

# The crystallization characteristics of polypropylene and low ethylene content polypropylene copolymer with copolyesters

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## Abstract

The crystallization characteristics of polypropylene (PP) and low ethylene content PP copolymers with and without nucleating agents were studied by differential scanning calorimetry (DSC). PP and PP copolymers was blended with three different kinds of co[poly(butylene terephthalate-*p*-oxybenzoate)] copolyesters, designated B28, B46, and B64, with the copolyester level varying from 5 to 15 wt.%. All samples were prepared by solution blending in hot xylene solvent at 50 °C. The crystallization behavior of samples was then studied by DSC. The results indicate that these three copolyesters accelerate the crystallization rate of PP and PP copolymers in a manner similar to that of a nucleating agent. The acceleration of crystallization rate was most pronounced in these blend systems with a maximum level at 5 wt.% of B28. The observed changes in crystallization behavior are explained by the effect of the composition and the amount of copolyester in the blends. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Crystallization rate; Copolyester; Blend; Liquid crystalline polymer

## 1. Introduction

Polypropylene (PP) has many advantages as a matrix resin for thermoplastics composites owing to its relatively low cost and high chemical resistance coupled with ease of fabrication. A major limitation of PP is that its glass transition is below room temperature, consequently its dimensional stability is limited. Copolymerization of propylene with other olefins to improve the impact properties of PP is a useful method for PP modification. Random or block propylene copolymers with low content ethylene are commercially extremely important since they improve impact properties of PP with seriously detracting from other desirable properties [1–3].

The crystallization behavior of these copolymers will change owing to the existence of ethylene sequence resulting in the decrease of structural regularity of copolymer. Usually, the overall crystallization rate of these

copolymers is depressed, which may affect their mechanical properties and their cycle time of fabrication processes. Efforts to alleviate this problem have included the addition of nucleation agents to these modified PP to increase the crystallization rate. For a modified polymer material, monitoring the change of its crystallization rate brought about by a modifier such as comonomers in copolymers or another component in a blend system is particularly important.

The kinetics of crystallization in PP with nucleating agents has been thoroughly studied, mainly with regard to isothermal process [4–6]. The nonisothermal crystallization behaviors are reported in several literatures to describe nonisothermal crystallization kinetics. Based on the Avrami equation, Ziabicki [7,8] and Ozawa [9] have their theories, respectively, to treat the case where the substances crystallize in the nonisothermal conditions.

The crystallization can be increased by the addition of nucleating agents such as sodium benzoate and talc, which are two effective nucleating agents of PP homopolymer [10]. Three types of co[poly(butylene terephthalate-*p*-oxybenzoate)] copolyesters (POB–PBT) were synthesized according to the procedure reported in our

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previous study [11]. The crystallization rate of PET or PBT blend with these copolyester varying from 1 to 15 wt.% were accelerated [12,13]. Blends of PET with a liquid crystalline polymer, LCP60–80 (blend of LCP60 and LCP80 in 50/50 wt.%), at several compositions were studied by Sukhadia et al. [14]. They reported that the heat of fusion ( $\Delta H_f$ ) was seen to increase with increasing the LCP60–80 content. Other PET/LCP blends of PET/VLC (trade name Vectra A900) and PET/KLC (PHB/PET = 80/20 molar ratio) were studied by Sharma et al. [15]. VLC and KLC act like nucleating agents for PET crystallization and this effect probably reaches a maximum at a LCP level between 0 and 5 wt.%. In the range from 10 to 15 wt.%, VLC and KLC possibly destroy the symmetry of PET, thus resulting in the decreases in  $\Delta H_f$ ,  $\Delta H_c$ , and  $T_m$ . From these earlier results, it is seen that the crystallization behavior of PET blends is influenced by the composition and amount of the second component, chemical compatibility, and the degree of dispersion achieved in the mixing process.

In this study, we report the crystallization behavior of a commercial PP and PP copolymers resin blended with three types of co[poly(butylene terephthalate-*p*-oxybenzoate)] copolyesters (POB–PBT). The objective of this investigation was to elucidate the effects of composition and amount of the copolyester component on the PP crystallization behaviors.

## 2. Experimental

### 2.1. Materials

Three POB–PBT copolyesters, designated B28, B46, and B64, were synthesized according to the procedure reported in our previous study [11]. These copolyesters contain different POB/PBT molar ratios: 20/80 in B28, 40/60 in B46, and 60/40 in B64. PP and PP copolymers, designated PPB and PPR, were commercial products from the Taiwan Polypropylene Co. (Kaushon, Taiwan). Their characteristics are list in Table 1.

### 2.2. Blending method

The copolyester were added to solutions of PP and PP copolymers in 50 °C xylene. These solutions were

stirred for 3 h and then dried in a vacuum oven at 50 °C for at least one week. The pure PP and PP copolymers was also subjected to identical processing in the xylene solvent in order to nullify the effects of thermal history.

### 2.3. Differential scanning calorimetry

The dynamic crystallization was carried out in the sample pan of DuPont 2000 calorimeter with ~10 mg sample. Each sample was heated to from 30 to 200 °C at a heating rate of 10 °C/min under a nitrogen atmosphere, held for 3 min to destroy anisotropy, and then cooled at 10 °C/min to 30 °C. Both thermal and crystallization parameters were obtained from the heating and cooling scans.  $T_m$  was considered to be the maximum of the endothermic melting peak from the heating scans and  $T_c$  that of the exothermic peak of the crystallization from the cooling scans. The heat of fusion ( $\Delta H_f$ ) and crystallization heats ( $\Delta H_c$ ) were determined from the areas of melting peaks and crystallization peaks. The  $\Delta H_c$  and  $\Delta H_f$  are referred the whole blends. All results are the average of three samples.

## 3. Results and discussion

### 3.1. Melting and crystallization characteristics of PP and PP copolymers

The results of DSC heating and cooling scans for PP and PP copolymers are shown in Fig. 1(a) and (b), respectively. It is evident that there is a endothermic melting peak in all the heating scan, and there is a distinct exothermic crystallization peak in all the cooling scans. The various melting and crystallization parameters determined from heating and cooling scans for all blends are given in Table 2. It has been demonstrated that there is very little difference between PP homopolymer and PP block (PPB) copolymer in their onset temperature of melting,  $T_m$ ,  $\Delta T_m$  and  $\Delta H_c$ . The onset temperature of melting and melting peak width ( $\Delta T_m$ ) are related to the least stability and distribution of crystallites, respectively. These results indicate that the least stability, distribution and the perfection of crystallites in PP and PPB are comparable with each other. The other hands, the fact that the onset temperature of melting,  $T_m$  and  $\Delta H_f$  of PP random (PPR) copolymer are smaller than those of PP and the  $\Delta T_m$  of PPR are broader than that of PP reveals the perfection of crystallites of PP is better than those of PPR.

The crystallization peak temperature ( $T_c$ ) represents the temperature at maximum crystallization rate. These temperatures for PP and PPB are higher by 8–10 °C than that of PPR (101 °C). Changes in the heat of crystalli-

Table 1  
PP and PP copolymers samples and their characteristics

| Samples | Description         | Ethylene content (mol%) | MI (G/10 min) |
|---------|---------------------|-------------------------|---------------|
| PP      | PP homopolymer      |                         | 1.5           |
| PPB     | PP block copolymer  | 7.8                     | 5.2           |
| PPR     | PP random copolymer | 3.2                     | 1.7           |

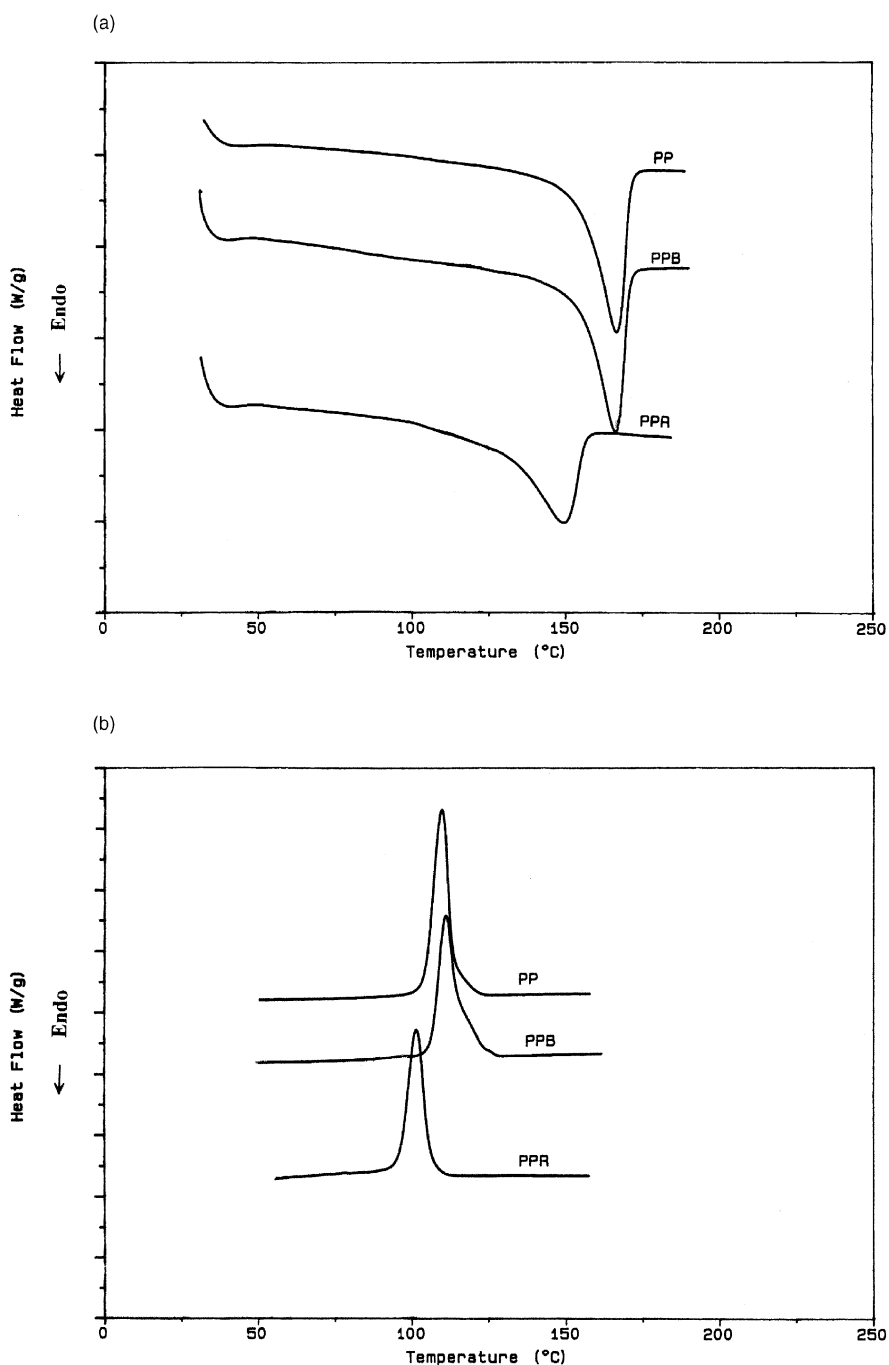


Fig. 1. DSC thermograms of PP homopolymer and copolymers: (a) heating scans and (b) cooling scans.

zation ( $\Delta H_c$ ) are related to the extent of crystallization. The values of  $\Delta H_c$  for PP and PPB are always larger than that of PPR (47.4 J/g). If the crystallization rate were defined as the heat of crystallization divided by time which is from the onset to completion of crystalli-

zation ( $\Delta H_c/\text{time}$ ). The crystallization rate for PP and PPB are greater than that of PPR (0.329 J/g/s). These results imply that the inclusion of ethylene unit in polypropylene chain results in the retardation of PP crystallization and lowering of its degree of crystallinity

Table 2  
DSC data of PP and PP copolymers

| Sample | Melting (from heating scans) |            |                   |                    | Crystallization (from cooling scans) |            |                   |                    |                                  |
|--------|------------------------------|------------|-------------------|--------------------|--------------------------------------|------------|-------------------|--------------------|----------------------------------|
|        | Onset (°C)                   | $T_m$ (°C) | $\Delta T_m$ (°C) | $\Delta H_f$ (J/g) | Onset (°C)                           | $T_c$ (°C) | $\Delta T_c$ (°C) | $\Delta H_c$ (J/g) | $\Delta H_c/\text{time}$ (J/g s) |
| PP     | 142                          | 167        | 34                | 49.1               | 123                                  | 109        | 25                | 61.2               | 0.408                            |
| PPB    | 142                          | 166        | 33                | 48.3               | 129                                  | 111        | 27                | 54.2               | 0.334                            |
| PPR    | 122                          | 150        | 40                | 35.5               | 114                                  | 101        | 24                | 47.4               | 0.329                            |

and crystallization rate in PP block and random copolymers.

### 3.2. Block polypropylene blended with 5 wt.% copolyester

There was a melting endothermic peak in heating scans, and there was only a distinct crystallization exothermic peak in the cooling scans like PPB as shown in Fig. 1(a) and (b) for PPB blends with 5 wt.% different copolyesters in the differential scanning calorimetry (DSC) thermograms. The melting and crystallization parameters are given in Table 3.

A shift in the crystallization onset temperature represents modification of the nucleation process. It is clear that the nonisothermal crystallization behavior of PPB is not altered significantly by blending with 5 wt.% copolyesters, in terms of the onset temperature of crystallization. The  $T_c$  for the blends are higher by 9–11 °C than that of pure PPB (111 °C). Changes in the crystallization peak width ( $\Delta T_c$ ) and the heat of crystallization ( $\Delta H_c$ ) are related to the overall crystallization rate and the extent of crystallization, respectively. The  $\Delta T_c$  for the blends are narrower by 6–9 °C than that of pure PPB (27 °C) and the values of  $\Delta H_c$  are always greater than that of PPB (54.2 J/g). The crystallization rate ( $\Delta H_c/\text{time}$ ) for all blends are greater than that of PPB (0.334 J/g s). In programmed cooling, the crystallization temperature reflects the overall crystallization rate due to the combined effects of nucleation and growth. Thus the degree of supercooling ( $\Delta T = T_m - T_c$ ) may be a

measurement of a polymer's crystallizability, i.e., the smaller the  $\Delta T$ , the higher the overall crystallization rate. The  $\Delta T$  for the blends are smaller by 10–11 °C than that of pure PPB (55 °C). These results reveals that the crystallization rate may be accelerated by blending with 5 wt.% copolyesters: e.g., B28, B46, and B64. Furthermore, the acceleration of PPB crystallization is most pronounced in the 95/5 PPB/B28 blend, because it exhibits the highest  $T_c$ , the narrowest crystallization width, the greatest  $\Delta H_c/\text{time}$  and the smallest  $\Delta T$  among all blends.

### 3.3. Composition effect by blending with different wt.% of B28 copolyester

To confirm the composition dependence of the crystallization of PP and PP copolymers in the blends, the PP/B28, PPB/B28 and PPR/B28 blends were subjected to further studies. Three compositions were prepared in weight ratios of 95/5, 90/10, and 85/15. There was a melting endothermic peak in all heating scans, and there was only a distinct crystallization exothermic peak in all the cooling scans like as shown in Fig. 1(a) and (b). The various melting and crystallization parameters are summarized in Table 4.

For the PP/B28 blends, the crystallization onset temperatures are higher by 7–8 °C than that of pure PP in all three compositions. The  $T_c$  are higher by 14–15 °C than that of pure PP (109 °C) and shows a maximum at ~5 wt.% (see Fig. 2). The  $\Delta H_c/\text{time}$  are always greater

Table 3  
DSC data of PPB and PPB blends with 5 wt.% different copolyesters

| Composition (95/5) | Melting (from heating scans) | Crystallization (from cooling scans) |            |                   |                    |                                  |                   |
|--------------------|------------------------------|--------------------------------------|------------|-------------------|--------------------|----------------------------------|-------------------|
|                    | $T_m$ (°C)                   | Onset (°C)                           | $T_c$ (°C) | $\Delta T_c$ (°C) | $\Delta H_c$ (J/g) | $\Delta H_c/\text{time}$ (J/g s) | $\Delta T^a$ (°C) |
| PPB                | 166                          | 129                                  | 111        | 27                | 54.2               | 0.334                            | 55                |
| PPB/B28            | 166                          | 130                                  | 122        | 18                | 58.1               | 0.538                            | 44                |
| PPB/B46            | 165                          | 132                                  | 121        | 21                | 55.6               | 0.441                            | 44                |
| PPB/B64            | 164                          | 129                                  | 120        | 22                | 54.3               | 0.411                            | 45                |

<sup>a</sup>  $\Delta T = T_m - T_c$ .

Table 4  
DSC data of PP and PP copolymers blends with different wt.% of B28

| Composi-<br>tion | Melting<br>(from heat-<br>ing scans) | Crystallization (from cooling scans) |            |                   |                    |                                  |                   |                         |
|------------------|--------------------------------------|--------------------------------------|------------|-------------------|--------------------|----------------------------------|-------------------|-------------------------|
|                  | $T_m$ (°C)                           | Onset (°C)                           | $T_c$ (°C) | $\Delta T_c$ (°C) | $\Delta H_c$ (J/g) | $\Delta H_c/\text{time}$ (J/g s) | $\Delta T^a$ (°C) | $\Delta H_{cc}^b$ (J/g) |
| <i>PP/B28</i>    |                                      |                                      |            |                   |                    |                                  |                   |                         |
| 100/0            | 167                                  | 123                                  | 109        | 25                | 61.2               | 0.408                            | 58                | 61.2                    |
| 95/5             | 165                                  | 131                                  | 124        | 18                | 64.8               | 0.600                            | 41                | 59.2                    |
| 90/10            | 166                                  | 131                                  | 124        | 18                | 59.6               | 0.552                            | 42                | 57.2                    |
| 85/15            | 165                                  | 130                                  | 123        | 19                | 58.7               | 0.515                            | 42                | 55.2                    |
| <i>PPB/B28</i>   |                                      |                                      |            |                   |                    |                                  |                   |                         |
| 100/0            | 166                                  | 129                                  | 111        | 27                | 54.2               | 0.334                            | 55                | 54.2                    |
| 95/5             | 166                                  | 130                                  | 122        | 18                | 58.1               | 0.538                            | 44                | 52.6                    |
| 90/10            | 166                                  | 131                                  | 122        | 17                | 53.8               | 0.527                            | 44                | 50.9                    |
| 85/15            | 166                                  | 131                                  | 122        | 18                | 56.4               | 0.522                            | 45                | 49.2                    |
| <i>PPR/B28</i>   |                                      |                                      |            |                   |                    |                                  |                   |                         |
| 100/0            | 150                                  | 114                                  | 101        | 24                | 47.4               | 0.329                            | 49                | 47.4                    |
| 95/5             | 149                                  | 123                                  | 113        | 20                | 49.0               | 0.408                            | 36                | 46.1                    |
| 90/10            | 149                                  | 122                                  | 113        | 21                | 49.1               | 0.390                            | 36                | 44.8                    |
| 85/15            | 149                                  | 122                                  | 112        | 21                | 48.5               | 0.385                            | 37                | 43.5                    |

<sup>a</sup>  $\Delta T = T_m - T_c$ .

<sup>b</sup>  $\Delta H_{cc}$ : computed  $\Delta H_c$ .

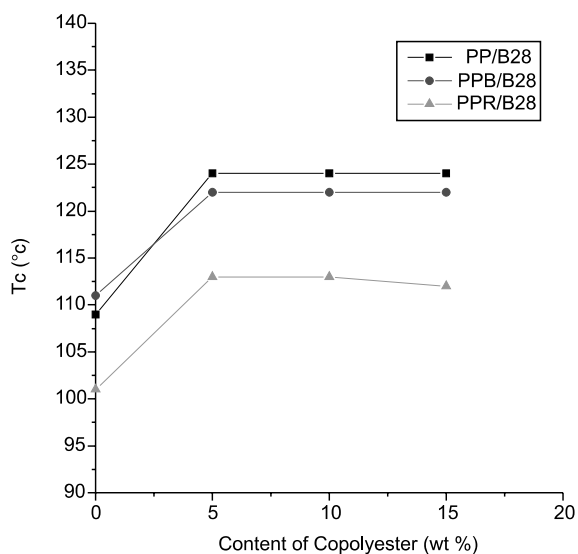


Fig. 2. Crystallization temperature of PP blends with 5–15 wt.% of B28 copolyester. The point at 0 wt.% corresponds to pure PP.

than that of pure PP and shows a maximum at ~5 wt.% copolyester (see Fig. 3). The  $\Delta T$  are smaller by 16–17 °C than that of pure PP (58 °C) and shows a minimum at ~5 wt.% copolyester (see Fig. 4). From the values of  $\Delta H_c$  for B28 is 21.5 J/g [16]. The computed value of  $\Delta H_c$  ( $\Delta H_{cc}$ ) by using the rule of additivity and after normal-

izing for their respective weight fractions varies with the blend composition as given in Table 4 (for instance  $\Delta H_{cc} = 59.2 = 61.2 \times 0.95 + 21.5 \times 0.05$  for 95/5 PP/B28 blend). PP/B28 blends exhibit a higher experimental  $\Delta H_c$  than those  $\Delta H_{cc}$  over the level of 5–15 wt.% of copolyester, indicating that PP is crystallized to a greater extent than expected, by blending with B28 at the level of 5–15 wt.%. These results reveal that the crystallization rate of PP was accelerated by blending with B28 at the level of 5–15 wt.%. The 95/5 PP/B28 blend exhibits a most significant acceleration of PP crystallization because it exhibits the highest  $T_c$ , the greatest  $\Delta H_c/\text{time}$  and the smallest  $\Delta T$  in the PP/B28 blends.

For the PPB/B28 blends, the crystallization onset temperatures are higher by 1–2 °C than that of pure PPB. The values of  $T_c$  are 122 °C for all three compositions and higher than that of pure PPB. The  $\Delta H_c/\text{time}$  are always greater than that of pure PPB and shows a maximum at ~5 wt.% copolyester (see Fig. 3). The  $\Delta T$  are smaller by 10–11 °C than that of pure PPB and shows a minimum at ~5 wt.% copolyester (see Fig. 4). The PPB/B28 blends exhibit a higher experimental  $\Delta H_c$  than those  $\Delta H_{cc}$  over the level of 5–15 wt.% of copolyester, indicating that PPB is crystallized to a greater extent than expected, by blending with B28 at the level of 5–15 wt.%. These results reveal that the crystallization rate of PPB was accelerated by blending with B28 at the level of 5–15 wt.%. The 95/5 blend exhibits a most significant acceleration of PP crystallization because it exhibits the greatest  $\Delta H_c/\text{time}$  and the smallest  $\Delta T$  in the PPB/B28 blends.

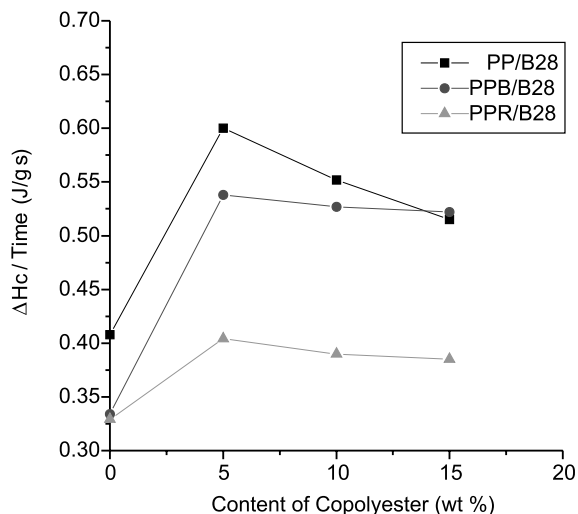


Fig. 3. The  $\Delta H_c/\text{time}$  (J/g·s) of PP blends with 5–15 wt.% of B28 copolyester. The point at 0 wt.% corresponds to pure PP.

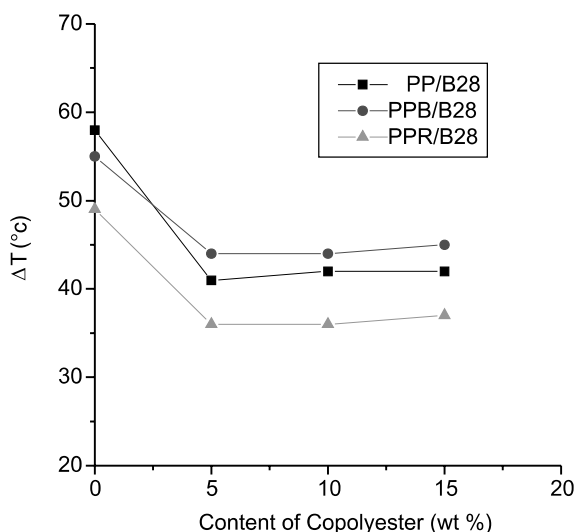


Fig. 4. The supercooling ( $\Delta T$ ) of PP blends with 5–15 wt.% of B28 copolyester. The point at 0 wt.% corresponds to pure PP.

For the PPR/B28 blends, the crystallization onset temperatures are higher by 8–9 °C than that of pure PPR. The  $T_c$  are higher by 11–12 °C than that of pure PPR and shows a maximum at ~5 wt.% copolyester (see Fig. 2). The  $\Delta T_c$  are narrower by 3–4 °C than that of pure PPR (24 °C). The  $\Delta H_c/\text{time}$  are always greater than that of pure PPR and shows a minimum at ~5 wt.% copolyester (see Fig. 3). The  $\Delta T$  are smaller by 12–13 °C than that of pure PPR and shows a maximum at ~5 wt.% copolyester (see Fig. 4). The PPR/B28 blends exhibit a higher experimental  $\Delta H_c$  than those  $\Delta H_{cc}$  over the

level of 5–15 wt.% of copolyester, indicating that PPR is crystallized to a greater extent than expected, by blending with B28 at the level of 5–15 wt.%. These results reveal that the crystallization rate of PPR was accelerated by blending with B28 at the level of 5–15 wt.%. The 95/5 blend exhibits a most significant acceleration of PPR crystallization because it exhibits the highest  $T_c$ , the greatest  $\Delta H_c/\text{time}$  and the smallest  $\Delta T$  in the PPR/B28 blends.

The crystallization rate of PP in PP homopolymer, block copolymer and random copolymer was accelerated by blending with B28 over the content range from 5 to 15 wt.%. This may be explained as follows: from the  $T_c$  of B28, B46, and B64 are 185, 164 and 154 °C [16], respectively. PP crystallizes in the presence of the solid state of these second component. It seems that the copolyesters content less than 15 wt.% may not destroy the symmetry of PP that result in the decrease of crystallization. But the dispersed copolyester, which exhibit high degree of molecular order of anisotropic phase even liquid crystalline (B46 and B64) increases the nucleating spot and accelerates the nucleation and growth process in a manner similar to that of a nucleating agent.

#### 4. Conclusions

It is known that the crystallization behavior of a polymer becomes modified in a blend because of the presence of the other component. The results of the present investigation clearly indicate that this modification depends on composition and amount of the second component. It was found that B28 copolyester accelerates the crystallization rate of PP and PP copolymers more significantly than the other samples, i.e. B46, and B64, when it is blending into PPB copolymers at a level of 5 wt.%. The crystallization rate of PP, PPB and PPR were accelerated by blending with B28 at the level of 5–15 wt.% and the 95/5 blend exhibits a most significant acceleration.

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