PII: S0032-3861(97)00441-2

Polymer Vol. 39 Nos. 8–9, pp. 1697–1702, 1998

0032-3861/97/$17.00+0.00

Structure of isotactic polypropylene/ hydrogenated oligo(cyclopentadiene) blends: 1. Polypropylene-rich blends

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(Revised 12 May 1997)

Blends of isotactic polypropylene (iPP) and hydrogenated oligo(cyclopentadiene) (HOCP) containing 30% or less HOCP have been studied by small-angle X-ray scattering in the temperature range 25 to 160°C. The structure of blends has been analysed in terms of a pseudo two-phase model consisting of stacks of lamellae whose thickness is a function of temperature and composition. Structural parameters of the model have been derived and their temperature and composition dependences have been interpreted in the light of existing theories. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polymer blends; small-angle X-ray scattering; lamellar structure)

INTRODUCTION

In general, both the amorphous and crystalline phases contribute to the final properties of polymer blends. The already excellent chemical, mechanical, physical and electrical properties of isotactic polypropylene (iPP) can be improved by blending it with proper plasticizers, additives, modifiers, etc. Films of iPP blended with hydrogenated oligo(cyclopentadiene) (HOCP) are used in the packaging industry owing to their reduced permeability to oxygen and flavourings compared with plain iPP films. These blends have been carefully studied[1,2] from the morphological and mechanical points of view and, more recently, a preliminary structural study by means of small-angle X-ray scattering (SAXS) has been published[3].

In particular, a good deal of attention has been paid to the study of the phase diagram. The original idea that iPP and HOCP were completely miscible in the melt and that their melt solidified forming one amorphous phase (made with amorphous iPP and HOCP) was soon abandoned in favour of a more complex phase diagram showing both an upper (UCST) and a lower (LCST) consolution point. The latter corresponds to a process of phase separation in the condensed state involving the formation of two phases, one rich in iPP and the other rich in HOCP, while the former corresponds to a similar process involving liquid phases. According to the phase diagram, iPP and HOCP, for any composition, are miscible at temperatures higher than ≈240°C and lower than ≈ 90°C, whereas the system undergoes phase separation at intermediate temperatures. Depending on temperature, blend composition and preparation conditions, systems with different structures, morphologies and properties can be obtained. According to such a phase diagram, the blends with HOCP content less than about 20% (w/w) should always form a homogeneous melt. Even at room temperature, these blends are characterized by crystalline iPP in a miscible amorphous phase formed by non-crystalline iPP and HOCP. From blends containing more than about 25% HOCP, either a homogeneous or a phase-separated melt can be obtained, depending on temperature and composition.

In a preliminary SAXS study of iPP/HOCP blends[3] we found that for pure iPP and for the iPP/HOCP blends containing more than 75% of iPP, the Lorentz-corrected scattering curves show a single peak which can be fitted well with a single Gaussian. For blends containing less than 75% iPP, the Lorentz-corrected scattering curve shows two peaks which can be fitted with two Gaussians. By computing the long period for all the samples studied, we noticed that, for the samples showing two peaks, the short long period falls on a master curve containing values for all samples (also those whose Lorentz-corrected scattering curves show only a peak), while the thicker long periods fall on a different master curve. The temperature dependence of both long periods is similar (both increase with increasing temperature), although the growth rate is different for the two periods. These structural results seem to indicate that blends containing 20% or less HOCP form, in the condensed state, a stack of layers of crystalline iPP of thickness l_c separated by layers of amorphous iPP or iPP/HOCP of thickness l_a. For blends containing more than 30% of HOCP there is a wide region of the phase diagram characterized by two kinds of crystallite formed by lamellae of iPP and amorphous material rich in iPP and HOCP, respectively. Blends containing 25% or 30% HOCP act as borderline cases.

The analysis presented so far does not allow a separate evaluation of l_c and l_a. In addition, it would be interesting to gain additional structural information on the transition layer between l_a and l_c, on the degree of crystallinity and on the

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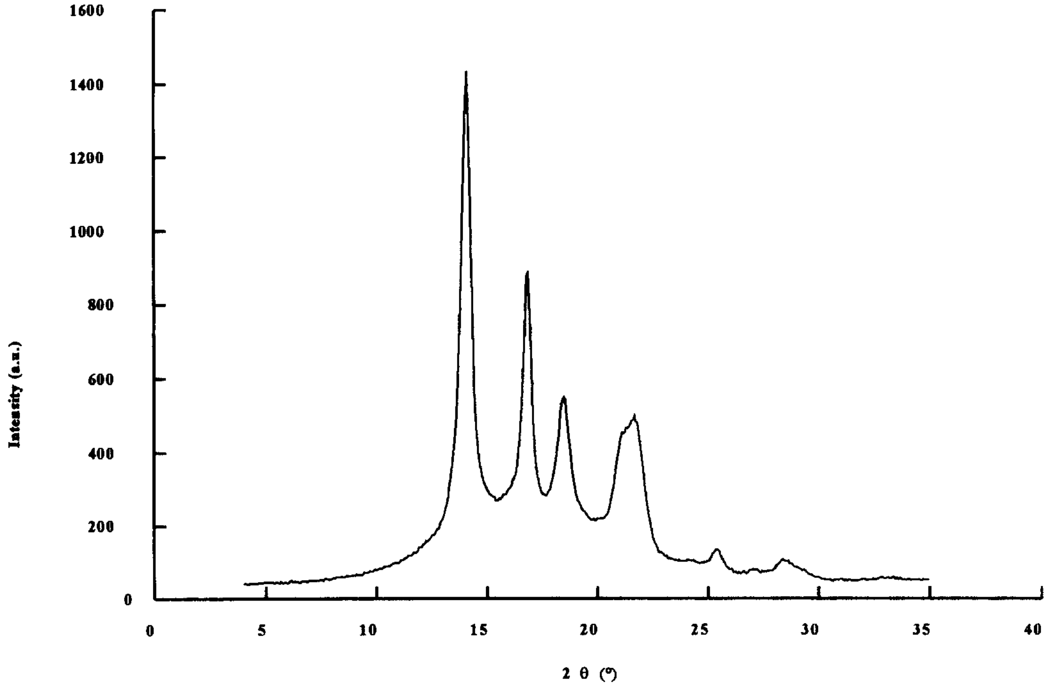

Figure 1 One dimensional WAXS pattern from a sample of pure iPP at 25°C, after quenching. 2θ is the scattering angle

curvature of the lamella surface. Therefore in this paper we extend the previous SAXS study, covering a wider range of temperatures (25–160°C), but limiting the structural analysis to iPP-rich blends (100–80% w/w in iPP). For these blends, in agreement with the phase diagram, the two components are miscible for any temperature and composition. A preliminary structural analysis of the 70/30 blend is also reported. We point out that this material may show phase separation, but it was prepared in such a way as to be a homogeneous amorphous phase at room temperature. In a forthcoming paper, the structure of the blends at higher HOCP content will be reported. The influence of the phase separation phenomena on the structural parameters will be discussed as function of temperature, composition and preparation conditions, which determine the miscibility of the two components in the amorphous phase.

EXPERIMENTAL

Materials and methods

Isotactic polypropylene (Moplen T30S, Montedison) with weight-average molecular weight (M_w) of 3.0×10^5 D and a hydrogenated mixture of isomers of cyclopentadiene (Escorez, Esso Chemical Co.) with M_w = 630 D, glass transition temperature (T_g) of 85 ± 5°C and density of 1.07 g cm^{-3} were used.

The blends were prepared by extruding the two components with a twin extruder at about 280°C. After extrusion the blends were cooled to room temperature and granulated. The compositions (%w/w) of the iPP/HOCP blends studied were 100/0, 95/5, 85/15, 80/20 and 70/30. The samples, consisting of discs about 1 cm diameter and 1 mm thick, were obtained by melting the granulated blends at about 240°C and then quickly quenching them in H_2O/methanol at −20°C. They were kept at this temperature until ready for measurements.

SAXS studies were performed with the 10 m SAXS camera of the Oak Ridge National Laboratory, TN, USA[4]. The system uses pin-hole collimation, and therefore there is no need for slit smearing correction, and is equipped with a two-dimensional position-sensitive detector. The sample-to-detector distance varied between 2 and 5 m (3.12 m for most samples) and Cu K_α radiation produced with a 12 kW rotating anode was used. The samples were contained in stainless steel cells equipped with Kapton windows. The scattered intensity of all the samples was isotropic and the radial average was performed on the data corrected for electronic background, scattering of the cell, transmission and thickness. Scattering cross-sections were obtained by calibration with secondary standards[5]. Samples were studied as a function of the temperature (from 25 to

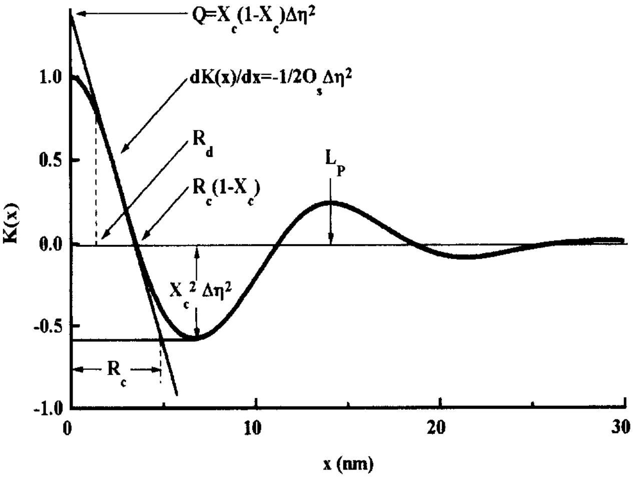

Figure 2 Experimental correlation function, $K(r)$, obtained for a 95/5 (w/w) iPP/HOCP blend, at 95°C. The geometrical construction has been implemented in a FORTRAN code

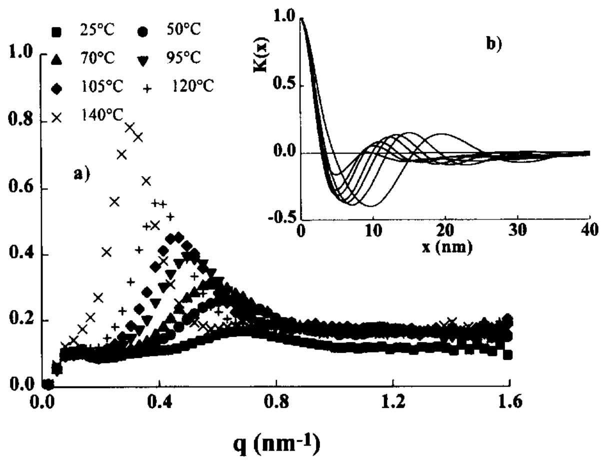

Figure 3 (a) Lorentz-corrected SAXS intensities for 80/20 (w/w) iPP/HOCP blend. (b) Experimental correlation functions, $K(r)$s, for the 80/20 (w/w) iPP/HOCP blend, as calculated at the various temperatures investigated

160°C). In the starting material, the polypropylene always crystallizes in the monoclinic α form[6–8], as evidenced from wide-angle X-ray scattering (WAXS) measurements, see *Figure 1*. Samples were crystallized isothermally and several 30 min scattering patterns were recorded at each temperature and summed after reaching constant count rate. After changing the temperature the procedure was repeated. Usually, it took a few minutes to reach thermal equilibrium and constant count rate.

Table 1 Long periods (nm) obtained from Lorentz-corrected experimental SAXS patterns. Numbers in parentheses refer to long periods derived via Fourier inversion (see text for further details)

T (°C)	100% iPP	95% iPP	85% iPP	80% iPP
25	11.1 (11.0)	11.5 (11.7)	9.9 (9.6)	9.8 (9.4)
50	12.7 (12.6)	12.0 (12.1)	10.6 (10.6)	10.2 (10.1)
70		12.9 (12.8)	11.6 (11.7)	11.2 (11.3)
75	13.2 (13.1)			
95	14.3 (14.0)	14.3 (14.1)	13.4 (13.2)	12.5 (12.3)
105	15.0 (14.7)	15.5 (15.2)	14.4 (14.1)	13.6 (13.3)
120	16.0 (15.7)	17.4 (16.9)	16.7 (16.2)	15.5 (15.1)
130	17.4 (16.9)	18.9 (18.3)	19.3 (18.7)	
140		21.6 (20.9)	21.8 (20.9)	20.4 (19.6)
150				23.3 (22.3)
155	22.0 (21.2)			25.0 (23.7)
160	22.9 (22.3)		35.5 (33.3)	28.0 (26.3)

Data analysis

According to Strobl and Schneider[9], structural information on a lamellar system characterized by a single type of lamella can be obtained by computing the electron density autocorrelation function, $K(r)$, which turns to be the cosine Fourier transform of the diffraction pattern, i.e.

$$K(r) = \frac{1}{2\pi^2}\int_0^\infty I(q)q^2 \cos(2\pi qr)\,\mathrm{d}q$$

Geometrical features of the electronic density self-correlation function, $K(r)$, can be interpreted in terms of structural parameters of the lamellar system, characterizing the blend's thermodynamic state. In *Figure 2*, we report a

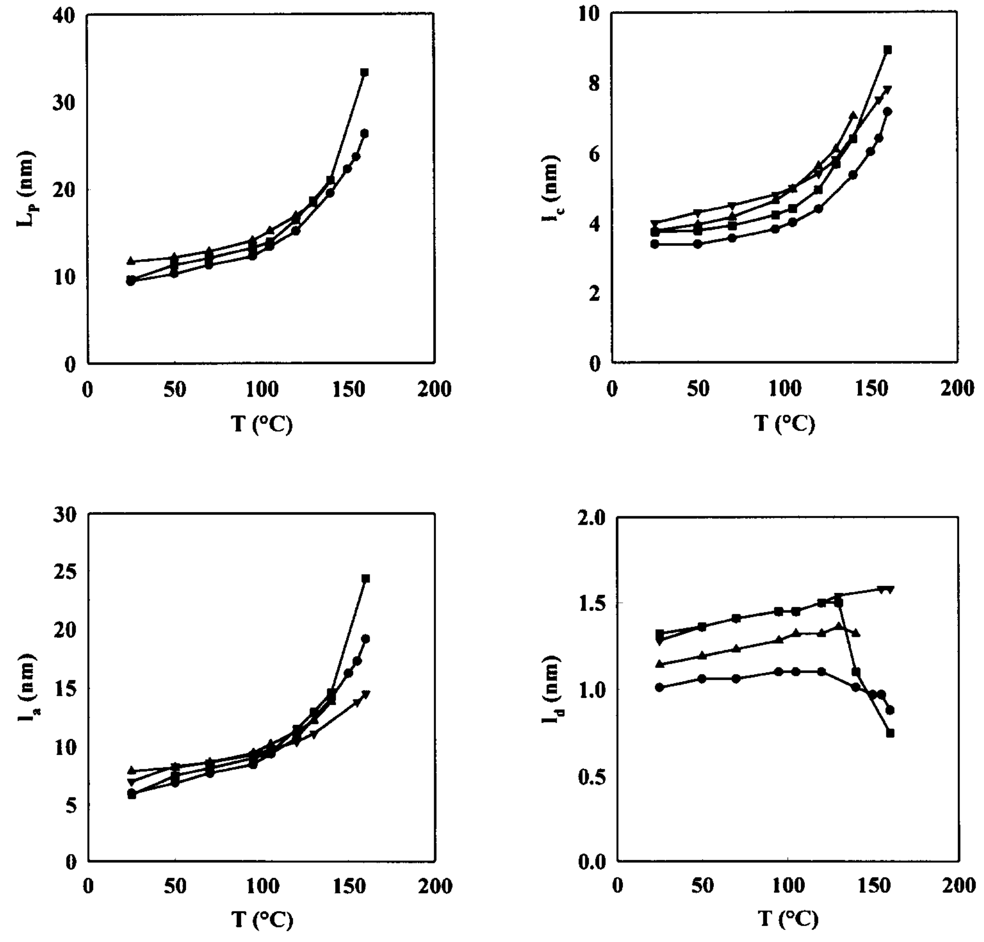

Figure 4 Evolution of structural parameters L_p, l_c, l_a and l_d with temperature for 100/0 (●), 95/5 (■), 85/15 (▲) and 80/20 (▼) iPP/HOCP blends. The lines are intended as a guide for the eye

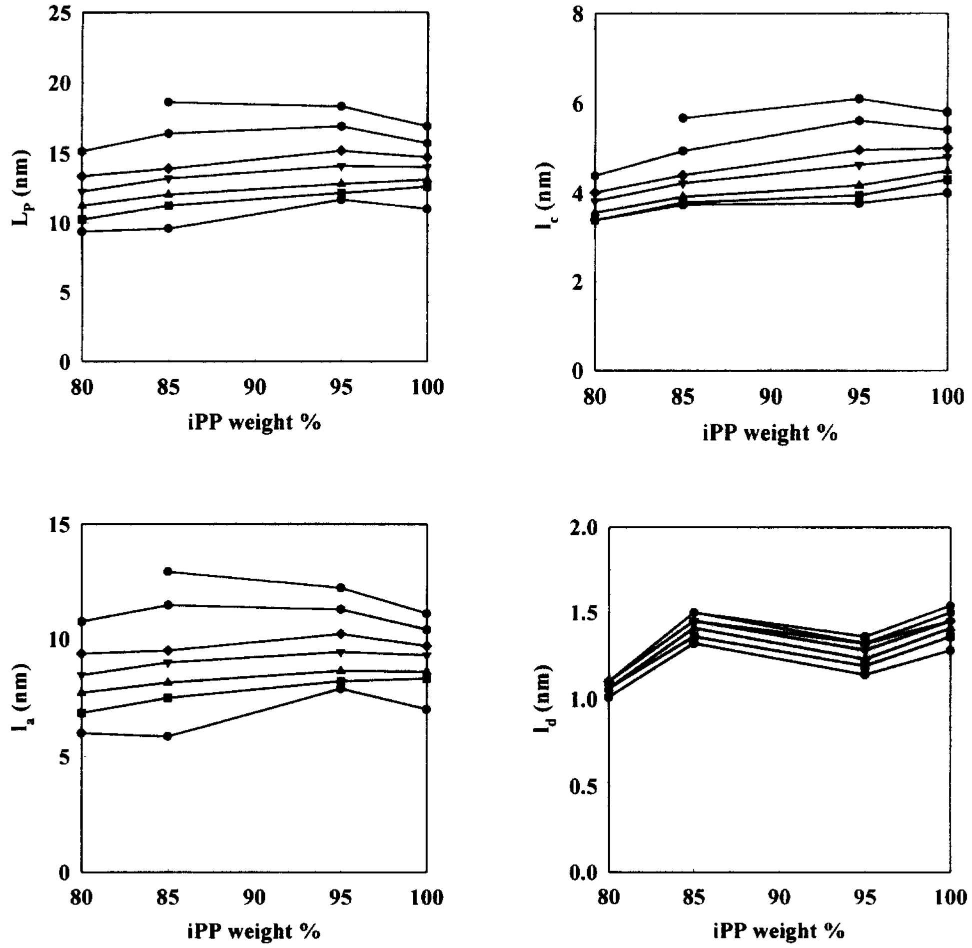

Figure 5 Evolution of structural parameters L_p, l_c, l_a and l_d with composition at T = 25°C (●), 50°C (■), 75°C (▲), 95°C (▼), 105°C (◆), 120°C (●) and 130°C (●). The lines are intended as a guide for the eye

typical self-correlation function obtained for a 5% HOCP/iPP blend at a temperature of 95°C. In this figure, we describe the way structural features can be derived from geometrical characteristics of experimental $K(r)$ curves.

One of the most easily obtainable parameters from $K(r)$ curves is L_p, the long period of the lamellar system, which turns to be the average period of the macrolattice formed by the centres of adjacent lamellae. L_p is related to the abscissa of the maximum of $K(r)$.

In an ideal two-phase system with crystalline and amorphous layers alternating with each other, $K(r)$ should appear as a sequence of triangular impulses. Deviations from such a behaviour are due to various effects such as finite stack length, polydispersity in the thickness of both crystalline and amorphous layers, etc. As a consequence, care must be taken in deriving structural parameters from $K(r)$ analysis. In this paper, we characterize the so-called[9] *baseline* in $K(r)$ as the horizontal line across the minimum of $K(r)$. Strictly speaking, to detect the correct baseline would necessitate *a priori* knowledge of the index of crystallinity of the blend. On the other hand, various experimental techniques yield different values of the crystallinity index, X_c. In addition, we checked a few samples and found that the structural parameters obtained with our approach were in agreement with the ones obtained by deriving the baseline by means of differential scanning calorimetry (d.s.c.) measurements of X_c[10].

By analysing the electron density functions obtained for all the samples under the experimental conditions described earlier, we derived the thicknesses of the crystalline (l_c) and amorphous ($l_a = L_p - l_c$) layers, the thickness of the diffusion layer between the crystalline and amorphous layers (l_d), the electron density contrast between crystalline and amorphous phases ($\Delta\eta$) and the specific interface between the two phases (O_s). Details of the analysis of these parameters are reported in the following section.

RESULTS AND DISCUSSION

Figure 3a shows typical Lorentz-corrected intensities for the 80/20 iPP/HOCP blend at several temperatures as a function of the scattering variable $Q = 4\pi \sin\theta/\lambda$, where 2θ is the scattering angle. For any temperature a single sharp peak is observed whose position and intensity change with changing temperature; similar results were obtained for all the samples. From the peak position, using Bragg's law, the long period (L_B) is obtained. The values of L_B obtained for the whole set of samples are reported in *Table 1*.

The autocorrelation functions, $K(r)$, for the 80/20 iPP/HOCP blend at different temperatures are reported in *Figure 3b*. Again similar curves were obtained for all the samples. In analogy with the behaviour of the Lorentz-corrected scattering curves, the $K(r)$ curves of the pure iPP and the always homogeneous blends present a single maximum for all temperatures. The abscissae of the maximum, which correspond to the average distances of periodicity (L_p), are in excellent agreement with the values of the L_B obtained by use of Bragg's law, as can be seen in *Table 1*.

By using the relationship described above, the thicknesses of the crystalline lamellae, amorphous layers and transition layers have been obtained for all temperatures and compositions. In *Figures 4 and 5* we report the temperature and composition dependences of these parameters. For all samples, l_c increases with temperature. The same is true for l_a and l_d, with l_a increasing with temperature more rapidly than l_c. Also, $\Delta\eta^2$ is an increasing function of temperature. This corresponds to a greater thermal expansivity of the amorphous phase with respect to the crystalline one, in agreement with the literature[11].

The increase of the amorphous and diffusion regions with temperature is mostly due to thermal expansion, whereas the increase of crystal thickness with temperature is due mainly to reorganization of the lamellae as a consequence of annealing phenomena, in agreement with the chain-folding theory[12,13] of polymer crystallization.

For any temperature, a slight but continuous decrease of l_c and l_d is observed with increasing HOCP content. As reported in a previous paper[3], the presence of up to 30% HOCP in the composition disturbs the iPP crystallization process. In particular, the HOCP causes a reduction of the spherulite growth rate as it acts as diluent for the iPP, inducing an increase of the energies related to the formation of a nucleus of critical size and to motion of the macromolecules in the growing crystals, in agreement with the crystallization theory of polymer blends[14]. Hence thinner crystalline layers could be expected, taking into consideration that the HOCP has no marked effect on the equilibrium melting point.

The trend of l_a with composition and temperature is far more complex. At temperature above 75°C l_a decreases with composition, for temperatures between 95°C and 120°C l_a is almost composition-independent and finally, at higher temperatures, a continuous increase of l_a with composition is observed. The decrease of l_a with composition at low temperatures could be explained by considering that the HOCP molecules which replace the amorphous iPP molecules in the blends are at a temperature lower than the glass transition temperature; therefore they occupy a smaller volume than the iPP chains, giving rise to a contraction of the amorphous material. At higher temperatures the HOCP is in the rubbery phase and, being a low-molecular-weight material, has an expansivity higher than that of the polypropylene chains.

The crystallinity index, X_c, see *Figure 6*, increases with temperature and, at a given temperature, decreases with HOCP content. The trend of X_c with temperature is certainly related to the enhancement of order obtained by increasing the temperature. In fact, additional crystallinity develops from portions of the rubbery phase which failed to crystallize at lower temperature and from the improvement of poorly formed crystals, as confirmed by the increase of l_c.

A very interesting parameter from a structural point of

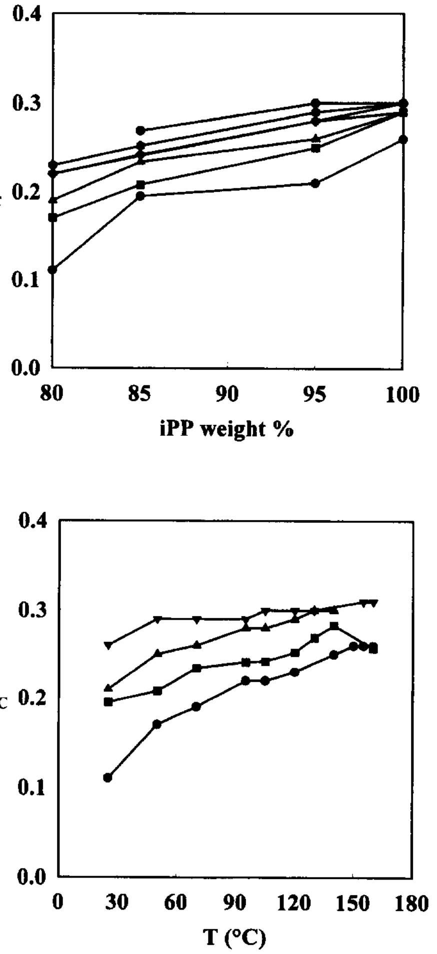

Figure 6 Evolution of the structural parameter X_c with: (a) composition, at $T = 25°C$ (●), 50°C (■), 75°C (▲), 95°C (▼), 105°C (◆), 120°C (●) and 130°C (●); and (b) temperature, for 100/0 (▼), 95/5 (▲), 85/15 (△) and 80/20 (●) iPP/HOCP blends. The lines are intended as a guide for the eye

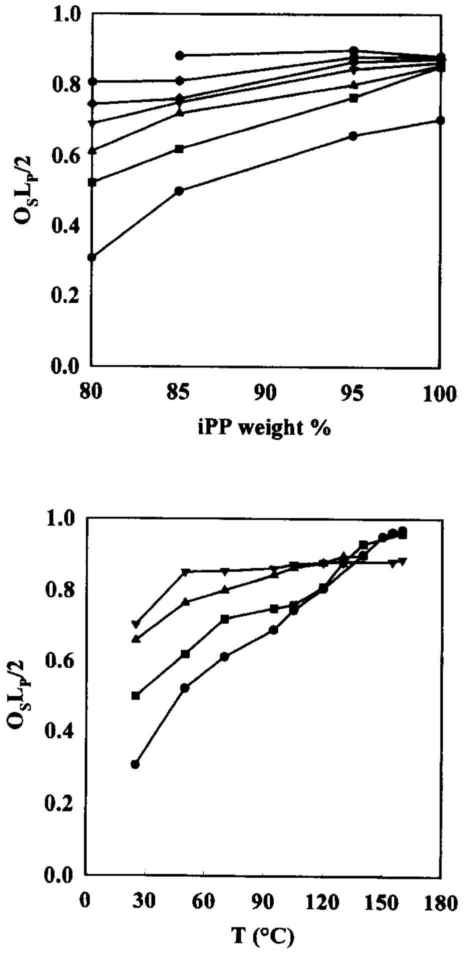

Figure 7 Evolution of the structural parameter $O_sL_p/2$ with: (a) composition, at T = 25°C (■), 50°C (●), 75°C (▲), 95°C (▼), 105°C (◆), 120°C (●) and 130°C (●); and (b) temperature, for 100/0 (▼), 95/5 (▲), 85/15 (■) and 80/20 (●) iPP/HOCP blends. The lines are intended as a guide for the eye

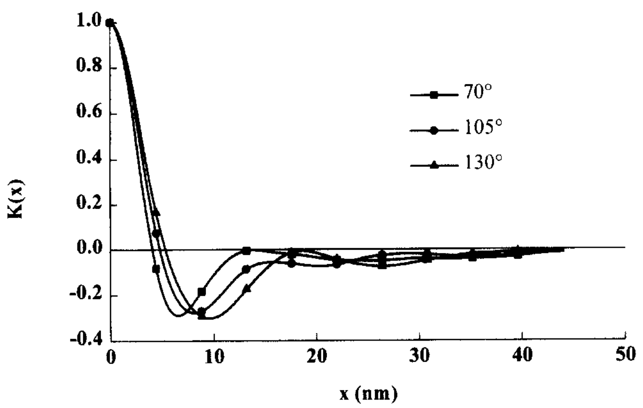

Figure 8 Experimental correlation functions for a 70/30 (w/w) iPP/HOCP blend in three different thermodynamic conditions: 70, 105 and 130°C

view can be obtained by multiplying the specific surface, O_s, by $L_p/2$. Values of $O_sL_p/2$ greater than 1 would indicate the presence of curvature on the crystallite surfaces, whereas values less than 1 would indicate that the distribution function of the long period is not symmetrical; i.e. in particular, a mean value higher than the most probable one[9]. In *Figure 7*, the dependence of $O_sL_p/2$ on temperature and composition is reported. All the values are below 1, indicating that all the surfaces of the crystallites are flat and hence that the fold surfaces are regular. For all the samples, $O_sL_p/2$ increases with temperature and approaches 1 at higher temperature. This result indicates that, upon increasing temperature, there is an increase in the symmetry of the distribution of the long period, in accordance with the increase of crystallinity and l_c. In [15], Albrecht and Strobl derive the parameter $O_sL_p/2$ for pure iPP, obtaining a different temperature dependence; in any case, differences can easily be due to the difference in thermal treatment between samples.

The shape of the self-correlation function for the 70/30 blend depends on temperature (see *Figure 8*). At $T < 95°C$ $K(r)$ shows a single peak. Increasing the temperature, two peaks are observed. For even higher temperature a single peak is again obtained. According to the phase diagram this blend should present a homogeneous amorphous phase at temperature below 100°C and fall inside the three-phase region for sufficiently higher temperature. At 70°C the system is composed of iPP crystals and a single amorphous phase. A single type of lamella is probably present as indicated by the single maximum in $K(r)$. Increasing the temperature to 105°C, the first crystals formed thicken but the amorphous phase undergoes a phase separation. Two phases are present, one rich in iPP and the other rich in HOCP. Part of the iPP in the iPP-rich phase can, at these temperatures, crystallize to form a second type of lamella. Two maxima in $K(r)$ are consequently present. At 130°C, the earlier formed crystals continue to thicken, while the ones formed by phase separation are not present any more (a single maximum in $K(r)$ is observed). They probably melt at these temperatures, as confirmed by d.s.c. results[10]. The preliminary results on the 70/30 blend indicate that the phase separation phenomena influence the structural parameters. Work is in progress to analyse the structure of blends at higher HOCP content as a function of temperature, composition and preparation conditions which, in turn, determine the miscibility in the amorphous phase of the two components.

CONCLUSION

The X-ray analysis has indicated that the structure of the iPP/HOCP system is complex and strongly dependent not only on temperature and composition but also on the phase structure and physical state of the blend components. For the blends with low HOCP content (< 20%), the experimental autocorrelation function is consistent with a structure of alternating amorphous and crystalline layers separated by a diffusion region. For these blends, at any composition, an increase of the structural parameters was found with temperature. The dependence on composition of such parameters is more complex. The thickening of crystalline layers with temperature, thermal expansion together with the possible changes of the physical state of the blend components were invoked to explain all the results. The preliminary results on the 70/30 blend seem to indicate that a second crystallization process takes place, following the phase separation, in the iPP-rich phase. During this crystallization, which is induced by demixing, new lamellae are formed. The evolution of the lamallae dimensions and the other structural parameters for the blends at higher HOCP content, as a function of temperature, composition and preparation conditions, will be presented in a forthcoming paper.

REFERENCES

1. Cimmino, S., Di Pace, E., Karasz, F. E., Martuscelli, E. and Silvestre, C., *Polymer*, 1993, **34**, 972.
2. Cimmino, S., Martuscelli, E. and Silvestre, C., *Macromol. Symp.*, 1994, **78**, 115.
3. Caponetti, E., Chillura Martino, D., Cimmino, S., Floriano, M. A., Martuscelli, E., Silvestre, C. and Triolo, R., *J. Mol. Struct.*, 1996, **383**, 75.
4. Wignall, G. D., Lin, J. S. and Spooner, S., *J. Appl. Crystallogr.*, 1990, **23**, 241.
5. Wignall, G. D. and Bates, F. S., *J. Appl. Crystallogr.*, 1986, **20**, 28.
6. Vittoria, V. and Riva, F., *Macromolecules*, 1986, **19**, 1975.
7. Natta, G., Peraldo, M. and Corradini, P., *Rend. Acc. Naz. Lincei*, 1959, **26**, 14.
8. Fichera, A. and Zanetti, R., *Makromol. Chem.*, 1975, **176**, 1885.
9. Strobl, G. R. and Schneider, M., *J. Polym. Sci.: Polym. Phys. Edn*, 1980, **18**, 1343.
10. Unpublished results.
11. Van Krevelen, D. W., *Properties of Polymers*. Elsevier Scientific Publishing Company, Amsterdam, 1976.
12. Wunderlich, B., *Macromolecular Physics*, Vol. II. Academic Press, New York, 1976.
13. Mandelkern, L., *Crystallization of Polymers*. McGraw-Hill, New York, 1964.
14. Silvestre, C., Cimmino, S. and Di Pace, E., in *The Polymeric Materials Encyclopedia: Synthesis, Properties and Applications*, ed. J. C. Salamone. CRC Press, Inc., Boca Raton, FL, 1996, pp. 689–703.
15. Albrecht, T. and Strobl, G., *Macromolecules*, 1995, **28**, 5267.