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Isothermal crystallisation of iPP/Vectra blends by DSC and simultaneous SAXS and WAXS measurements employing synchrotron radiation

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Abstract

The isothermal crystallisation behaviour and morphology of blends of isotactic polypropylene, iPP, and a liquid crystal polymer, Vectra A950, has been studied using differential scanning calorimetry, optical microscopy and simultaneous WAXS and SAXS in real-time measurements using synchrotron radiation. It has been observed that Vectra domains act as sites for the nucleation of iPP, and the rate of crystallisation is enhanced with increasing Vectra content in the blend. The presence of the α crystalline form in pure iPP, and both α and β forms for iPP in iPP/Vectra blends has been found. The SAXS patterns for iPP/Vectra blends containing β iPP are characterized by two different long period values that were related to the α and β lamellae. The secondary crystallisation mechanism has been investigated by SAXS/WAXS experiments. It is shown that, in contrast to primary crystallisation, secondary crystallisation of iPP is not affected by the presence of the thermotropic liquid crystalline polymer. As already known from pure iPP, the main process of secondary crystallisation is the growth of new lamellar stacks within remaining amorphous regions in the iPP spherulites.

Keywords: α-Polypropylene; β-Polypropylene; Liquid crystalline polymer

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1. Introduction

The solid state properties displayed by semicrystalline polymers are fundamentally defined by the crystalline morphology developed during the crystallisation process [1,2]. In polymer blends where one of the components is a semicrystalline polymer the presence of the second component has a considerable influence on the crystallisation process. This process is very complex since it is governed by many factors [3] such as the content of the second component, the degree of miscibility between components, the thermal history, the processing conditions, the degree of dispersion, etc. Thermotropic liquid crystalline polymers (LCP) have been used as the second component in blends with semicrystalline thermoplastics mainly because of their ability to enhance processing conditions by reducing the melt viscosity, and their reinforcement of the modulus and strength of the thermoplastic matrices [4–8]. From the literature [4,5,9–12], it can be deduced that these blends are usually two phase systems, since both polymers are generally immiscible or only partially miscible. Moreover, in some cases even small amounts of a thermotropic LCP can significantly affect the crystallisation process of the thermoplastic matrix [13–17].

One of the significant technological advantages of isotactic polypropylene is the relative ease with which its properties can be improved by the presence of additives. In this respect, LCP's are interesting fillers for iPP. This work deals with blends of iPP and a commercial thermotropic copolyester based on *p*-hydroxybenzoic acid and 2,6-hydroxynaphthoic acid (Vectra A950) as a minor constituent. Vectra has a nematic melt of low viscosity, excellent chemical resistance and thermal stability, and it has been used to reinforce conventional thermoplastics [4,5,18]. There are several reports on the influence of Vectra on the crystallisation behaviour of semicrystalline polymers. In these blends the presence of Vectra induces different nucleation mechanisms, e.g. in Nylon 6 [19,20] the anisotropic organization of the LCP plays an important

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role in the kinetics of the crystallisation process; the nucleation process could be initiated on the ordered state of the LCP despite the lack of well-developed three dimensional crystals. On the contrary, in poly(ethylene terephthalate) (PET) [21] delay in the crystallisation of the PET component has been found. The rate of crystallisation and the crystalline morphology are strongly determined by the presence of Vectra. Most work on iPP/Vectra blends [13,22,23] has studied the rheological and mechanical properties, and there is little data [24] on the crystallisation behaviour. It has been reported [25,26] that the internal organization of iPP spherulites is strongly disturbed by the presence of inclusions of the dispersed component.

Isotactic polypropylene exhibits several crystalline forms: monoclinic or α-form, trigonal or β-form and triclinic or γ-form, depending on specific crystallisation conditions. Varga [27] reports differences in the physical properties of α and β forms of iPP. In the crystallisation of iPP essentially the α modification occurs, but when selective β nucleating agents are present, the α modification may be accompanied by an amount of β. In the previous paper [28] we have reported the influence of the thermal history and content of the Vectra component on the polymorphic behaviour of iPP. It was shown that Vectra was able to nucleate both α and β forms. In order to understand the role of Vectra A950 on the development of the α and β microcrystalline structures in iPP a kinetic analysis of the primary and secondary crystallisation is essential. Whereas primary crystallisation of plain iPP has been extensively studied [27,29–31], there is little information on secondary crystallisation. Recently Kolb et al. [32] have analysed this process at low supercooling.

In the present paper a kinetic analysis of the primary and secondary crystallisation of iPP/Vectra A950 blends has been done. Changes in the crystallisation rate as well as crystal morphology, lamellar size and degree of crystallisation with time and crystallisation temperature as well as the LCP concentration, have been studied. The crystallisation experiments have been carried out by differential scanning calorimetry (DSC), optical microscopy and simultaneous wide-angle X-ray scattering (WAXS) and small-angle X-ray scattering (SAXS) using synchrotron radiation.

2. Experimental

The iPP, was a commercial grade provided by REPSOL-YPF in pellet form. This polymer had an isotacticity of 95% and a viscosity average molecular weight of 164.700. The characterization has been described elsewhere [33]. The LCP was Vectra A950, a wholly aromatic polyester type thermotropic mainchain LCP obtained from Hoechst Iberica S. A. This copolymer is based on *p*-hydroxybenzoic acid (73 mol%) and 2,6-hydroxynaphthoic acid (27 mol%). iPP/Vectra blends were prepared in a Minimax CS-183 MMX mixer equipped with a 4 cm^3 head. The temperature of blending was 290 °C for 4 min with a rotor speed of 50 rpm. The LCP content in the blends was of 0.5, 1, 2 and 5% by weight.

A Pyris 1 DSC instrument was used for thermal analysis. The DSC was calibrated using indium and zinc as standards. The weight of the samples was between 5 and 8 mg. All measurements were conducted under a nitrogen atmosphere. For isothermal crystallisation studies, the samples were first heated to 210 °C, and kept at this temperature for 5 min to eliminate the previous thermal and/or mechanical history. Then, the samples were quenched at 80 °C/min to the desired temperature, T_c, and maintained for the predetermined crystallisation time. The crystallisation curves were then recorded as a function of time.

The nucleation behaviour and crystalline morphology of iPP and iPP/Vectra blends were analysed by polarised light microscopy. A Leitz Aristomet microscope equipped with cross-polarizers and a Wild M46 photographic camera was employed. A Mettler FP80 programmable hot stage was used to control the temperature. The samples were prepared by melting the materials between a glass slide and a coverslip to obtain thin films, held for 5 min at 210 °C, and then cooled quickly to the crystallisation temperature, T_c.

Simultaneous wide and small angle X-ray patterns were recorded using synchrotron radiation at the polymer beam line at Hasylab, DESY, Hamburg. The details of the instrument are given elsewhere [34]. The synchrotron beam was monochromatized by Bragg reflection through a germanium single crystal, resulting in a wavelength of 0.15 nm, in order to focus the beam in the horizontal direction. Focusing in the vertical direction was achieved with a Ni-mirror. The SAXS and WAXS curves were detected with two linear Gabriel detectors. The SAXS detector was placed at a distance of 235 cm from the sample and was calibrated with the different orders of the long spacing of rat-tail cornea ($L = 65$ nm). The WAXS detector was placed to cover a 2θ range from about 10 to 32° and was calibrated with the crystalline diffraction peaks of PET. In order to consider the change of the intensity of the primary beam during the scattering measurements, the scattering intensity was divided by the intensity of the primary beam detected by an ionisation chamber in relative units. The background scattering obtained when no sample was present in the beam was subtracted from all measured experimental data after an appropriate correction for absorption.

3. Results and discussion

In the present study, the crystallisation kinetics of the iPP component in the iPP/Vectra blends was analysed from DSC data obtained under isothermal conditions. The thermal behaviour was analysed from the data obtained in a temperature interval ranging from 125 to 135 °C for all blend compositions studied. Fig. 1 shows DSC thermograms

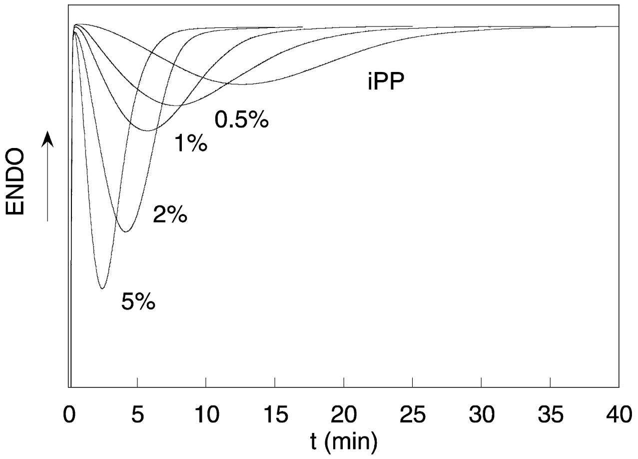

Fig. 1. DSC thermograms for iPP component in pure iPP and its blends with Vectra A950 isothermally crystallised at 129 °C.

of the isothermal crystallisation at 129 °C for pure iPP and iPP/Vectra blends. It can be seen that by increasing Vectra content in the blend the overall crystallisation time is significantly shorter. From this figure it is deduced that iPP crystallisation in the blends is completed before the crystallisation conversion of pure iPP had reached 30–95%. The morphological features of the iPP/Vectra blends have been previously studied by scanning electron microscopy, SEM [28]. It was found that blends consisted of two separate phases indicating that both polymers were immiscible, and the Vectra domains appear as spherical droplets in the iPP matrix. The size of these Vectra droplets varied between 1 and 25 μm. Consequently, it is suggested from the above results that the Vectra domains, present in the iPP matrix act as heterogeneous nucleating agents for iPP. The same behaviour was also observed at different crystallisation temperatures for all the iPP/Vectra blends.

The experimental data, for each T_c, have been analysed according to the equation proposed by Avrami [35–37]:

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

where $X(t)$ is the fraction of material crystallised after time t; k is a constant related to the rate of crystallisation and n defines the mechanism of crystallisation which depends on both the mode of nucleation and growth of crystals.

From the slope of the plot $\log(-\ln(1 - X(t)))$ against $\log t$ the values of n can be obtained. An Avrami exponent of 3 was obtained for pure iPP and did not vary significantly with the addition of Vectra for all the crystallisation temperatures. According to this value, the crystallisation for iPP component corresponds to heterogeneous nucleation with three-dimensional spherulitic growth. Similar values of n have been reported by several authors for pure iPP in a wide crystallisation temperature range [27,38–41].

The values of the constant of crystallisation rate (k), obtained according to equation (1), decreased exponentially with the crystallisation temperature for iPP component in all the samples studied. It was also found that k increased with the content of Vectra in the blend. Crystallisation rates of polymers can be expressed in terms of the half times of crystallisation, $\tau_{0.5}$, obtained from DSC crystallisation isotherms as the time for which $X(t) = 0.5$. Fig. 2 shows the changes in the half time of crystallisation of pure iPP and iPP/Vectra blends as a function of the crystallisation temperature. This figure clearly shows that $\tau_{0.5}$ increases exponentially with the temperature in all cases, and it is evident that the half time of crystallisation decreases monotonically with the increasing Vectra content in the blend. From the above results it can be concluded that Vectra A950 acts as a heterogeneous nucleating agent for iPP by providing nucleation sites. On increasing the Vectra content the number of nucleation sites and the crystallisation rate of iPP will be increased. However, the decrease of the half time of crystallisation in iPP/Vectra blends is much smaller than that observed for efficient nucleating agents of iPP as sorbitol derivatives [42–44] and an organic phosphate derivative [43] at similar concentrations.

The crystalline morphology obtained during the isothermal crystallisation process confirms the nucleation of iPP spherulites on Vectra domains dispersed in the polymeric matrix. Fig. 3 shows a polarised light microphotograph of iPP/Vectra (95/5) blend after isothermal crystallisation at 129 °C for 3 min. In this figure it can be clearly seen the Vectra domains dispersed in the polymeric matrix and the growing iPP spherulites. The microphotographs demonstrate that the crystallisation of spherulites of iPP can be nucleated by the surface of the Vectra domains, and it can be concluded that Vectra is a weak or moderate nucleating agent since a considerable proportion of the liquid crystal polymer domains do not appear to promote the nucleation of iPP spherulites. This effect was observed for all iPP/Vectra blends in the present study. Polarised light microphotographs after isothermal crystallisation at 125 °C for pure iPP, and blends of iPP/Vectra (99/1) and (95/5) are shown in Fig. 4, where it can be observed that on increasing

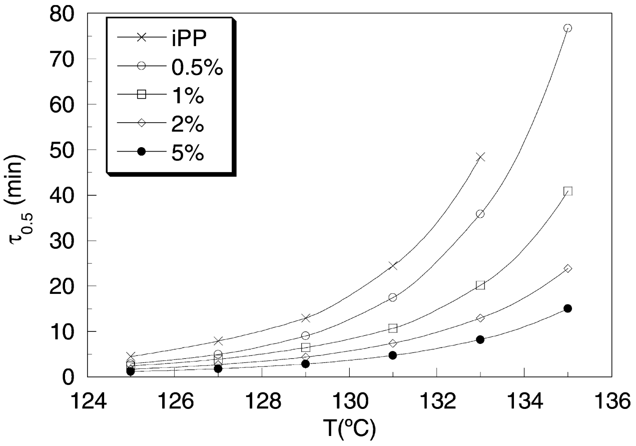

Fig. 2. Representation of $\tau_{0.5}$ versus crystallisation temperature for pure iPP and its blends.

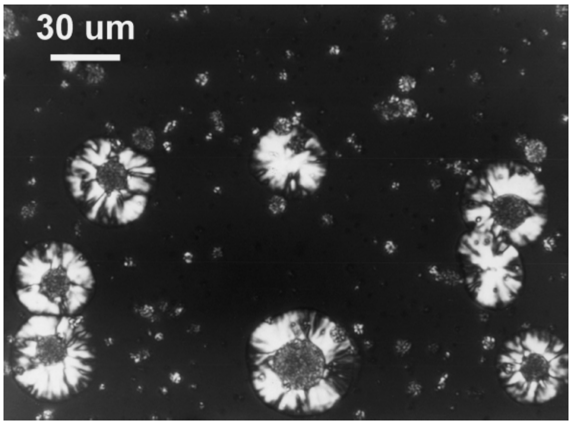

Fig. 3. Polarised light microphotographs of the isothermal crystallisation of the iPP/Vectra (95/5) blend crystallised at 129 °C for 3 min.

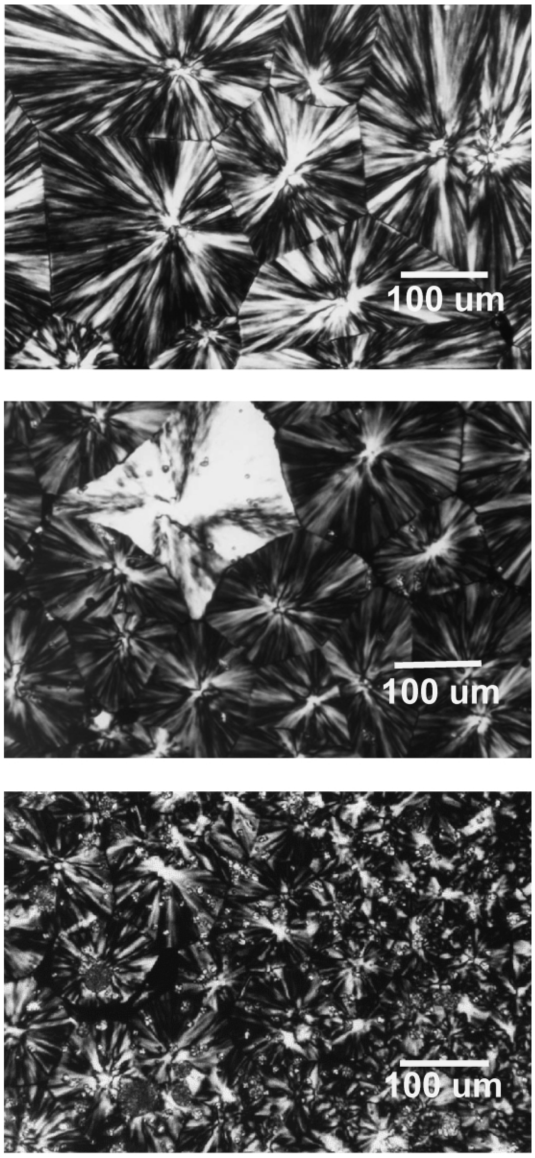

Fig. 4. Polarised light microphotographs after isothermal crystallisation at 125 °C of the: (a) pure iPP, (b) PP/Vectra (99/1) blend and (c) PP/Vectra (95/5) blend.

the Vectra content in the blend the number of crystallites was significantly increased and their size reduced.

The radial growth rate of α iPP spherulites for pure iPP and its blends was investigated at different isothermal crystallisation temperatures by polarised optical microscopy. Fig. 5 represents the spherulitic radius versus the crystallisation time for pure iPP and iPP/Vectra (99/1) and (95/5) blends crystallised at 129 °C. From this figure, it can be deduced that the spherulitic growth rate at a particular isothermal crystallisation temperature is not influenced by the presence of the LCP. The same behaviour also occurred at other temperatures, and thus it can be concluded that the spherulitic growth only depends on the isothermal crystallisation temperature. From the above results it is deduced that the increase observed in the overall crystallisation rate for the blends is related to an increase in the nucleation density due to the nucleation ability of Vectra domains present in the polymeric matrix and it is not related to a variation of the radial growth rate of the α spherulites since it is not affected by Vectra. The same behaviour has been reported for iPP with other nucleating agents by several authors [45–48].

Other crystallisation characteristics of pure iPP and iPP/Vectra blends were analysed by X-ray diffraction. Simultaneous SAXS and WAXS measurements were performed during isothermal crystallisation using synchrotron radiation. Fig. 6 shows the evolution of the WAXS and SAXS patterns during the isothermal crystallisation of iPP/Vectra (99/1) blend at 121 °C. In Fig. 6a the recorded WAXS intensity, $I(2\theta)$, is presented. Fig. 6b shows the SAXS intensity after Lorentz correction, $I(s)s^2$ versus the modulus of the scattering vector, $s = (2/\lambda)\sin(\theta/2)$, with λ being the wavelength of radiation and θ being the scattering angle. Progress of crystallisation can be observed from both the evolution of a long period peak in the SAXS and the growth of crystalline reflections on the amorphous halo of the WAXS.

The WAXS patterns obtained after isothermal crystal-

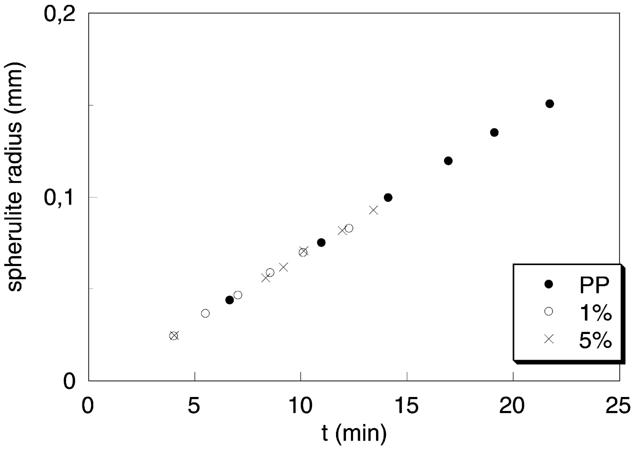

Fig. 5. Spherulite radius as a function of crystallisation time for pure iPP and iPP/Vectra (99/1) and (95/5) blends isothermally crystallised at 129 °C.

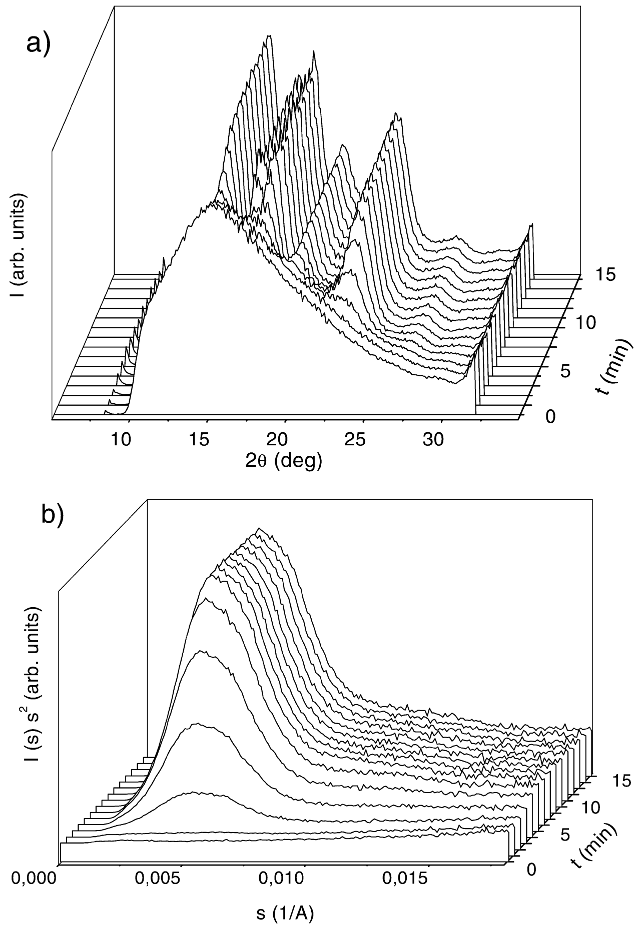

Fig. 6. Development of WAXS and SAXS during isothermal crystallisation of iPP/Vectra (99/1) blend at 121 °C: (a) WAXS, and (b) SAXS.

lisation of pure iPP and its blends showed the presence of one or two crystalline forms. The characteristic reflections of the α form of iPP can be found at scattering angles 2θ of 14° (1 1 0), 17° (0 4 0), 18.5° (1 3 0), 21° (1 1 1) and 22° $(\bar{1}\ 3\ 1)$ and (0 4 1) [49] for all the samples. However, for iPP/Vectra (99.5/0.5), (99/1) and (98/2) blends the β form was also obtained. The β form is characterized by reflections at 2θ 16° (3 0 0) and 21° (3 0 1) [49]. On the other hand, pure iPP and the iPP/Vectra (95/5) blend only showed crystalline reflections corresponding to the α form. The disappearance of β crystalline form for iPP/Vectra (95/5) blend was discussed in a previous paper [28]. This behaviour may be explained due to the higher density of Vectra domains present at higher PCL concentrations and to the lower β nucleation rate, although once nucleated β spherulites grow faster than α ones [50,51]. Then, higher density of α nuclei is obtained at the early stage of the crystallisation for iPP/Vectra (95/5) blend and the growing fronts of the α spherulites could enclose other Vectra domains, of which, some would have nucleated β spherulites and therefore less β content was obtained after complete crystallisation. In Fig. 7 WAXS diffraction patterns for pure iPP and iPP/Vectra (99/1) and (95/5) after isothermal crystallisation at 125 °C are shown. In the case of the iPP/Vectra (99/1) blend a strong reflection can be observed near 2θ 16° which corresponds to β form of iPP. From the WAXS patterns of the blends, the relative proportion of the β form was calculated using the Turner–Jones parameter [46], k_β, which is given by:

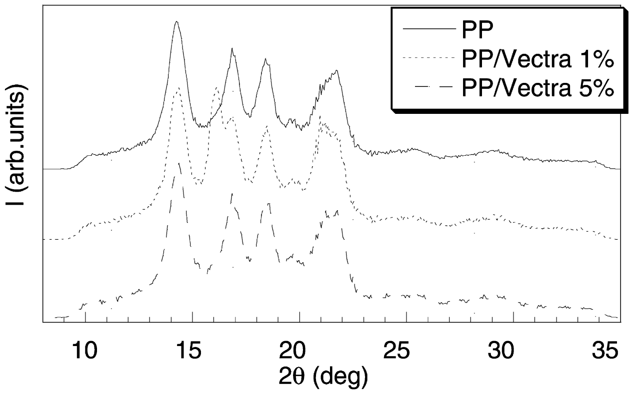

Fig. 7. Wide angle X-ray scattering patterns for iPP and iPP/Vectra (99/1) and (95/5) blends obtained after isothermal crystallisation at 125 °C.

$$k_\beta = [I_{\beta 1}/[I_{\beta 1} + (I_{\alpha 1} + I_{\alpha 2} + I_{\alpha 3})]] \tag{2}$$

where $I_{\beta 1}$ is the intensity of the (3 0 0) reflection of the β phase and $I_{\alpha 1}$, $I_{\alpha 2}$ and $I_{\alpha 3}$ are the intensities of the (1 1 0), (0 4 0) and (1 3 0) reflections of the α modification, respectively. Depending on the crystallisation temperature, different k_β values were obtained for each blend. For iPP/Vectra (99.5/0.5), (99/1) and (98/2) blends k_β varied from 0.09 to 0.20, 0.11 to 0.22 and 0.09 to 0.13, respectively.

From the position, $s_{\max}$, of the strong SAXS long period peak in Fig. 6b it is possible to determine an average long period, $L = 1/s_{\max}$. This repeat is related to the distance between adjacent crystalline lamellae. Fig. 8 shows the long period values obtained for pure iPP and its blends with Vectra during isothermal crystallisation at 121 °C as a function of the crystallisation time. A slight decrease in the value of the long period with crystallisation time is observed

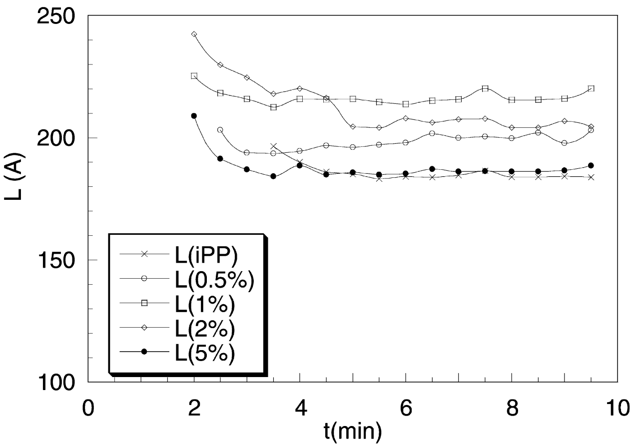

Fig. 8. Change of the long period values against crystallisation time for pure iPP and its blends with Vectra during isothermal crystallisation at 121 °C.

for the samples. A decreasing long period during the course of crystallisation has frequently been related to the obvious fact of increasing crystallite population [52–56], or to the perfectioning of lamellae with respect to local defects, flatness and extension [57,58]. A decision cannot be made on the basis of simple analysis of peak position, but requires advanced method of SAXS data analysis that is beyond the scope of this paper and considers the distribution of long periods [59]. An application to the crystallisation of polymers has recently been published by García et al. [60]. Furthermore, as can be seen in this figure the long period values for iPP/Vectra (99.5/0.5), (99/1) and (98/2) blends are larger than those corresponding to the long period of pure iPP, whereas for the iPP/Vectra (95/5) blend the value of *L* is similar to that of pure iPP. It becomes clear from the comparison between WAXS and SAXS results that for the iPP/Vectra blends containing the β crystalline form, the long period value obtained after isothermal crystallisation is higher.

It is well known that the β crystalline form has a lower melting temperature than the α form. Therefore, we have heated isothermally crystallised samples in order to analyse the effect of the β phase on the value of the long period. The variation of the long period with temperature during heating for pure iPP and iPP/Vectra (99/1) and (95/5) blends crystallised isothermically at 121 °C, is illustrated in Fig. 9. It was found that the long period increased on increasing temperature for all the samples. According to Hsiao et al. [55] this behaviour could be related to the thermal expansion of both crystalline and amorphous components on increasing temperature and also to melting of the thinnest lamellae formed during the isothermal crystallisation process, leaving behind the thicker lamellae in stacks, resulting in an increase of the long period. As can be seen in this figure, the long period values for plain iPP and the iPP/Vectra (99/1) blend were found to converge at about 150 °C. This value of the temperature is in good agreement with the melting temperature for the β crystalline form obtained from separate DSC thermograms under the same experimental conditions.

As seen earlier, the WAXS patterns showed the crystalline modifications obtained for the samples after crystallisation process. Time-resolved WAXS patterns for an iPP/Vectra blend containing α and β modifications during heating permits the analysis of the melting behaviour of each crystalline form. Fig. 10 shows time-resolved WAXS patterns for the iPP/Vectra (99/1) blend during heating at 5°/min after isothermal crystallisation at 121 °C. The characteristic reflection at 2θ 16° which corresponds to the β form can be clearly seen at 121 °C. On increasing temperature, at 141 °C the intensity of this reflection decreased, disappearing at around 150 °C. This melting value for the β crystalline form is in good agreement with that obtained by DSC and SAXS. Thus, the decrease of the long period at about 150 °C seems to be related to melting of the β modification, and it can be concluded that the higher *L* value for iPP/Vectra (99/1) blend with regard to *L* for pure iPP was due to the presence of the β crystalline form obtained during the isothermal crystallisation process. Fig. 9 also shows the variation of the long period with temperature for the iPP/Vectra (95/5) blend. From the WAXS curve for this blend only the reflections of the α crystalline form were found. In this case, the variation of *L* with the temperature was similar to the variation for pure iPP. These results suggest that the *L* values for iPP and its blends with Vectra and the variation of the long period with the temperature for the melting process are related to the presence of α and β forms in each sample. Taking into account that the crystallisation of α and β spherulites probably takes place in independent stacks, it

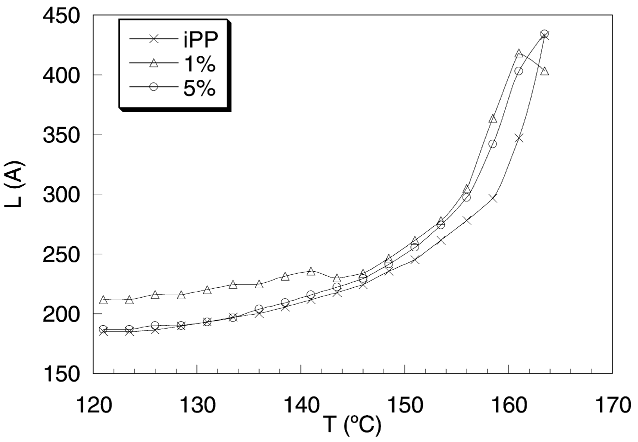

Fig. 9. Variation of the long period values versus temperature for pure iPP and iPP/Vectra (99/1) and (95/5) blends during heating at 5°/min after isothermal crystallisation at 121 °C.

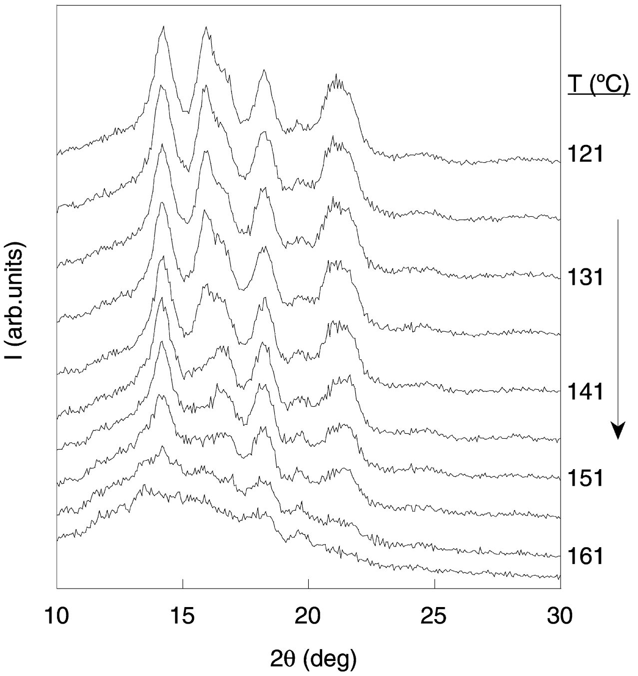

Fig. 10. Change of WAXS intensity for iPP/Vectra (99/1) blend during heating at 5°/min after isothermal crystallisation at 121 °C.

can be expected that two types of lamellar stacks were formed during the isothermal crystallisation process. It could be assumed that the long period for α form in the blends, which have both crystalline forms, has the same value of L as in the pure iPP, which is only formed by α phase. Then, the long period for the β form would be larger than for the α form. As can be seen in Fig. 9, after the melting of the β lamellar stacks at about 150 °C, the long period showed a small decrease, and L for the iPP/Vectra (99/1) blend and for pure iPP converged since only α lamellar stacks would be present in the samples. On increasing temperature α lamellar stacks would be melted which resulted in a progressive increase in the value of the long period.

A careful examination of the shape of the SAXS patterns corresponding to the blends with a high proportion of the β form suggested the possibility that the SAXS data were the sum of two contributions related to the presence of two stack populations, α and β. Piccarolo et al. [61,62] also suggested the presence of two populations of stacks in quenched samples of iPP, one being related to the α lamellar periodicity and the other to the lamellae of the mesomorphic phase. Fig. 11 shows SAXS patterns of pure iPP and iPP/Vectra (99/1) and (95/5) blends after isothermal crystallisation at 121 °C. The results obtained by WAXS demonstrated that in pure iPP and the iPP/Vectra (95/5) blend only the α crystalline form was present since in this figure it can be observed that identical SAXS patterns were obtained for both samples. However, it became clear from the comparison between SAXS patterns for the iPP/Vectra (99/1) blend and pure iPP that for the blend containing α and β forms the SAXS profile showed a different shape. This difference is related to the presence of the β crystalline form in the blend. Similar SAXS patterns were obtained for all iPP/Vectra blends containing considerable amount of the β crystalline form. The occurrence of two scattering components in these blends can be explained by the presence of two stack populations, α and β forms, and with two long periods associated to them. From the shape of the SAXS patterns of the iPP/Vectra (99/1) blend shown in Fig. 11 and the evolution of the long period on heating for the same blend shown in Fig. 9, it can be suggested that the long period of the β lamellae is substantially larger than in that of the α lamellae. Busse et al. have reported the occurrence of two different long periods derived from SAXS measurements for isothermally crystallised iPP samples containing α and β modifications with the one which correspond to the β crystalline form much larger [63]. A similar conclusion has been suggested by Vleeshouwers [64] and Kotek et al. [65]. This behaviour explains the decrease observed at 150 °C for the long period of the iPP/Vectra blend on heating due to the melting of β modification and the disappearance of the long period at 165°C due to the melting of the α modification. Similar melting temperatures were also obtained by DSC for each crystalline form.

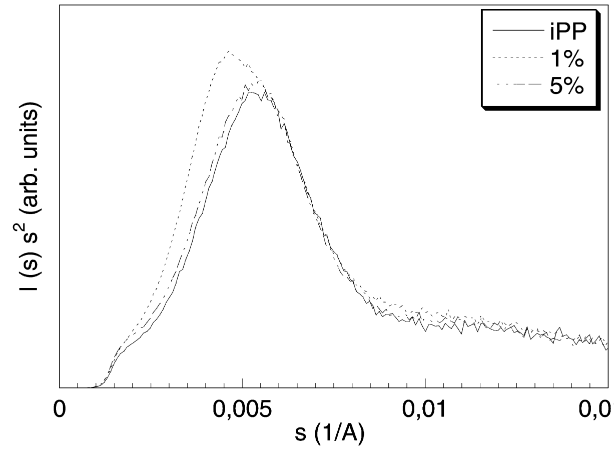

Fig. 11. Representative SAXS patterns for pure iPP and iPP/Vectra (99/1) and (95/5) blends after isothermal crystallisation at 121 °C.

By the simultaneous study by SAXS and WAXS it is possible to distinguish between the primary and secondary crystallisation, and to determine the mechanisms that contribute to the second process [52,57,58,66,67]. In the course of polymer crystallisation two different stages can be observed. During primary crystallisation the spherulites grow until they impinge on each other. In this case the degree of crystallinity, Xc, shows a rapid increase. The secondary crystallisation is due to additional crystallisation within the spherulites. This process is characterized by a very slow increase of X_c. The degree of crystallinity can be defined by the following expression [52]:

$$X_c = X_s X_L X_{cL} \tag{3}$$

where X_s is the volume fraction filled with spherulites, X_L the volume fraction transformed into lamellar stacks and X_{cL} is the crystallinity within the lamellar stacks. In the primary crystallisation process X_s increases from 0 to 1 and X_L can be considered almost constant. During secondary crystallisation X_s stays constant and equal to 1 but X_L and/or X_{cL} slowly increase. Three different processes can take place at this stage: (a) the crystals may become thicker while the amorphous regions become thinner, (b) new lamellar stacks may be formed if the spherulites were not completely filled, (c) new crystals may grow between the lamellar stacks. The simultaneous measurements of SAXS and WAXS allow us to determine the process that contributes to the secondary crystallisation. Therefore, the values of the intensity of the crystal reflections obtained from WAXS, the scattering power and the long period obtained from SAXS were compared for iPP and its blends with Vectra to analyse the effect of the Vectra content on the secondary crystallisation mechanism of iPP.

The area under the crystalline reflections, A_c, which can be related to the degree of crystallinity, was obtained from the WAXS patterns as follows:

$$A_c = \int_0^\infty I_c(s) s^2 \mathrm{d}s \tag{4}$$

where $I_c(s)$ is the scattering intensity of the crystal reflections, s the scattering vector.

The scattering power, Q, can be obtained from the corresponding SAXS experiments, which may be defined as [68]:

$$Q = 4\pi \int_0^\infty I(s)s^2 \mathrm{d}s \quad (5)$$

Here $I(s)$ is the SAXS intensity normalized to the volume of the sample and the intensity of the primary beam. The scattering power, Q, may also be defined as [52]:

$$Q = X_s X_L X_{cL}(1 - X_{cL})(\Delta\rho)^2 \quad (6)$$

where $\Delta\rho$ is the difference between the densities of the amorphous and crystalline regions.

Fig. 12 shows the values of A_c, Q and L against crystallisation time for iPP and iPP/Vectra (95/5) blend crystallised isothermically at 121 °C. A_c and Q were normalized so that the same value is obtained at a crystallisation time corresponding to twice the half time of crystallisation, $\tau_{1/2}$. Values of the half time of crystallisation were 5.6 min for pure iPP and 2.6 min for the iPP/Vectra (95/5) blend. During the primary crystallisation, Q is proportional to X_s due to the small variation with X_L and X_{cL}, and A_c follows the same variation as X_s. Therefore, the values of A_c and Q increased in the same way during the primary crystallisation for all samples studied, as can be seen in this figure. Both curves (iPP and iPP/Vectra (95/5)) are sigmoidal, which can be explained on the basis of the Avrami theory applied to the crystallisation of spherulites. After twice $\tau_{0.5}$, the primary crystallisation can be considered to be finished. During secondary crystallisation, the long period stays constant with the crystallisation time for pure iPP and all its blends with Vectra. Therefore, the formation of new crystals within the lamellar stacks can be excluded since this crystallisation process would cause a decrease of L. In this time, Q and A_c show the same variation with time and remained nearly constant. This behaviour proves that new lamellar stacks were formed into the spherulites. A similar trend was also observed previously for iPP and PVF$_2$ at high crystallisation temperatures by Kolb et al. [32]. These authors observed that X_c and Q remained almost constant during secondary crystallisation. Furthermore, they did not observe changes in the full width at half maximum from the WAXS curves, so they concluded that growth of new lamellae within remaining amorphous regions inside the spherulite was the secondary crystallisation process. It is to be noted, that these authors investigated iPP crystallisation behaviour at high crystallisation temperatures. In the present study lower temperatures were used but iPP shows similar crystallisation behaviour. The above results show that the secondary crystallisation of iPP seemed not to be affected by the presence of Vectra domains and the mechanism of this process was the formation of new lamellar stacks, which are formed within the spherulites since these crystalline entities were not completely filled.

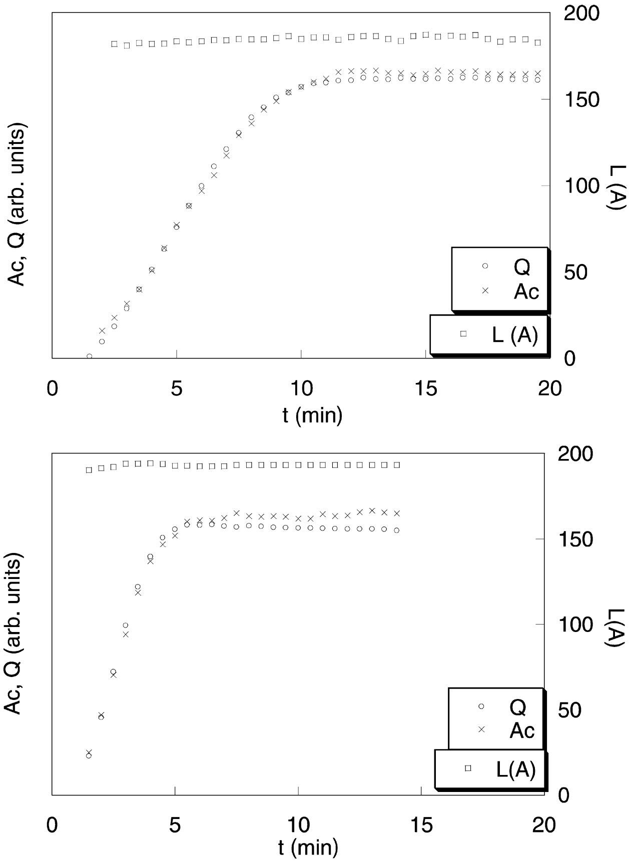

Fig. 12. Long period value, L, scattering power, Q, and integral intensity of crystal reflection, A_c, as a function of time during isothermal crystallisation at 121 °C of: (a) pure iPP and (b) iPP/Vectra (95/5) blend.

Furthermore, in this figure it can be observed that the A_c and Q values for iPP/Vectra (95/5) blend increased more rapidly than for pure iPP. This result is due to the presence of Vectra in the blend. The liquid crystal polymer acts as nucleating agent for iPP spherulites and the crystallisation rate is increased. The same behaviour is obtained for all blend compositions. These results are in agreement with those obtained by DSC and optical microscopy.

4. Conclusions

It was shown that the liquid crystal polymer, Vectra A950, has an important effect on the crystallisation behaviour of iPP polymer for iPP/Vectra blends with low Vectra content. The rate of crystallisation was enhanced with increasing Vectra content in the blend however, identical Avrami exponents, ($n = 3$), were obtained in all the samples. The Vectra domains acted as nucleation sites for iPP spherulites in iPP/Vectra blends.

By simultaneous measurements of WAXS and SAXS, detailed information on the molecular processes during crystallisation can be obtained. The WAXS data demonstrated that the different crystalline polymorphs of iPP, α and β, were obtained in the blends and the relative proportion of the β form varied depending on the Vectra content in the blend and the isothermal crystallisation temperature. The results obtained from SAXS data demonstrated the presence of two different populations of lamellar stack for blends containing the α and β crystalline forms. Our results indicate that the long period value for the β phase is higher than that corresponding to the phase.

Secondary crystallisation mechanisms for iPP and iPP/-Vectra blends were studied by simultaneous WAXS and SAXS measurements. The results obtained show that the principal mechanism for secondary crystallisation was the growth of new lamellar stacks within the remaining amorphous regions inside the spherulites. It was observed that the presence of the liquid crystal polymer in the blends had no influence on the mechanism of the secondary crystallisation process.

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