 min isothermal holding step after the first heating step.

The isothermal crystallisation temperatures (covering the range from 190 to 195°C) have been approached with a cooling temperature of $80^{\circ}\text{C min}^{-1}$. Though the isothermal crystallisation of the PBTs, produced by polycondensation, might have been studied in a broader temperature range, for sake of comparison the same temperature interval was selected in which the crystallisation of the pCBTs could be studied properly.

For the non-isothermal investigations, the following cooling rates were selected: 2, 3, 5, 10 and $20^{\circ}\text{C min}^{-1}$.

Results and discussion

Isothermal crystallisation

The crystallisation kinetics of polymers under isothermal conditions for various modes of nucleation and growth can well be approximated by the known Avrami equation [11, 12]:

$$X_t = 1 - \exp(-kt^n) \quad (1)$$

where X_t is the relative crystallinity at different crystallisation times, n is a constant depending on the mechanism of nucleation and the form of crystal growth, and k is the crystallisation rate constant re-

lated to nucleation and growth parameters. X_t can be calculated according to Eq. (2):

$$X_t = Q_t / Q_{\infty} = \int_0^t (dH/dt) dt / \int_0^{\infty} (dH/dt) dt \quad (2)$$

where X_t is thus the ratio of the heat generated at time t and infinite time t_{∞} , respectively. As the heat of crystallisation after infinite time t_{∞} is not available, the heat of crystallisation of the respective material measured under dynamic conditions with $2^{\circ}\text{C min}^{-1}$ heating rate was applied.

The Avrami equation can be linearised as follows:

$$\log\{-\ln[1-X_t]\} = n \log t + \log k \quad (3)$$

From a plot of $\log\{-\ln[1-X_t]\}$ vs. $\log t$, n (the slope of the straight line) and the crystallisation rate constant k (the intersection with the y -axis) can be obtained.

The crystallisation traces of the isothermal holding step used for the evaluation of the Avrami parameters is shown for all materials in Figs 1–6. Common is, for all materials, that the Avrami parameters can be extracted

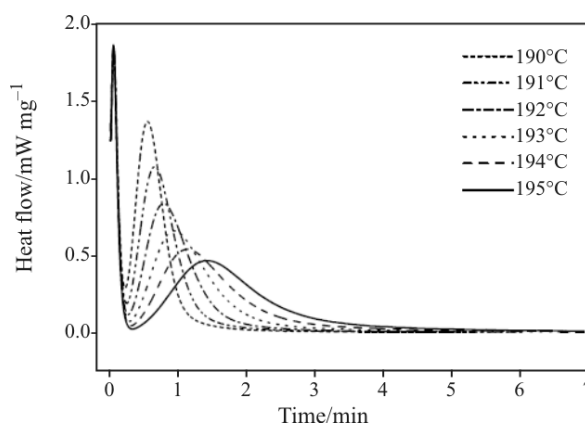


Fig. 1 Crystallisation traces of the isothermal measurements of pCBT 160, 0 min 250°C

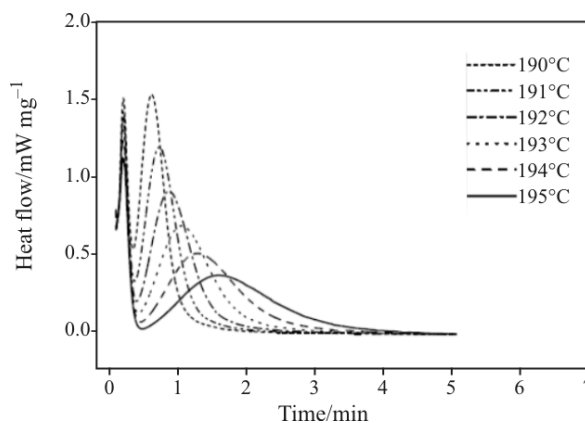


Fig. 2 Crystallisation traces of the isothermal measurements of pCBT 160, 15 min 250°C

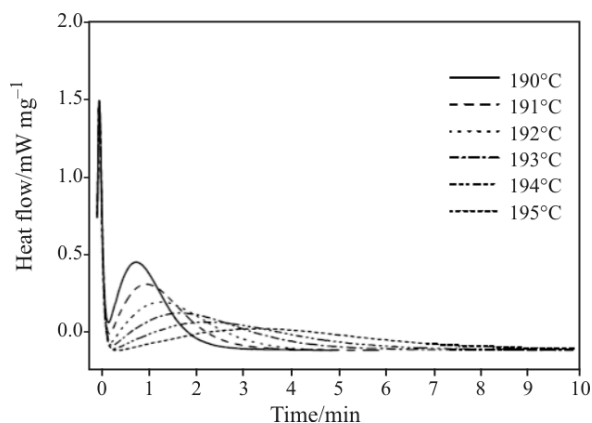


Fig. 3 Crystallisation traces of the isothermal measurements of pCBT XB3-CA4, 0 min 250°C

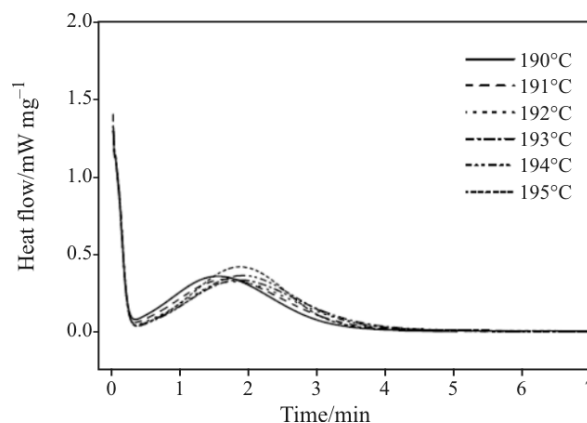


Fig. 6 Crystallisation traces of the isothermal measurements of PBT6550

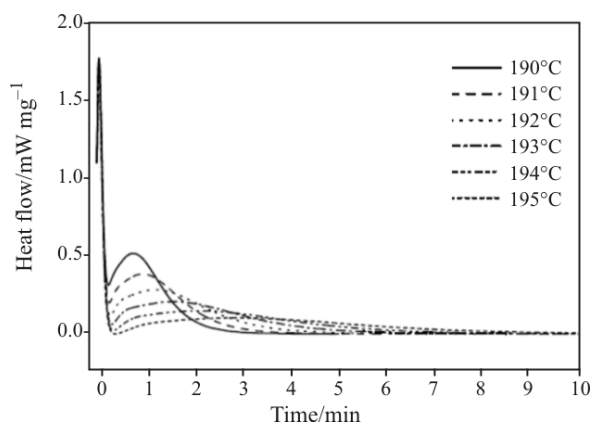


Fig. 4 Crystallisation traces of the isothermal measurements of pCBT XB3-CA4, 15 min 250°C

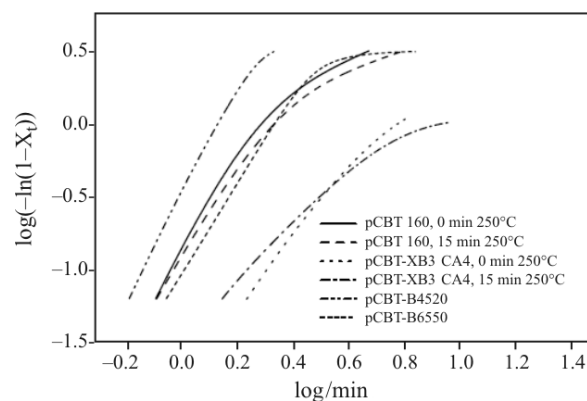


Fig. 7 Avrami plot of all investigated materials as obtained at 195°C

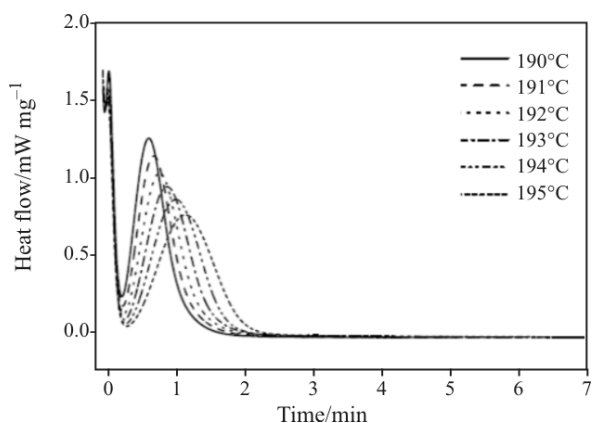


Fig. 5 Crystallisation traces of the isothermal measurements of PBT4520

most precisely when the crystallisation traces at 195°C are considered. This is due to the fact that the DSC signal is not significantly distorted by the transient signal of the DSC machine. According to Lorenzo *et al.*, the crystallisation traces at temperatures below 195°C lead to an error of around 20% in values of n and k [13].

Therefore, the most reliable Avrami parameters can be obtained from the tests at 195°C.

The Avrami plot for all pCBTs and PBTs at 195°C is shown in Fig. 7. In the diagram the plot covers the range of crystallisation from 5 to 95%. Deviations from linearity of the Avrami-plot at later stages of crystallisation have been neglected in the evaluation. Usually, the deviation from linearity is assigned to the beginning of secondary crystallisation. This occurs at very high crystallinities in our polymers, except in the case of pCBT XB3-CA4.

As mentioned before, the Avrami parameters at temperatures lower than 195°C in Table 1 have to be interpreted with caution due to the overlapping transient signal of the DSC machine at the beginning of isothermal crystallisation at these temperatures. Nonetheless, based on the results listed in Table 1 conclusions may be drawn.

The temperature dependence of the overall crystallisation is linked solely with the constant k in Eqs (1) and (3). But this holds only under the prerequisite that the morphology of the growing crystals do not change with the crystallisation temperature. If this is the case, a master curve should be obtained by moving the

Table 1 Parameters of isothermal crystallisation from the Avrami equation (T_c : the crystallisation temperature, $\ln k$: the crystallisation rate constant, n : the Avrami exponent, $t_{0.5}$: the crystallisation half-time)

Material	$T_c/^\circ\text{C}$	n	$\ln k$	$t_{0.5}/\text{min}$
pCBT 160 0 min 250°C	190	3.74	0.64	0.55
	191	3.20	0.20	0.65
	192	3.25	-0.07	0.78
	193	3.28	-0.32	0.93
	194	3.36	-0.58	1.13
	195	3.31	-0.87	1.41
pCBT 160 15 min 250°C	190	3.70	0.66	0.54
	191	3.28	0.26	0.65
	192	3.33	-0.02	0.79
	193	3.28	-0.31	0.97
	194	3.24	-0.63	1.21
	195	3.03	-0.93	1.52
pCBT XB3-CA4 0 min 250°C	190	2.16	-0.32	0.84
	191	2.25	-0.53	1.05
	192	2.22	-0.80	1.36
	193	2.06	-1.04	1.73
	194	2.17	-1.35	2.24
	195	2.11	-1.60	3.43
pCBT XB3-CA4 15 min 250°C	190	2.01	-0.27	0.84
	191	1.80	-0.68	1.03
	192	1.80	-0.68	1.22
	193	1.70	-0.87	1.66
	194	1.78	-1.13	2.08
	195	1.80	-1.42	2.99
PBT B4520	190	4.03	0.44	0.67
	191	4.04	0.29	0.73
	192	3.69	-0.04	0.81
	193	3.78	-0.12	0.92
	194	3.85	-0.29	1.04
	195	3.83	-0.49	1.19
PBT B6550	190	2.62	-0.80	1.53
	191	2.70	-0.90	1.64
	192	2.77	-1.00	1.76
	193	2.83	-1.05	1.86
	194	3.03	-0.93	1.88
	195	3.12	-1.05	1.86

Avrami-lines along the time axis. As can be seen from the data in Table 1, the two pCBT materials (pCBT XB3-CA4 and pCBT 160, at both polymerisation holding temperatures) and the PBT B4520 allow the construction of a master curve. In contrast, the PBT B6550 shows a continuously decreasing Avrami exponent with decreasing temperature. In this case, it has to be surmised that the geometry of the growing crystal phase depends on the crystallisation temperature.

The deviation from linearity of the Avrami plot of the pCBT XB3-CA4 may suggest some influence of the catalyst or of the molecular mass distribution. Either fractions of pCBT XB3-CA4 with low molecular mass or of the catalyst are not incorporated in the crystallised polymer consisting of macromolecules with considerably higher molecular mass. This can be explained with the increasing mobility with decreasing

ing molecule size. Eventually, the concentrations of catalyst and/or of fractions with low molecular mass increase in the remaining molten phase and consequently retard the complete crystallisation. The effect is frequently observed in other polymer systems, too [14]. This arguing, being speculative, should be checked next based on gel permeation chromatographic (GPC) and wide angle X-ray scattering (WAXS) studies.

A nucleation effect can be excluded when considering the results with pCBT 160, which also contained catalyst. This corroborates our suggestion that the early deviation from linearity of the pCBT XB3-CA4 is due to considerably stronger fractionation.

Compilations of the crystallisation kinetics data of various polymers show that the dependence of the crystallisation half time follows a clear pattern with increasing molecular mass [15, 16]. The double logarithmic plot of the crystallisation half time over the molecular mass yields a parabola. The shape of the parabola changes with decreasing crystallisation temperature, such that the arms get farther away from each other and additionally, the average crystallisation half time is reduced.

From these usually observed crystallisation behaviours, it can be assumed that the molecular mass of the polymerised pCBT XB3-CA4 is higher than that of the pCBT 160. This is due to the fact that the crystallisation half times $t_{0.5}$ increase with increasing crystallisation temperature stronger for pCBT XB3-CA4 than for the pCBT 160. Unfortunately, no direct (from GPC measurements) or indirect (from rheological tests following exactly the DSC testing conditions) experimental proofs are available for the authors at present to substantiate the above suggestion.

From the above mentioned dependence of the crystallisation half time $t_{0.5}$ with respect to the molecular mass, nothing can be deduced to compare the molecular mass of the pCBTs with the PBTs. Noteworthy are observations showing that in general the molecular mass of the in situ polymerised pCBT is higher than of PBTs [17].

The same analysis as performed for the pCBTs is applicable for the PBTs. The PBT B6550 should have a higher molecular mass compared to the PBT B4520, applying the general behaviour of the recrystallisation temperature half time dependence with molecular mass: the crystallisation half time of the PBT B6550 is higher than that of the PBT B4520 for every crystallisation temperature as should be the case for high molecular mass fractions.

At 195°C the Avrami exponent allows some conclusions with respect to crystal growth. Interesting is the distinct difference in Avrami exponents between the

pCBT 160 and the pCBT XB3-CA4. For both pCBT materials, the type of nucleation can be assumed to be athermal due to the presence of the catalyst. Then, the pCBT 160 shows an Avrami exponent of $n \approx 3$, corresponding to spherical crystal growth and the pCBT XB3-CA4 exhibits an Avrami exponent of $n \approx 2$, indicating two dimensional plate-like crystal growth. The influence of the polymerisation conditions (i.e. holding time in the melt) on the Avrami exponent is different for the investigated pCBTs. For the pCBT 160, no change was detected in the crystallisation behaviour. For the pCBT-XB3-CA4 the Avrami exponent decreases slightly after subjecting the material to the 15 min at 250°C holding step prior to cooling to the crystallisation temperature. However, an interpretation of these differences without knowing the molecular mass distribution is not possible.

The commercial PBT B4520 displays an Avrami exponent of $n \approx 4$, leaving only thermal nucleation with spherical crystal growth according to the Avrami theory. For the other reference, PBT B6550, the Avrami exponent is $n \approx 3$, indication either athermal nucleation with three dimensional crystal growth or thermal nucleation with two-dimensional crystal growth.

Until now, the predicted crystal morphology by the Avrami theory could not be confirmed by direct observation.

Non-isothermal crystallisation

Even more important for the praxis is the kinetic behaviour of the polymer under non-isothermal crystallisation conditions. There are several modes for the studying the non-isothermal crystallisation kinetics of polymers. Ozawa [18] amended the Avrami approach such that the effect of the heating or cooling rate is taken into account, assuming that the mathematical derivation from Evans [19] is valid. The extended Avrami equation according to Ozawa is:

$$X_T = 1 - \exp[-K_T/\Phi^m] \quad (4)$$

where X_T is the crystallinity at a given temperature but varying cooling rate, Φ is the cooling rate, m is the Ozawa exponent that depends on the crystal growth and nucleation mechanism and K_T is the crystallisation rate constant.

The double logarithmic transformation, used to obtain the Ozawa plot, yields:

$$\ln\{-\ln[1-X_T]\} = \ln K_T - m \ln \Phi \quad (5)$$

In Table 2 the Ozawa parameters for all materials are given for the temperature range from 190 to 195°C. Note that only PBT B4520 and PBT B6550 have practically the same slope m , so the related Ozawa plots yield a series of parallel lines.

Table 2 Parameters of non-isothermal crystallisation from the Ozawa equation (T_c : the crystallisation temperature, $\ln K_T$: the crystallisation rate constant, m : the Ozawa exponent)

Material	$T_c/^\circ\text{C}$	m	$\ln K_T$
pCBT 160 0 min 250°C	190	5.40	14.42
	191	4.51	10.75
	192	2.88	5.88
	193	3.27	6.32
	194	3.59	6.53
pCBT 160 15 min 250°C	195	3.31	5.13
	190	3.93	10.05
	191	2.45	5.58
	192	2.85	6.08
	193	3.27	6.57
pCBT XB3-CA4 0 min 250°C	194	3.04	5.79
	195	3.44	6.01
	190	1.77	3.37
	191	2.04	3.63
	192	2.30	3.86
pCBT XB3-CA4 15 min 250°C	193	2.54	4.00
	194	2.74	3.99
	195	2.85	3.76
	190	2.52	5.26
	191	2.31	4.57
PBT B4520	192	2.47	4.56
	193	2.61	4.46
	194	1.92	2.70
	195	2.16	2.73
	190	3.21	5.77
PBT B6550	191	3.13	5.08
	192	3.29	4.88
	193	2.92	3.71
	194	3.10	3.47
	195	3.28	3.16
	190	2.18	3.01
	191	1.96	2.44
	192	2.00	2.20
	193	2.08	1.98
	194	2.20	1.79
	195	2.07	1.30

For the pCBT materials, a distinct change in Ozawa exponent is observed from 190 to 191°C in most cases. The different melt prehistories (0 or 15 min at 250°C) change the crystallisation kinetics considerably, although, incidentally, some matching in the Ozawa parameters may be noticed. Further investigations will be necessary to gain insight in the dynamic crystallisation of the pCBT materials.

For direct comparison with the Avrami results, only the Ozawa plot at 195°C is shown in Fig. 8. Clearly, the results show that secondary crystallisation as influencing parameter can be excluded. The Avrami (cf. Fig. 7) and Ozawa plots (cf. Fig. 8) of the pCBTs and PBTs are sufficiently linear.

For an ideal material, the Ozawa exponent should match with the Avrami exponent. However, the agreement between the Ozawa exponent m and the Avrami

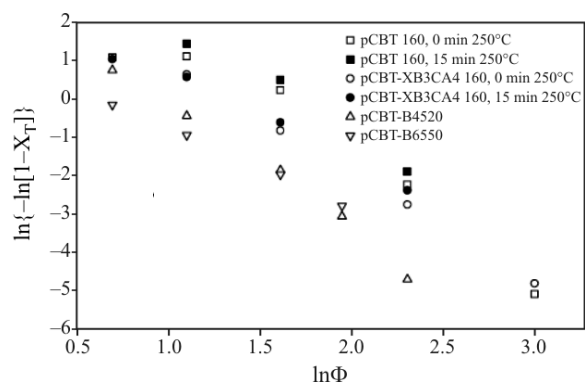


Fig. 8 Ozawa plot for all investigated materials as obtained at 195°C

exponent n occurs for each material at different temperatures and the Ozawa exponent m changes stronger with temperature than the Avrami exponent n (cf. Tables 1 and 2). This may suggest that the activation energy changes in the investigated temperature range.

At every crystallisation temperature, the cooling rate function K_T for the pCBT 160 is larger than for the pCBT XB3-CA4. This indicates that the pCBT 160 crystallises faster than pCBT XB3-CA4. This conclusion is in agreement with the results of the Avrami analysis.

The deviation from the 'ideal' material (i.e. with identical Avrami and Ozawa parameters) may be due to the small amount of catalyst which is necessary for the bulk polymerisation of CBT. The catalyst residue may work as heterogeneous nuclei for crystallisation. Note that the content of any catalyst or additive within PBT B4520 and PBT B6550 were not known.

Activation energy

An additional way to gain more information about the differences between isothermal and non-isothermal crystallisation is the determination of the activation energy. A method often used to evaluate the activation energy at various cooling rates is the method proposed by Kissinger [20]:

$$d[\ln(\Phi/T_p^2)]/d(1/T_p) = -\Delta E/R \quad (6)$$

where R is the universal gas constant and E is the activation energy of crystallisation. The activation energies of the non-isothermal crystallisation are calculated with the data from the plot of $\ln(\Phi/T_p^2)$ vs. $1/T_p$ (Fig. 9).

Equation (6) predicts a negative slope due to the fact that initially only melting processes were investigated. The slope for all materials is positive in this case because the recrystallisation temperature decreases rather than increases with higher cooling rates. Obviously, two distinctly different ranges can be observed for all material variations, i.e. above and

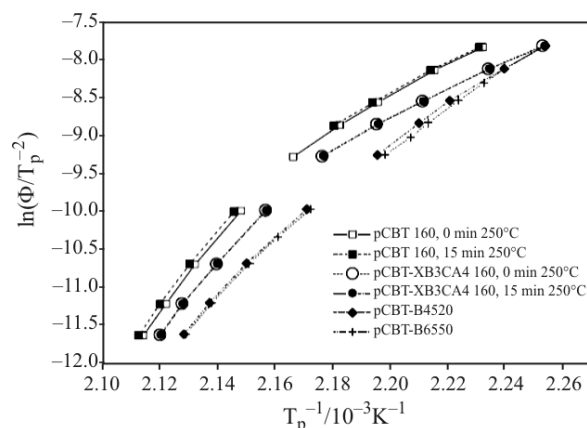


Fig. 9 Kissinger graph for evaluating the non-isothermal crystallisation activation energy

Table 3 Activation energies E_c evaluated according to the Kissinger method

Material	$E_c/\text{kJ mol}^{-1}$ for $\ln(F/T_p^2) > -9.5$	$E_c/\text{kJ mol}^{-1}$ for $\ln(F/T_p^2) < -9.5$
pCBT 160, 0 min 250°C	400	181
pCBT 160, 15 min 250°C	408	181
pCBT XB3-CA4, 0 min 250°C	367	156
pCBT XB3-CA4, 15 min 250°C	367	156
PBT B4520	217	203
PBT B6550	217	218

below the ordinate value of $\ln(\Phi/T_p^2) \approx -9.5$. The activation energies have been calculated in these regions and are listed in Table 3.

At high temperatures the crystallisation occurs easily in the commercial PBTs while the pCBTs are almost incapable of crystallisation. At lower temperatures ($\leq 190^\circ\text{C}$), the scenario changes completely. The pCBTs crystallise slightly easier than the commercial PBTs. Possible explanations for the higher activation energy at temperatures $\geq 190^\circ\text{C}$ of the pCBTs may be related to their inherent higher molecular mass and readiness to pronounced fractionation of the molecules during polymerisation compared to PBTs. The observed activation energies match sufficiently well with other PBT variations. e.g. an activation energy of $E_c = 275 \text{ kJ mol}^{-1}$ has been found for the PBT 1097A [21] and $E_c = 260 \text{ kJ mol}^{-1}$ for bulk polymerised PBT [22]. A precise comparison with the results obtained in this work with the above one is not possible because the details of the Kissinger analysis (peak temperatures and corresponding heating rates) were not disclosed in the cited works.

Conclusions

Commercial PBT and in situ polymerised pCBT materials were investigated in this study with respect to their isothermal and non-isothermal crystallisation behaviours. To produce pCBTs two different kinds of CBT oligomers were used. The isothermal crystallisation has been evaluated by using the Avrami analysis whereas for the non-isothermal crystallisation the Ozawa method was adopted. Additionally, the activation energy has been calculated according to the Kissinger method.

It was established that the crystallisation of pCBTs depend more strongly on the experimental conditions than the PBTs. The results of the pCBTs indicated that the crystallisation occurs in a temperature range where a change in the activation energy takes place. This complicates the data reduction using the Avrami and Ozawa equations. So, the activation energies were determined for two temperature ranges, viz. above and below 190°C. Noteworthy is that the activation energy for the pCBT produced from the higher molecular mass CBT oligomer (CBT 160) was higher compared to the counterpart with low molecular mass (CBT XB3-CA4).

For the resulting crystallisation kinetics, the polymerisation conditions are of crucial importance, as evidenced by the different results obtained with varying in situ polymerisation conditions.

The commercial PBTs B4520 and B6550 show a more stable crystallisation behaviour compared to the investigated pCBTs. Their behaviour obey to the Avrami, Ozawa and Kissinger formalism better than the pCBTs.

Acknowledgements

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