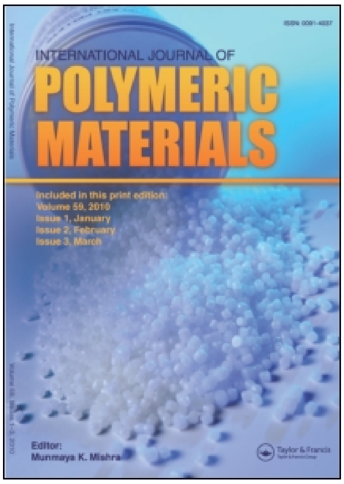

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Thermal Transitions of Polypropylene in Blends and Composites with Polypyrrole and Polypyrrole/Montmorillonite

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Thermal transitions of the semi-crystalline isotactic polypropylene, in polypropylene/polypyrrole blends and polypropylene/polypyrrole/montmorillonite composites, processed by two different ways, were investigated by differential scanning calorimetry. Glass transition temperature of polypropylene was found to remain unchanged at 269 K, whereas the crystallization rate was found to be higher in the blends and composites, which is explained in terms of increased concentration of extrinsic crystallization nuclei. The effect is larger in the materials processed by mixing and subsequent compression molding as compared to the materials prepared directly by compression molding. The degree of crystallinity of polypropylene did not show any systematic variation with composition, whereas it is slightly higher for the samples prepared by direct compression molding, being in the range of 50–59%. The polypropylene in the blends and the composites crystallizes in the stable α form, whereas metastable crystallites of the β form were observed as a minor component, depending on the thermal history of the samples. The results are discussed on the basis of the picture emerging from morphological studies.

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Keywords: crystallization rate, differential scanning calorimetry, montmorillonite, polypropylene, polypyrrole

INTRODUCTION

The main objective of the formation of polymer blends or composites is to prepare new polymeric materials with interesting combinations of physical properties. Conductive polymer materials have been obtained by blending polypyrrole with polypropylene [1]. Recently the preparation of composites containing a nearly constant amount of montmorillonite in a polypropylene matrix and variable amount of polypyrrole has been reported. The presence of montmorillonite was found to increase the conductivity, as compared to the polypropylene/polypyrrole blends [2]. Electrical conductivity in both blends and composites was found to be influenced by the way of material processing, which results in different final morphology.

The glass transition of the polymer matrix in polymer composites is affected by the presence of and interactions with the filler and its investigation may provide significant information on polymer–filler interactions and on morphology. The same is true also for the crystallization and melting transitions in semi-crystalline polymer matrices [3].

In the polypropylene matrix blends and composites the crystallization process, the degree of crystallinity and the crystalline morphology of the polymer may be influenced by the presence of the additional components, and/or the way of material processing. The crystallization of polypropylene was found to accelerate in blends with random ethylene-propylene copolymer [4], styrene-ethylene-butylene-styrene copolymer [5] and poly(vinylidene fluoride) [6], and in composites with single wall carbon nanotubes [7], montmorillonite [8–9] and in-situ prepared silica nanoparticles [10]. Reduction of the crystallization rate of polypropylene has also been reported by the addition of low and high density polyethylene [11–12], polystyrene [13], and organosilica [14]. The presence of additional components in polypropylene matrix has been found to influence also the polymorphism of polypropylene. Enhancement, reduction, or no formation of the β form of isotactic polypropylene, depending on the morphology, has been found in composites with single wall carbon nanotubes, montmorillonite, and glass beads [7–9,15], whereas in the article published by Menyhard et al. [16] the influence of a second polymer on the β form of polypropylene was reported. Because the crystalline structure plays a significant role for most physical and mechanical properties of semi-crystalline polymers, a study of crystallization phenomena is of great importance.

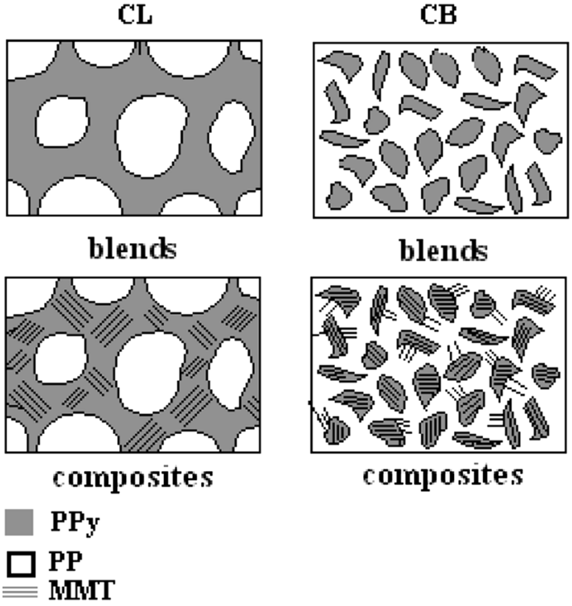
In the present study differential scanning calorimetry (DSC) was employed to investigate thermal transitions of the semi-crystalline isotactic polypropylene matrix in polypropylene/polypyrrole blends and polypropylene/polypyrrole/montmorillonite composites. The results are discussed in correlation to the morphological characterization of those new types of materials [2].

EXPERIMENTAL

Materials

Polypropylene/polypyrrole (PP/PPy) blends and polypropylene/montmorillonite/polypyrrole (PP/MMT/PPy) composites were prepared by oxidative polymerization of pyrrole in the presence of PP, or PP and MMT, respectively. Ferric chloride was used as oxidant, whereas PP or PP and MMT, in the case of blends and composites, respectively, were suspended in an aqueous solution of pyrrole in presence of the anionic surfactant dodecylbenzenesulfonic acid (DBSA). The montmorillonite content and the amount of conductive polypyrrole were varied in the range of 4.5–4.0 wt% and 4.8–16.7 wt%, respectively. The preparation of the samples has been described in detail elsewhere [1–2]. PP was treated in the same way as composite samples. PP powder was dispersed in water/DBSA solution, followed by filtration and drying. The blends and the composites were processed by two ways: (a) by compression molding after addition of stabilizers at 453 K for 2 min (code CL), or (b) by melt mixing in a 30 ml cell of the Plasti-Corder kneading machine PLE 330 (Brabender, Germany) at 463 K, 75 rpm for 10 min with stabilizers, and then by compression molding (code CB). The blends and the composites are named PP/XPPy and PP/XPPy/YMMT, respectively. X and Y denote the amount of PPy and MMT in weight percent, respectively.

Results of morphological characterization [2] showed that the final morphology of the prepared materials is significantly affected by the method of processing. Direct compression molding of the samples results in formation of agglomerates and a very inhomogeneous distribution of polypyrrole or polypyrrole/montmorillonite particles in the polypropylene matrix in the blends and composites, respectively. After melt processing the polypyrrole phase is homogeneously distributed in the blends in the form of small islands, whereas in the composites mixing results in a break up of large agglomerates and in a more homogeneous distribution of the montmorillonite layers (covered by



SCHEME 1 Schematic representation of the morphology of the blends and composites studied.

polypyrrole) in the polypropylene matrix. In Scheme 1 the morphology of the studied materials is schematically presented.

Method

Samples of weight varying between 5 and 7 mg, measured with an accuracy of 10^{-4} g (Mettler), were sealed in aluminium pans and placed in the sample holder of a differential scanning calorimeter (model Pyris 6, Perkin Elmer). Nonisothermal and isothermal measurements were performed. In both cases the samples were heated to 463 K at a rate of 20 K/min to erase their thermal history and eliminate any crystalline phase initially present in the sample. For the non isothermal measurements samples after holding for 1 min at 463 K, were cooled at a rate of 20 K/min to 223 K and the heat flow versus temperature was recorded, where the crystallization and the glass transition were followed. The samples were subsequently heated at 463 K at a rate of 20 K/min and the heat flow versus temperature was recorded, where the glass transition and the melting were recorded. For the isothermal measurements the samples, after holding for 1 min at 463 K, were cooled at a rate of 40 K/min to the predetermined crystallization temperature, ranging from 388 K to 40 K for neat polypropylene and from 398 K to 403 K for the blends and the composites, where they were isothermally crystallized. The samples crystallized isothermally at each temperature were subsequently heated at 5 K/min to 463 K to follow the melting of the crystallites formed. All the experiments were performed in a nitrogen environment.

RESULTS: NONISOTHERMAL DSC EXPERIMENTS

Crystallization

In Figures 1 and 2 heat flow versus temperature, upon cooling with a rate of 20°K/min, is presented for the neat isotactic polypropylene, the blends and the composites prepared by mixing and compression

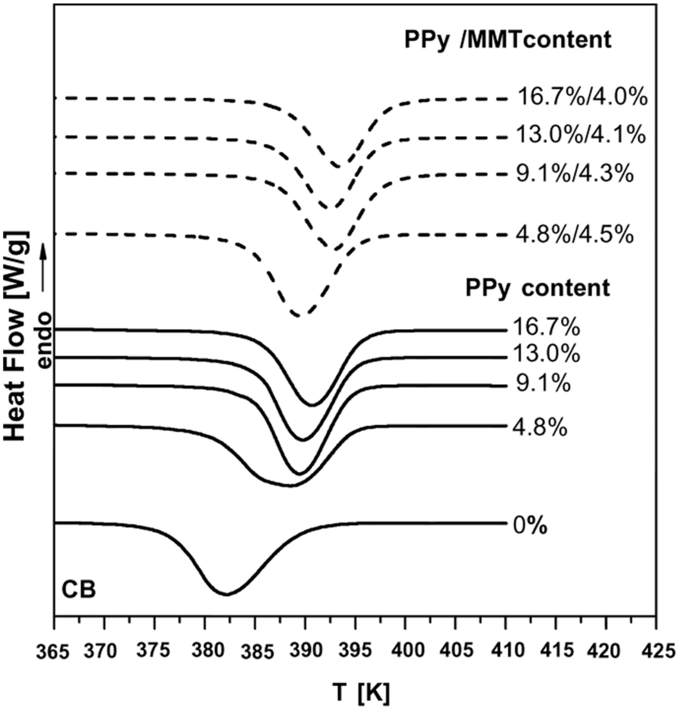


FIGURE 1 DSC thermograms in the region of crystallization of polypropylene for the samples prepared by mixing in Brabender and subsequent compression molding (CB), both blends and composites, arbitrarily shifted vertically (cooling rate 20°K/min).

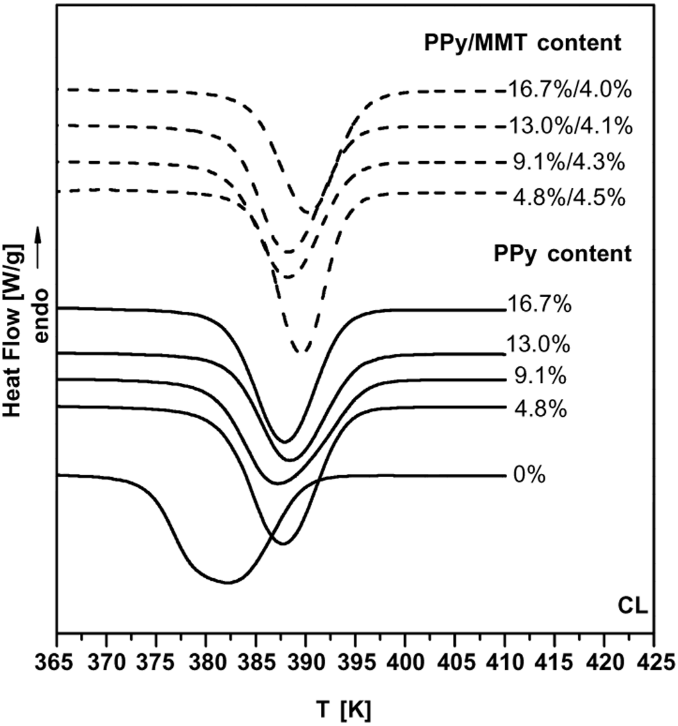


FIGURE 2 DSC thermograms in the region of crystallization of polypropylene for the samples prepared by direct compression molding (CL), both blends and composites, arbitrarily shifted vertically (cooling rate 20°K/min).

molding and by direct compression molding, respectively. The exothermic peak detected in all the samples is attributed to the crystallization of polypropylene. The peak is located at higher temperatures in the blends and the composites as compared to the neat polypropylene. A peak shift of 6 K is observed for the lowest content of polypyrrole (4.8%). The shift can be explained in terms of increased concentration of extrinsic crystallization sites at the interfaces between the polypropylene matrix and the polypyrrole or polypyrrole/montmorillonite lonite inclusions, in the blends and the composites, respectively. The effect is larger in the mixed and compression molded materials than in the direct compression molded. This can be understood considering the different final morphology achieved by the two different ways of preparation (Scheme 1). In the compression molded materials the interface between polypyrrole or polypyrrole/montmorillonite phase and the PP matrix is smaller, as polypyrrole covers polypropylene particles, while by mixing, polypyrrole or polypyrrole/montmorillonite phase is homogeneously distributed in the PP matrix, introducing larger interface. Generally, in the composites the crystallization peak is located at higher temperatures than in the blends.

In the blends processed by mixing and subsequent compression molding (Figure 1, solid lines) a slight shift of the peak with increasing polypyrrole content is observed. In the corresponding composites (Figure 1, dashed lines) less systematic variation of peak position with composition is detected, with the composites with polypyrrole content higher than 4.8% showing the peak at higher temperatures as compared to the corresponding blends. In the direct compression molded blends (Figure 2, solid lines) no composition dependence of peak position is observed (except for the shift to higher temperatures, as compared to neat polypropylene), whereas in the composites (Figure 2, dashed lines) the peak is observed at slightly higher temperatures than the blends, although without systematic shift with composition.

The crystallization peak is symmetric for all the samples, except for PP/4.8PPyCB and PPCB, and PP/9.1PPyCL, which show a shoulder at the low and high temperature side, respectively. The symmetry of the crystallization peak indicates a continuous size distribution of crystallites, whereas the double structure of the peak may reflect the existence of two populations of crystallites with different sizes formed during cooling. Excluding the materials mentioned earlier, the crystallization peak is narrower, whereas the slope of its initial portion is larger in the blends and composites as compared to that of neat polypropylene. In the blends and composites processed by mixing and compression molding narrower crystallization peak is observed as compared to that of the materials processed by direct compression molding.

If one considers the slope of the initial portion of the exotherm as an indication of the initial process of crystallization, nucleation (larger slope indicates faster nucleation), the result for the size distribution can be understood in terms of a faster nucleation, which results in almost simultaneous creation of most crystallites that subsequently grow to form a more uniform crystallite size distribution [17].

Melting

Figures 3 and 4 show the DSC melting endotherms upon heating the samples crystallized at a rate of 20 K/min, as described earlier. In all the samples an intense melting peak is detected, at 435–438 K. This peak corresponds to the melting of the stable α form crystallites,

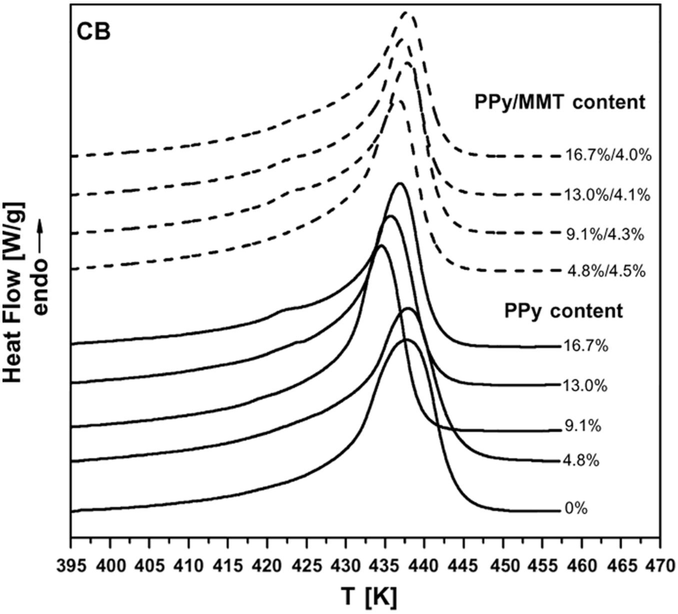


FIGURE 3 DSC thermograms during second heating of the samples prepared by mixing in Brabender and subsequent compression molding (CB), both blends and composites, arbitrarily shifted vertically (heating rate 20°K/min).

known to be formed in isotactic polypropylene [18–19]. The peak is located at the same or slightly lower temperatures in the blends and composites as compared to the neat polypropylene. Larger dispersion of melting temperatures is observed in the blends processed by mixing and compression molding as compared to the rest of materials, although without systematic variation with polypyrrole content. The shift of the melting peak at lower temperatures can be understood in terms of melting of smaller and/or less perfect crystallites in the blends and composites as compared to the neat polypropylene.

At the low temperature side of the main melting peak a shoulder peak is detected, located at 420–423 K, which corresponds to the melting of the metastable β form crystallites of polypropylene [18–19]. The shoulder is detected for all the blends and the composites processed by direct compression molding, even for the neat polypropylene, whereas for the mixed and compression molded materials it is detectable only for polypyrrole content higher than 4.8%. The shoulder is located at higher temperatures as compared to the neat polypropylene. The effect is larger for the composites.

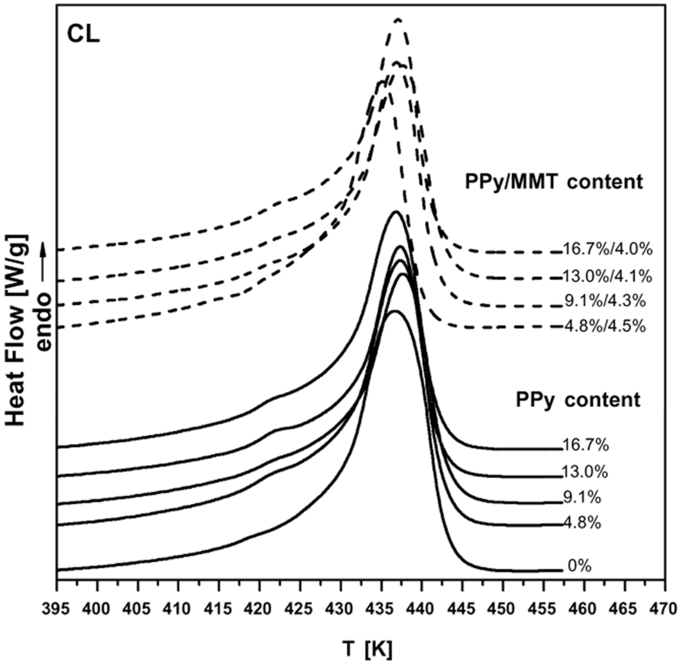


FIGURE 4 DSC thermograms during second heating of the samples prepared by direct compression molding (CL), both blends and composites, arbitrarily shifted vertically (heating rate 20°K/min).

The degree of crystallinity of α and β forms of polypropylene is calculated according to

$$X\% = \frac{\Delta H}{\Delta H_{\infty} w} \times 100 \tag{1}$$

where ΔH and ΔH_{∞} are the heat of fusion of the sample and of the completely crystallized one, respectively. The ratio of the heats of fusion is divided by w, the weight fraction of polypropylene in the sample, in order for the degree of crystallinity in the blends and composites be normalized to the polypropylene content.

No separate calculation of fusion heat of α and β phase was possible, so the total fusion heat was calculated by integrating the DSC thermogram from 395 to 455 K, whereas ΔH_{∞} was taken from the literature for the heat of fusion of the α form crystallites of polypropylene (major component), equal to 177 J/g [20]. No systematic variation of the degree of crystallinity with composition was observed, being in the range of 50–55% in the materials processed by mixing and subsequent compression molding, and 51–59% in the direct compression molded. Higher values were found for the direct compression molded materials as compared to the mixed and compression molded, even for the neat polypropylene.

The melting peak is narrower in the blends and composites as compared to the neat polypropylene, except for the samples showing double structure in the crystallization peak, already mentioned. The effect is larger for the materials processed by mixing and subsequent compression molding, however, without systematic variation with composition.

The step in heat capacity due to the glass transition of polypropylene is too weak, because of the high degree of crystallinity, and as a consequence a low fraction of amorphous polypropylene and determination of the glass transition temperature was possible only by differentiation of the signal. The glass transition temperature was found for all the samples to be 269 K, in the temperature range of the glass transition temperature reported for polypropylene (303–293 K, depending on the tacticity and thermal history of the sample) [21].

RESULTS: ISOTHERMAL DSC EXPERIMENTS

Crystallization

The heat flow versus time isotherms, at four crystallization temperatures, is shown in Figure 5 for the neat polypropylene processed by mixing and subsequent compression molding. The time $t = 0$ is taken as the time of the DSC oven stabilization. As may be observed in Figure 5, the time for complete crystallization increases with crystallization temperature.

As the temperature increases the induction period of crystallization increases, as a result of the increase of the nucleation barrier with decreasing supercooling. The temperature that was selected to observe the evolution of crystallization in all the samples was a result of a compromise between a full observation of crystallization and measurable heat flow signal. Figure 6 shows the heat flow versus time isotherms at 403 K for the neat isotactic polypropylene and the blends processed by mixing and subsequent compression molding and by direct compression molding. As can be seen in Figure 6, the time needed for the crystallization of polypropylene to be completed in the blends is much shorter than that for neat polypropylene. The induction time and the time for complete crystallization are larger in

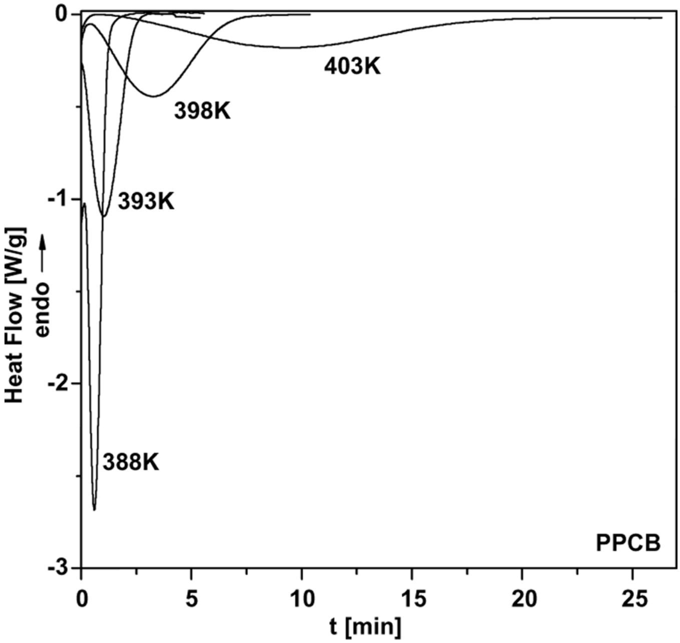


FIGURE 5 DSC thermograms during evolution of the crystallization process at four different temperatures for neat isotactic polypropylene processed by mixing in Brabender and subsequent compression molding, CB.

the direct compression molded materials as compared to the mixed. The time for complete crystallization is composition dependent for the mixed materials, decreasing with increasing polypyrrole content, although it seems to be independent of composition for the direct compression molded. Interestingly, the peak for PP/4.8 PPyCB and PP/9.1 PPyCL shows an asymmetric broadening at long times, in accordance with the double structure of the crystallization peak upon cooling at constant rate for the same materials, already mentioned (Figures 1 and 2). This can be understood in terms of the formation of crystallites of smaller size at longer times.

The isothermal data at 403 K were analyzed by means of the Avrami equation [20], which can be written as

$$X(t) = 1 - \exp(-kt^n) \tag{2}$$

where k is the kinetic growth rate constant (min^{-n}) and n is the Avrami exponent characteristic of the mechanism that controls the crystallization process, homogeneous/heterogeneous, in one or more dimensions.

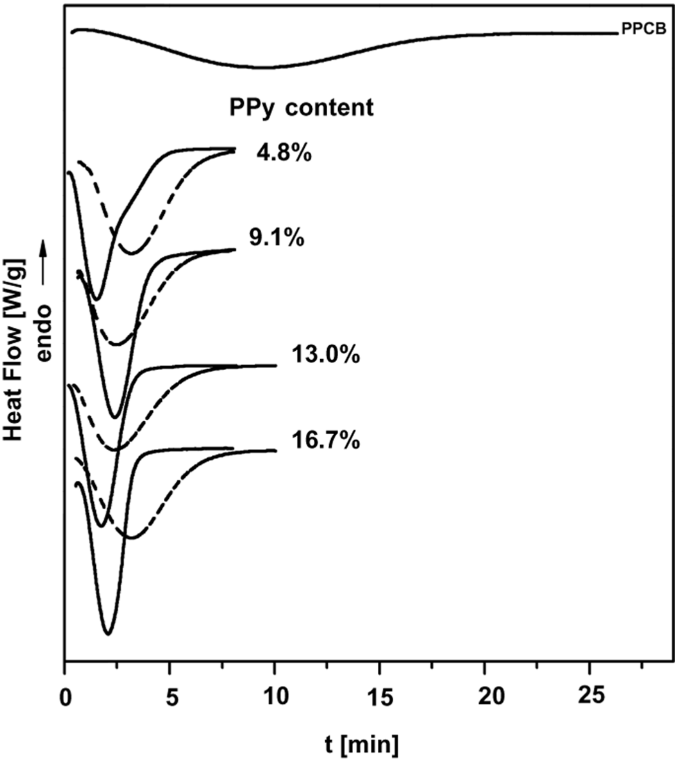


FIGURE 6 DSC thermograms during evolution of the crystallization process at 403°K for the mixed and compression molded, CB (solid line) and direct compression molded CL (dashed line) blends.

To evaluate properly the Avrami parameters it is necessary to register the complete crystallization peak. According to Figure 5, this condition is fulfilled at 403 K. At lower temperatures, the initial part of the crystallization peak is not observed because polymer crystallization starts before the temperature of the DSC oven is stabilized.

The normalized degree of crystallinity, $X(t)$, of the samples was determined from the heat flow versus time isotherms using the following equation

$$X(t) = \frac{X_t}{X_\infty} = \frac{\int_0^t \left(\frac{dH}{dt}\right)dt}{\int_0^\infty \left(\frac{dH}{dt}\right)dt} \tag{3}$$

where X_t and X_∞, are the weight fractions of crystalline polypropylene at times t and ∞, respectively.

The Avrami equation can be written also in a more convenient form for determination of the parameters k and n:

$$\ln\{-\ln[1 - X(t)]\} = \ln k + n \ln t \tag{4}$$

The half crystallization time $t_{1/2}$, which is defined as the time at which $X(t) = 0.5$ and is used to characterize crystallization rate, can be determined from the values of k and n by the expression:

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \tag{5}$$

The values of n and k, as well as the time of half crystallization, are listed in Table 1.

The values of n and k were calculated according to Eq. (4) as the slope and intersect of the linear fit in $\ln\{-\ln[1 - X(t)]\}$ vs. In t plot, respectively. The time of half crystallization, $t_{1/2}$, was calculated by Eq. (5), and, for comparison, as the time at which $X(t) = 0.5$.

Non integer values for the Avrami exponent, n, close to 3 were calculated for all the samples, except for the samples with 9.1 and 16.7% of polypyrrole processed by mixing and subsequent compression molding, for which values close to 4 were calculated. A value of 3 for the Avrami exponent indicates homogeneous growth of crystallites in three dimensions (spherulites), as has been reported by many authors for isotactic polypropylene, whereas the value 4 indicates heterogeneous growth in three dimensions [18]. The values determined for $t_{1/2}$ by the two ways described earlier are in excellent agreement,

TABLE 1 Parameters of Avrami Equation, Growth Rate Constant, k, and Exponent, n, and Time of Half Crystallization $t_{1/2}$ for the Isotherms at 403°K

Sample	k(min^{-n})	n	$t_{1/2}$(min)^a	$t_{1/2}$(min)^b
PPCB	0.0009	2.9	10	9.9
PP/4.8PPyCB	0.15	2.5	0.99	1.8
PP/9.1PPyCB	0.028	3.6	2.4	2.4
PP/13.0PPyCB	0.15	2.8	1.7	1.8
PP/16.7PPyCB	0.049	3.7	2.0	2.0
PP/4.8PPyCL	0.012	3.3	3.4	3.4
PP/9.1PPyCL	0.037	2.8	2.3	2.9
PP/13.0PPyCL	0.065	2.4	2.7	2.7
PP/16.7PPyCL	0.021	2.9	3.4	3.4

[a] Calculated by Eq. (5).

[b] t at $X(t) = 0.5$.

except for the samples PP/4.8PPyCB and PP/9.1PPyCL in which the value determined from n and k are lower than those calculated directly at $X(t) = 0.5$. This can be understood, if one considers the double structure of the crystallization peak detected for these samples. The time of half crystallization does not show any systematic variation with polypyrrole content in the blends; however, it is much lower than in neat polypropylene. In the meantime the values calculated for the mixed and compression molded materials are lower than those for the direct compression molded.

Melting

Figures 7 and 8 show DSC thermograms upon heating, with a rate of 5 K/min, the mixed and compression molded (solid lines, CB) and direct compression molded (dashed lines, CL) blends, which were isothermally crystallized at 398 and 403 K, respectively. At 398 K crystallites of the α and β form are created, which melt at 439 and 423 K, respectively. A symmetric melting peak at 439 K is observed in the direct compression molded materials, which is located at higher

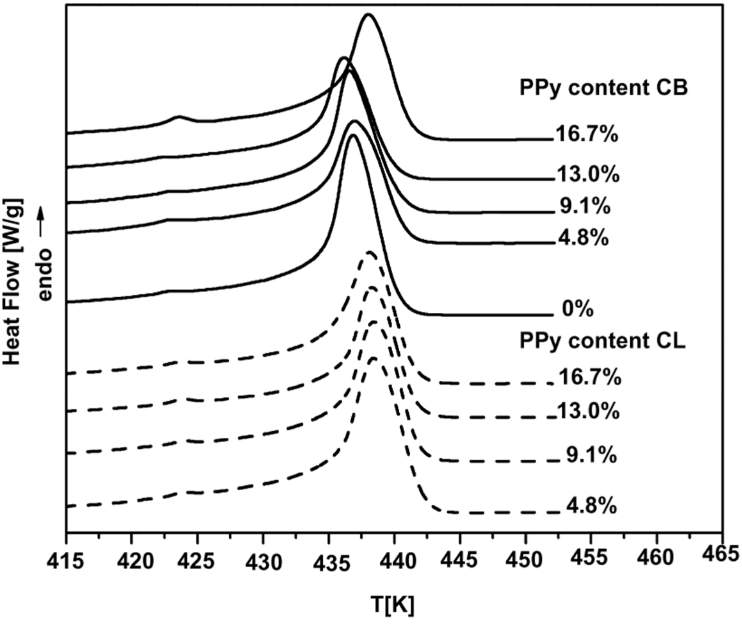


FIGURE 7 DSC thermograms during heating of the samples crystallized isothermally at 398°K (heating rate 5°K/min).

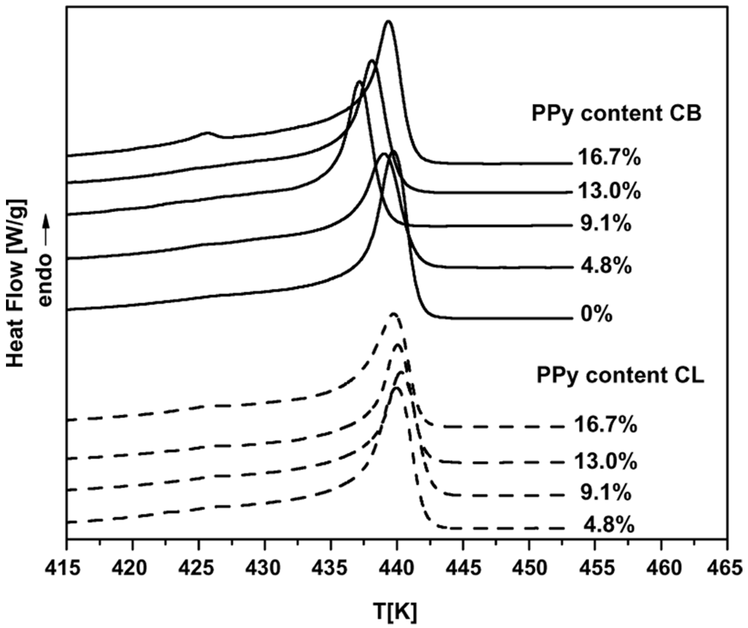


FIGURE 8 DSC thermograms during heating of the samples crystallized isothermally at 403°K (heating rate 5°K/min).

temperatures as compared to neat polypropylene and is composition independent. The main melting peak in the mixed blends shows a broadening at the high temperature side, which is attributed to the melting of crystallites formed after the recrystallization of the less ordered and/or smaller crystallites, melted a few degrees lower. Subsequent thermal treatment by a slow heating rate, here 5 K/min, allows crystallization to become more complete or may allow recrystallization of less stable crystals. In the mixed and compression molded blends the crystallites formed isothermally at 398 K melt at the same temperature as neat polypropylene does, except for PP/16.7PPy, which has a higher melting temperature. More perfect and/or larger crystallites are formed in the directly compression molded materials as compared to the mixed and compression molded, with the exception of PP/16.7PPyCB.

At 403 K crystallites of the α form are formed, except for the PP/16.7PPy, in which also melting of β form crystallites is clearly observed. Melting peaks are symmetrical (no recrystallization takes place) at almost the same position for the neat polypropylene and all the blends, except the mixed and compression molded blends with polypyrrole content of 9.1 and 13.0%, in which the melting peak is observed at lower temperatures.

DISCUSSION

Crystallization Rate

The overall crystallization rate increases in the blends and composites, processed by both ways: by mixing and compression molding and by direct compression molding, as compared to the neat isotactic polypropylene. This is indicated by the shift of the crystallization peak to higher temperatures (for the same cooling rate), in the non isothermal experiments (Figures 1 and 2), and to shorter times (for the same crystallization temperature), in the isothermal experiments (Figure 6), in the blends and composites as compared to the neat polypropylene. The crystallization rate may increase as a result of either enhanced nucleation rate or increased chain mobility. However, the crystallization rate is also dependent on temperature. The dependence is approximately parabolic, with zero value at the glass transition temperature T_g and at the melting temperature T_m, and maximum value at $T_{max} = (T_g + T_m)/2$ [22]. The presence of a second ingredient may affect the absolute value of T_g and/or T_m of the semi-crystalline ingredient, causing either an increase or a decrease of the crystallization rate, depending on the shift of T_{max} in relation to the isothermal crystallization temperature, T_i [22]. Chain mobility of polypropylene is not affected by the presence of the polypyrrole or polypyrrole/montmorillonite phase, as indicated by the glass transition temperature of polypropylene, found at 269 K for all the samples. The melting temperature is also not significantly affected. Thus, the increase of the overall crystallization rate in the blends and composites can be understood in terms of the increase of concentration of nuclei. Blending of polypropylene with polypyrrole or polypyrrole/montmorillonite results in the introduction of numerous new interfaces between the additional components and the semi-crystalline matrix.

Not all the interfaces can play a role as nucleation sites; only an interface that wets well with the semi-crystalline matrix (so that the crystalline chain can deposit on them) can cause heterogeneous nucleation. For isotactic polypropylene, an increase of crystallization rate was observed when mixed with styrene-ethylene-butylene-stryrene copolymer [5] or poly(vinylidene-fluoride) [6], although when mixed with low density polyethylene no such behavior was observed [11]. The interface between isotactic polypropylene and the polypyrrole or polypyrrole/montmorillonite sites can provide a nucleation center.

The area of the interface is dependent on the distribution of the additional components in the semi-crystalline matrix. In the blends and composites processed by mixing and compression molding, the polypyrrole or polypyrrole/montmorillonite phase is homogeneously distributed forming small islands within the polypropylene matrix introducing a larger interfacial area, whereas in the directly compression molded materials polypyrrole or polypyrrole/montmorillonite covers the polypropylene particles creating a smaller interfacial area. This could be an explanation for the higher overall crystallization rate observed in the blends and composites processed by mixing and compression molding as compared to those processed by direct compression molding. By increasing the amount of polypyrrole in the mixed and subsequently compression molded blends, the interfacial area becomes larger, as more islands of polypyrrole phase are formed, which results in an increase of crystallization rate with increasing polypyrrole content, as was observed. In the case of the direct compression molded materials the interfacial area remains almost unchanged as the addition of larger amounts of polypyrrole results only in a larger volume of polypyrrole phase, and this results in a constant crystallization rate, independent of polypyrrole content, observed in these materials.

Crystallites

Polypropylene within the blends and composites crystallizes in the stable α form. Crystallites of the unstable β form are observed for the blends and composites processed by mixing and compression molding with polypyrrole content higher than 4.8% and for all the samples processed by direct compression molding, even for neat polypropylene, when they are crystallized upon cooling at a constant rate of 20 K/min. However, the occurrence of the β form crystallites depends on the crystallization conditions and the composition. For example in polypropylene under compression the highest content of β form crystallites was found for isothermal crystallization at 393 K [23], whereas blends and composites can have their own optimal annealing temperatures for β crystal formation [15]. For the samples under investigation, the amount of β crystal within polypropylene in the polypropylene/polypyrrole blends is higher when they are crystallized at 398 K than in those crystallized isothermally at 403 K. However, for all the thermal treatments performed (cooling at constant rate of 20 K/min, isothermal crystallization at 398 and 403 K) the highest content of β form crystallites was found for the blends with high polypyrrole content.

The thermal history of the materials, which relates to the conditions of time and temperature under which they were crystallized and any subsequent thermal treatment, influences also the average size and the size distribution of crystallites. By reducing the crystallization temperature from 403 to 398 K the melting peak of α form crystallites shifts from 440 to 438 K, whereas the melting peak of β form shifts from 426 to 423 K. The effect is larger for the materials processed by mixing and subsequent compression molding. However, for all the thermal treatments performed the melting temperature of β form crystallites was found higher in the blends and composites than in neat polypropylene, indicating larger and/or more perfect β form crystallites in them.

The size distribution becomes narrower by reducing the crystallization temperature, as is indicated by the reduction of the width of the melting peak, as a result of the increase of nuclei concentration, which causes almost simultaneous creation of most crystallites that subsequently grow to form a more uniform crystallite size distribution. This gives rise to a morphology with a larger number of small (and of uniform size) crystallites. Independently of the thermal history, the materials processed by mixing and subsequent compression molding show a narrower size distribution of crystallites and a smaller average crystallite size suggesting morphology with a large number of small crystallites, whereas in the materials processed by direct compression molding small and large crystallites coexist. The double structure of the crystallization peak observed, in the nonisothermal and isothermal experiments, for the samples PP/4.8PPyCB, PPCB and PP/9.1PPyCL suggests the existence of two distinct populations of crystallites of different size. Similar results were also observed by Nowacki et al. in isotactic polypropylene based nanocomposites with montmorillonite [8].

The crystallites formed in the blends and composites are of spherulitic type, as indicated by the values of the Avrami exponent, as is also the case in neat polypropylene [18]. The crystallization takes place homogenously within the blends, except for those processed by mixing and subsequent compression molding with polypyrrole content 9.1 and 13.0%, in which heterogeneous crystallization takes place.

CONCLUSIONS

The thermal transitions of isotactic polypropylene in blends and composites with polypyrrole or polypyrrole/montmorillonite were studied by differential scanning calorimetry performing both nonisothermal and isothermal experiments.

Addition of polypyrrole or polypyrrole/montmorillonite into the polypropylene matrix introduces interfaces between them, which act as nucleation sites, resulting in an increase of crystallization rate. The interfacial area is dependent on the components and the distribution of the additional components in the semi-crystalline matrix. A different way of processing results in a different final morphology and so interfacial area, which has as a result in different crystallization rates. Higher acceleration of crystallization was observed in the mixed and compression molded materials, where the additional components are distributed in the polypropylene matrix forming small islands, as compared to the direct compression molded samples, where the polypyrrole phase forms large regions.

The degree of crystallinity and the size of crystallites formed within the polypropylene matrix are not significantly affected by the presence of the additional components. The polypropylene matrix crystallizes predominately in the α form, whereas as a minor component crystallites of β form are created, depending on the thermal history and material composition.

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