Effect of PTW on crystallization kinetics of toughened PBT/PC blends

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Abstract: Poly(butylenes terephthalate) (PBT)/polycarbonate (PC)/poly(ethylene-butylacrylate-glycidyl methacrylate copolymer) (PTW) blends containing PTW as toughening modifier were obtained by extrusion and injection molding. The effect of PTW on the melt rheology of PBT/PC blend was examined by means of capillary calorimetry. The rheological properties of the blends suggested high reactivity between epoxy groups in PTW and terminal carboxylic acid group and/or hydroxyl group of PBT inhibited transesterification between PBT and PC. The effect of PTW on the crystallization of PBT in the PBT/PC/PTW blends was investigated by crystallization kinetics analysis under isothermal and nonisothermal conditions. Isothermal crystallization experiments were performed at crystallization temperature and analyzed based on the Avrami equation. A decrease of the half time of PBT crystallization $t_{1/2}$, as well as an increase of the overall crystallization rate of PBT in the PBT/PC/PTW blends have been observed. Nonisothermal crystallization experiments were performed at given cooling rate. The Ozawa analysis is used to describe its nonisothermal crystallization behavior. It is observed that at a given cooling rate, the PTW increases the overall crystallization rate of PBT in the PBT/PC/PTW blends. This is consistent with the result obtained under isothermal crystallization condition.

Keywords: Poly(butylene terephthalate) (PBT), Polycarbonate (PC), Poly(ethylene-butylacrylate-glycidyl methacrylate copolymer) (PTW), isothermal crystallization, nonisothermal crystallization.

Introduction

Polymer blending has been a major path to tailor properties of polymer materials [1, 2]. Blends of poly(butylene terephthalate) (PBT) and polycarbonate (PC) materials are of commercial interest because of their potential in combination. The amorphous PC provides impact resistance and toughness while the crystalline PBT provides enhanced chemical resistance and thermal stability. PBT/PC blends with excellent balance of properties, like high toughness, good dimensional stability, high heat distortion temperature and good flow property are used for large exterior parts in the automotive industry. Unfortunately, simple molten blending of PBT and PC in a mixer will most probably produce a PBT/PC mixture with poor mechanical properties and thermal properties. Thus, the important issues in PBT/PC blends are to toughen PBT/PC with a third component. Rubber or elastomer modification is generally recognized to be a very effective method to toughen brittle materials. Functionalized rubbers have been used in attempts to toughen PBT [3-13]. The most common
functional groups used for grafting the rubbers are ester, maleic anhydride, and epoxy. Thus far, epoxide-containing elastomers are known to be very effective to toughen PBT or PET [14]. Attempts to toughen pure PBT and PBT blends using epoxide-containing rubbers and the melting and crystallization behavior of PBT in its blends have been reported [14-25]. Poly (ethylene-butylacrylate-glycidyl methacrylate copolymer) (PTW) is a copolymer with epoxy groups (glycidyl) that react with carboxyl (preferentially) or hydroxyl functional groups, and with butylacrylate segments that provides very good low temperature properties. Therefore, PTW is an attractive impact modifier because of both reactive processing and rubbery toughening. In our previous work, we reported the use of PTW as a toughening modifier for PBT/PC blends [26]. The blends were characterized by DMTA, DSC, and SEM. The results showed that the addition of PTW led to great increase in the impact strength, elongation at break, vicat temperature and a reduction in the tensile strength and flexural properties of PBT/PC blends. It was found that 7% (wt) was an optimum PTW content for toughening modification of PBT/PC (50/50 w/w) blend. The melting and glass transition behaviour (after crystallization) of PBT/PC/PTW blends were studied. Also, the blend morphology was observed by SEM and the dispersed phase average diameter was determined by image analysis. The relation between the impact resistance and the phase morphology was discussed, and the critical ligament size for PBT/PC was determined. The critical ligament thickness below which ductile behaviour occurs was determined to be around 0.4 mm for these blends. The fracture surfaces of the toughened PBT/PC/PTW blends showed extensive yielding of the matrix.

In practical processing, such as extrusion molding and filming, crystallization usually proceeds under isothermal and non-isothermal conditions. Isothermal crystallization measurements are usually used to study the crystallization behaviour of polymers, since their theoretical analysis is relatively easy. The treatment of nonisothermal crystallization data, in which the polymers are observed at a constant cooling rate, is theoretically more complicated [27]. But this type of crystallization approaches more closely the industrial conditions of polymer processing such as extrusion molding, melt-spinning of synthetic fibers. For crystalline polymer, such as PBT, the crystallization behaviour is vital to the performance of materials. Therefore, understanding the effect of PTW on crystallization kinetics of PBT/PC blend is important for optimizing the process conditions and establishing the relationship between thermal properties and structure of the PBT/PC blends. However, to the best of my knowledge, detailed analysis of these aspects has not been reported in the other literatures.

The present study is aimed at elucidating the crystallization kinetics of PBT in PBT/PC, PBT/PC/PTW blends using differential scanning calorimetry (DSC) measurement. Attention was focused on isothermal and non-isothermal crystallization process of PBT, PBT/PC, and PBT/PC/PTW blends in order to understand the effect of PTW on the kinetic parameters. The kinetic data on isothermal crystallization behavior of PBT and its blends have been interpreted by using the Avrami analysis. Also, based on the experimental results, the applicability of Ozawa equation to non-isothermal crystallization behavior of this system is presented. The isothermal and non-isothermal crystallization behavior of PBT/PC/PTW blends explains the various aspects of the nucleation and growth process, which helps in optimization of the final processing of the PBT/PC/PTW blends.
Results and discussion

Viscosity measurement

Figure 1 compares the apparent viscosity vs shear rate curves of PTW, PBT/PC (50/50 w/w), and PBT/PC/PTW (50/50/7 w/w/w) blends during melt mixing. It clearly shows that PTW individually has lower viscosity than that of PBT/PC blend. PBT/PC/PTW blend, however, has significantly higher viscosity than that of PBT/PC blend, indicating that the additional PTW in the PBT/PC blend results in an increase in viscosity of the PBT/PC blend. The viscosity changes can be attributed to the chemical reactions involved in these blend systems.

For PBT/PC blend, transesterification between PBT and PC during melting process can create some PBT-PC copolymers. Initially, these copolymers may act as interfacial agents to improve the compatibility between PBT and PC and increase the interfacial boundary strength, but, ultimately, transesterification will lead to an amorphous random copolymer of a phase-separated blend [31]. This results in lower viscosity of PBT/PC blend.

For PBT/PC/PTW blend, the reaction between the epoxy functional group in the PTW and PBT terminal carboxylic acid (–COOH) and/or hydroxyl (–OH) groups enhance the adhesion between PTW and the PBT/PC blend and results in an increase in viscosity. In addition, transesterification can also take place between the acrylate ester group and the terminal –OH and –COOH of polyesters reported previously [32-34]. These transesterification are believed to be much slower than the epoxy coupling reactions and can be neglected under an extended period time of melting [35]. These transesterification could not cause viscosity increase of the blends. The increase in viscosity of PBT/PC/PTW blend, compared to that of in PBT/PC blend, indicated that transesterification between PBT and PC may be efficiently inhibited, and reactions between PTW and PBT terminal –OH and –COOH groups are dominant reactions.

Isothermal crystallization analysis

Considering the importance of isothermal crystallization rate to the commercial utility
of thermoplastic polyester, an insight into the isothermal crystallization is necessary. Figure 2 shows the dependence of heat flow on crystallization time at different crystallization temperature for PBT and its blends. As can be seen, the crystallization exothermic peak between platforms and the time to reach the maximum degree of crystallization increase with increasing crystallization temperature.

**Fig. 2.** Heat flow as a function of time during isothermal crystallization at different crystallization temperature by DSC for PBT, PBT/PC, and PBT/PC/PTW blends.

The isothermal crystallization kinetics of a polymer can be analyzed by evaluating its degree of crystalline conversion as a function of time at a constant temperature. In analyzing, the relative crystallinity, \( X_t \), developed up to time \( t \) was the ratio of the areas between the heat flow-time curve and the baseline of the sample [36, 37].

\[
X_t = \frac{Q_t}{Q_\infty} = \frac{\int_0^t \frac{dH}{dt} dt}{\int_0^\infty \frac{dH}{dt} dt}
\]

(1)

where \( Q_t \) and \( Q_\infty \) are the heat generated at time \( t \) and infinite time, respectively, and \( \frac{dH}{dt} \) is the heat flow rate. The development of the relative crystallinity with time for PBT and its blends are plotted in Figure 3. The characteristic isotherms are shifted to right along the time axis with the increasing crystallization temperature, indicating progressively slower crystallization rate. After most of the crystallization had taken place, a slow increase of crystallinity with time was observed, which could be attributed to the presence to secondary crystallization [38].

The degree of crystallinity against time was analyzed using the Avrami equation [38-40], which can be expressed as:

\[
X(t) = 1 - \exp(-Kt^n)
\]

(2)

where \( K \) is the Avrami rate constant containing the nucleation and the growth parameters, \( n \) is the Avrami exponent dependent on the mechanism of nucleation, the form of crystal growth. Eq. (2) can also be converted to
\[ \log[-\ln(1-X(t))] = \log K + n \log t \]  

(3)

**Fig. 3.** Relative crystallinity vs. crystallization time for various crystallization temperature from DSC thermograms of PBT, PBT/PC (50/50 w/w) and PBT/PC/PTW (50/50/7 w/w/w) blends.

Plots of \( \log [-\ln(1 - X(t))] \) vs. \( \log t \) are shown in Figure 4. For comparison, the regime of about 10-80\% conversion in the curves for all the samples is chosen to determine the exponent \( n \) and \( K \) according to Eq.(3) and presented in Table 1.

It should be noted that \( T_c \) values were determined according to \( T_p \) values obtained at same cooling rate, and temperature intervals for PBT, PBT/PC, and PBT/PC/PC blends were 6 °C, 3 °C, and 4 °C, respectively.

The \( n \) values of pure PBT and its blends range between 2.0 and 4.0, and are higher than the values reported in literature [41]. For pure PBT and PBT/PC/PTW blend, the values of Avrami index \( n \) are noninteger. These noninteger values are generally accounted for mixed growth and/or surface nucleation modes and two-stage crystallization [42, 43]. As for pure PBT, the \( n \) values are in the range of 3.5-4.0, which is normally attributed to thermal nucleation followed by three-dimensional crystallization growth. [44] The similar phenomena in nylon 6 nanocompositions were observed by Fornes [45]. While PBT/PC blends show the \( n \) value of 3.0, indicating the three-dimension spherulite crystal growth and PBT/PC/PTW blends exhibit the \( n \) values of 2.2-2.3, corresponding to two dimensional plate-like crystal growth.

Another important parameter is the half-time of crystallization \( t_{1/2} \), which is defined as the time at which the extent of crystallization is 50\%. It can be conveniently extracted from the plots of relative crystallinity \( X(t) \) vs. time \( t \) in Figure 4. The relation between
\( t_{1/2} \) and \( K \) can be expressed

\[
K = \frac{\ln 2}{t_{1/2}}
\]

Fig. 4. Plots of log [\(-\ln (1-X(T))\)] vs. log \( t \) for PBT, PBT/PC and PBT/PC/PTW blends.

Tab. 1. Kinetic parameters of PBT, PBT/PC (50/50 w/w), and PBT/PC/PTW (50/50/7 w/w/w) blends from the analysis of isothermal crystallization.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( T_c ) (°C)</th>
<th>n</th>
<th>logk</th>
<th>( t_{1/2} ) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>198</td>
<td>3.5</td>
<td>-1.00</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>192</td>
<td>3.8</td>
<td>0.31</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>186</td>
<td>4.0</td>
<td>1.25</td>
<td>0.4</td>
</tr>
<tr>
<td>PBT/PC</td>
<td>186</td>
<td>3.0</td>
<td>-1.06</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>183</td>
<td>3.0</td>
<td>-1.21</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>3.0</td>
<td>-0.76</td>
<td>1.5</td>
</tr>
<tr>
<td>PBT/PC/PTW</td>
<td>186</td>
<td>2.3</td>
<td>-4.22</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>182</td>
<td>2.3</td>
<td>-4.47</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>178</td>
<td>2.2</td>
<td>-4.00</td>
<td>0.9</td>
</tr>
</tbody>
</table>

\(^a\) Determined from Figure 3

The values of \( t_{1/2} \) derived from experimental data are listed in Table 1. The \( t_{1/2} \) is directly employed to describe the rate of crystallization. The lower the value of \( t_{1/2} \) is, the greater the rate of the crystallization is. As shown in Table 1, compared to pure
PBT, the values of $t_{1/2}$ of PBT/PC blends increase, and the addition of PTW to the PBT/PC blend decreases the value of $t_{1/2}$, indicating that the PBT/PC/PTW blends have a greater rate of crystallization than PBT/PC blends. The reasons will be explained in following section.

**Nonisothermal crystallization analysis**

Nonisothermal crystallization kinetics of polymers is of importance in process modeling and crystallization control [46, 47]. Recently, the kinetic parameters derived from isothermal experiments were also used to predict the nonisothermal crystallization behaviour.

Figure 5 shows the DSC cooling thermograms of PBT, PBT/PC (50/50 w/w), and PBT/PC/PTW (50/50/7 w/w/w) blends. Table 2 gives a summary of the nonisothermal crystallization parameters according to the DSC thermograms.

As seen in Figure 5, only a single crystallization peak can be observed. $T_p$ value of PBT in PBT/PC/PTW blend is lower than that of pure PBT and that of PBT in PBT/PC. The $T_{onset}$ - $T_p$ value of PBT/PC is the biggest. It is related to transesterification between PC and PBT in melting process. Incorporation of PC inhibits the crystallization of PBT in the blends [48]. However, the addition of the PTW into PBT/PC blend decreases the $T_{onset}$ - $T_p$ value of PBT in PBT/PC/PTW blend. The
facts are related to the high reactivity between epoxy groups in PTW and terminal carboxylic acid group and hydroxyl group of PBT, and as a consequence, transesterification between PBT and PC may be efficiently inhibited as evidenced by melt viscosity measurement. Thus, Incorporation of PTW can greatly enhance the crystallization rate of PBT in the PBT/PC/PTW blends. The similar finding was also obtained in poly(ethylene glycol-co-cyclohexane-1,4-dimethanol terephthalate) (PETG)/polycarbonate (PC) blends [49]. The rate of nucleation ($S_i$) and the width at half-height of the exotherm peak ($\Delta W$) at a given cooling rate are also listed in Table 2. As can be observed, $S_i$ values of the PBT/PC/PTW blend is greater than that of the PBT/PC blend and $\Delta W$ values of the PBT/PC/PTW blends are smaller than that of PBT/PC blend. It is likely that the PTW in PBT/PC/PTW blends can prevent effectively transesterification between PBT and PC, enhancing the crystallization of PBT in the PBT/PC/PTW blend.

Tab. 2. Various parameters of PBT, PBT/PC (50/50 w/w), and PBT/PC/PTW (50/50/7 w/w/w) blends obtained from the nonisothermal crystallization exotherm at a cooling rate of 10 °C/min.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_p$ ($^\circ$C)</th>
<th>$T_{onset}$ ($^\circ$C)</th>
<th>$T_{onset}$ - $T_p$ ($^\circ$C)</th>
<th>$S_i$</th>
<th>$\Delta W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBT</td>
<td>190.0</td>
<td>196.5</td>
<td>6.5</td>
<td>1.4</td>
<td>5.9</td>
</tr>
<tr>
<td>PBT/PC</td>
<td>177.1</td>
<td>191.8</td>
<td>14.7</td>
<td>0.1</td>
<td>15.7</td>
</tr>
</tbody>
</table>

Fig. 6. Heat flow as a function of temperature during nonisothermal crystallization at different cooling rates (2.5, 5, 10, 20 °C/min) by DSC for PBT, PBT/PC (50/50 w/w) and PBT/PC/PTW (50/50/7 w/w/w) blends.

Figure 6 shows heat flow as a function of temperature during nonisothermal crystallization at different cooling rates by DSC for PBT and PBT/PC (50/50 w/w), and PBT/PC/PTW (50/50/7 w/w/w) blends. As can be seen, the crystallization of PBT could be carried out at lower temperature with increasing cooling rate for PBT, PBT/PC, and PBT/PC/PTW blends. The relative degree of crystallinity as a function of temperature for PBT and its blends at various cooling rates is shown in Figure 7. It can be seen that all the curves have similar sigmoidal shapes and that crystallization occurred at lower temperature with increasing cooling rate, indicating that at slower
cooling rates there is sufficient time to activate nuclei at higher temperatures, and thus, crystallization nucleates at higher temperatures with slower cooling rates [50].

Fig. 7. Development of relative crystallinity with temperature for nonisothermal crystallization of PBT, PBT/PC (50/50 w/w) and PBT/PC/PTW (50/50/7 w/w/w) blends.

Considering the effect of cooling rate on the nonisothermal crystallization, Ozawa [51] extended the Avrami theory from isothermal crystallization to nonisothermal crystallization by assuming that the nonisothermal crystallization process was composed of infinitesimally small isothermal crystallization steps. According to Ozawa theory, the relative crystallinity \( C(T) \), at temperature \( T \), can be calculated as [52]:

\[
\ln[-\ln(1-C(T))] = \ln H(T) - M \ln |\Phi| 
\]

where \( H(T) \) is the cooling function related to the all over crystallization rate, \( M=m+1 \) for the instantaneous nucleation and \( M=m+2 \) for the nucleation prolonged in time, \( m \) is the Ozawa exponent that depends on the dimensionality of crystallization and the nucleation mode, and \( \Phi \) is the cooling rate.

By plotting \( \ln[-\ln(1-C(T))] \) vs. \( \ln |\Phi| \), \( \ln H(T) \) and \( M \) parameters can be calculated. Plots of \( \ln[-\ln(1-C(T))] \) vs. \( \ln |\Phi| \) are shown in Figure 8.
Fig. 8. Ozawa plots of ln [-ln (1 - C (T))] vs. ln |Φ| at indicated temperature for PBT, PBT/PC (50/50 w/w), and PBT/PC/PTW (50/50/7 w/w/w) blends.

Due to the limited number of cooling rates available in practice in DSC experiments, the plot of ln [-ln(1-C(T))] vs. ln |Φ| at a given T appears as a succession of linear segments; each succession is approximated by a unique straight line. The slopes of these straight lines give the values of M at each temperature. Intersections of these lines permit to calculate the cooling function H(T). The results are illustrated in Figure 9 and Figure 10.

As shown in Figure 9, pure PBT shows average of M is 3.5 over 190 °C~200 °C, corresponding to instantaneous nucleation and growth of spheres in 3D; PBT/PC blend shows the average of M is 3.0 over 178 °C~208 °C, indicating the three-dimension spherulite crystal growth; PBT/PC/PTW blend exhibits the average of M is 2.0 over 171°C~191 °C, corresponding to plate-like crystal growth in 2D. These values are in agreement with the results of isothermal crystallization.

The cooling function H(T) is a function of nucleation and growth rate [51]. As shown in Figure 10, lnH(T) increase with decreasing temperature for PBT, PBT/PC (50/50 w/w), and PBT/PC/PTW (50/50/7 w/w/w) blends. In fact, the thermodynamic driving force for crystallization increases as the crystallization temperature lowers until the temperature which causes a big increment in the viscosity so that the transport of polymer chains to the growth point becomes very difficult. Therefore, the result in pure PBT is observed.
Fig. 9. Variations of $M$ vs. crystallization temperature for PBT, PBT/PC (50/50 w/w), and PBT/PC/PTW (50/50/7 w/w/w) blends crystallized with various cooling rates.

In comparison, while decreasing the crystallization temperature, the $ln[H(T)]$ in PBT/PC/PTW (50/50/7 w/w/w) blend increases more quickly than in PBT/PC (50/50 w/w) blend. This might result from the chain irregularity. Transesterification between PBT and PC hinders the polymer chains to pack each other in a regular manner.

Fig. 10. Variations of $ln[H(T)]$ vs. crystallization temperature for PBT, PBT/PC (50/50 w/w), and PBT/PC/PTW (50/50/7 w/w/w) blends crystallized at various cooling rates.
However, the addition of the PTW into PBT/PC blend can efficiently inhibit transesterification between PBT and PC. Thus, PBT/PC/PTW (50/50/7 w/w/w) blend takes relatively shorter time in the crystallization than does PBT/PC (50/50 w/w) blend. The results showed the addition of PTW can increase the crystallization rate of PBT in the PBT/PC/PTW blend, as can also be observed in the isothermal process.

Conclusions

PBT/PC/PTW blends containing PTW as toughening modifier were obtained by extrusion and injection molding. Incorporation of PTW can greatly influence the crystallization rate of PBT in PBT/PC/PTW blends. The facts are related to the high reactivity between epoxy groups in PTW and terminal carboxylic acid group and hydroxyl group of PBT. The effect of PTW on the melt rheology of PBT/PC/PTW blends was examined by means of capillary calorimetry. Enhanced viscosity of PBT/PC/PTW blends suggested that reaction between PTW and PBT is dominant reaction.

For the isothermal crystallization, the Avrami equation can be used to obtain the values of the Avrami exponent $n$ and the Avrami rate constant $K$ for pure PBT, PBT/PC, and PBT/PC/PTW blends. The values of $n$ are in the range of 3.5-4.0 for pure PBT, 3.0 for PBT/PC, and 2.2-2.3 for PBT/PC/PTW blends. In addition, the crystallization rate of PBT in pure PBT and its blends increases in following order: PBT/PC < PBT/PC/PTW < PBT.

For the nonisothermal crystallization for pure PBT, PBT/PC, and PBT/PC/PTW blends, the Ozawa equation is used to describe the nonisothermal crystallization process. The results show that the average values of $M$ are 3.5 for pure PBT, 3.0 for PBT/PC blend, and 2.2 for PBT/PC/PTW blend; PBT/PC/PTW blend requires shorter time in the crystallization as compared to those of PBT/PC blend. Thus, the PTW in the PBT/PC/PTW blends can enhance the crystallization rate of PBT. This is in agreement with the results observed under isothermal crystallization.

Experimental part

Materials

PBT was L2100G (Yi Zheng Chemical Fiber Group Corp., China) with a melt flow index (MFI) of 25 g/10min (235 °C×2.16 kg, ASTM D1238). PC was PC110 (Chimei-Asahi Corp., Taiwan, China) with a MFI of 10 g/10 min (300 °C×1.2 kg, ASTM D1238). PTW was Elvaloy PTW (Du Pont, USA) with a MFI of 12 g/10 min (ASTM D1238).

PBT and PC particulates were dried at 120 °C for 4 h in a vacuum oven before processing. The blends comprised 50 phr PBT, 50 phr PC, and 7 phr PTW by weight.

The blends were extruded using a Berstoff twin-screw extruder (type ZE25, L/D ratio 41, screw diameter 25 mm, Germany) at a screw speed of 300 rpm and torques of 50-70%. The temperature profile of the barrel was 40-230-230-235-235-240-240-245-250 °C from the hopper to the die. The extrudated blends were dried in an air oven for 4 h at 100 °C. Injection molding was carried out in a plastic injection molding machine (HTB110X/1, China). The barrel temperature profile for injection moulding was 240-250-250-250-259 °C, and the mould temperature was at 50 °C.
Viscosity measurement

Capillary rheological measurements were performed on a capillary rheometer (L/D ratio 40) from Instron 4450 at 235 °C.

Differential Scanning Calorimetry (DSC) analysis

A differential scanning calorimetry (Perkin-Elmer DSC-1, USA) was used to analyze the isothermal and nonisothermal crystallization. As a base of comparison, the pure PBT was also passed through the extruded at the same conditions. Samples weighing 6-8 mg for DSC analysis were cut from the injection molded bars. It is worth noting that each sample was used only once and all the runs were carried out under nitrogen atmosphere to prevent extensive thermal degradation.

The isothermal crystallization of PBT, PBT/PC, and PBT/PC/PTW blends were performed as follows: the samples were heated at 20°C/min from 20°C to 250°C and kept for 3 min to eliminate any previous thermal history; then they were cooled at 150°C/min to the predetermined crystallization temperature \( T_c \), and maintained at \( T_c \) for 15 min necessary for DSC trace return to the calorimeter baseline.

The nonisothermal crystallization process of PBT, PBT/PC, and PBT/PC/PTW blends were performed as follows: the samples were heated at 20°C/min from 20°C to 250°C and kept for 3 min to eliminate the thermal history before cooling at a specified cooling rate. The samples were then cooled to 20°C at constant cooling rate of 2.5, 5, 10, 20°C/min. The exothermal curves were recorded.

Nonisothermal crystallization parameters

From the DSC curves of samples crystallized from the melt state at a given cooling rate, some useful parameters can be obtained to describe the nonisothermal crystallization [28-30]

![Nonisothermal crystallization parameters](image)

**Fig. 11.** Schematic representation of all the parameters of crystallization during the nonisothermal crystallization process.

These parameters are defined as following and illustrated in Figure 11.

1. The peak temperature of crystallization \( T_p \), the temperature at which the value of the heat flow is maximum.
(2) The quantity \(T_{\text{onset}} - T_p\), where \(T_{\text{onset}}\) is the temperature at the intercept of the tangents at the baseline and the high-temperature side of the exotherm.

(3) The initial slope of the exotherm \((S)\), the slope at inflection on the high-temperature side of the exotherm.

(4) The width at half-height of the exotherm peak \((\Delta W)\) determined after normalization of the peak to a constant mass of the samples.

The parameter \(S\) is a measure of the rate of nucleation. The parameter \(T_{\text{onset}} - T_p\) is a measure of the overall rate of crystallization. The smaller \(T_{\text{onset}} - T_p\) is, the greater the crystallization rate is. \(\Delta W\) is a measure of the crystallite size distribution. The smaller \(\Delta W\) is, the narrower the crystallite size distribution is.

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