

Morphology, phase structure and thermal behaviour of films of isotactic polypropylene/hydrogenated oligocyclopentadiene blends: 1. Extruded isotropic films

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The effect of hydrogenated oligocyclopentadiene (HOCP) on the structure and morphology of isotropic isotactic polypropylene (iPP) films obtained by melt extrusion has been studied using wide-angle X-ray scattering, thermal analysis and electron microscopy. It was found that the addition of HOCP causes the formation of the smectic phase of iPP at temperatures where bulk iPP crystallizes only in the monoclinic form. The amount of smectic phase present in the blend is dependent on the blend composition. The spherulitic morphology of iPP is completely modified by the presence of HOCP. For blends containing up to 10% HOCP, the iPP spherulite dimensions are drastically reduced. In the case of blends of higher HOCP content, the film crystallinity is reduced, no spherulites are visible and the film surface appears smoother.

(Keywords: film; morphology; thermal behaviour; blends; polypropylene; oligocyclopentadiene)

INTRODUCTION

In previous papers^{1,2} the crystallization, thermal behaviour and phase structure of isothermally crystallized samples of isotactic polypropylene/hydrogenated oligocyclopentadiene (iPP/HOCP) blends have been studied as functions of composition and crystallization conditions. It was found that HOCP influences the spherulite growth rate G , the overall crystallization rate K_n and the melting temperature T_m of iPP. In particular, for a given crystallization temperature T_c , the values of G , K_n and T_m for the iPP in the blend were lower than the values for bulk iPP. These results, together with the detection of a single glass transition temperature, led to the conclusion that iPP and HOCP form a miscible blend in the amorphous phase. For isothermally crystallized blend samples it was found that the presence of HOCP during crystallization did not interfere with the apparent size of crystalline lamellae, whereas the long period increases as a function of HOCP content. Such a finding suggests that HOCP is mainly located in the interlamellar regions.

Moreover, mechanical tensile tests and fracture mechanics analysis at high speed were carried out on the same system³, to correlate the mechanical properties and the fracture parameters with different microstructures and morphologies. It was found that the addition of HOCP improved the low-strain properties (modulus and yield stress), whereas the fracture toughness parameters (G_c and K_{Ic}) decreased with increasing HOCP in the blend. The mechanical and fracture results were

explained by assuming the existence of a high degree of compatibility in the amorphous phase and interconnection in the material between lamellae, amorphous regions and spherulites. No information was obtained at that time about the influence of HOCP on the crystalline form adopted by iPP in the blends.

As reported by several authors⁴⁻⁸, depending on processing conditions iPP can crystallize in different forms, i.e. the thermodynamically stable crystalline α form, the metastable β form and the smectic form, believed to be only partially ordered compared to the α and β forms. A few cases have been reported in the literature^{9,10} where the presence of a second polymer component in a miscible amorphous blend affects the formation of different polymorphic forms of some polymers. The stabilization of the β form of poly(vinylidene fluoride) with poly(methyl methacrylate) and poly(ethyl methacrylate) has been reported, as well as the modification of the polymorphic behaviour of syndiotactic polystyrene with poly(phenylene oxide) (PPO).

The aim of this paper is to examine the influence of HOCP content on the overall morphology and phase structure of isotropic iPP/HOCP blend films obtained by melt extrusion using wide-angle X-ray scattering, thermal analysis and optical and electron microscopy.

EXPERIMENTAL

Materials and blend preparation

The materials used in this study were a commercial

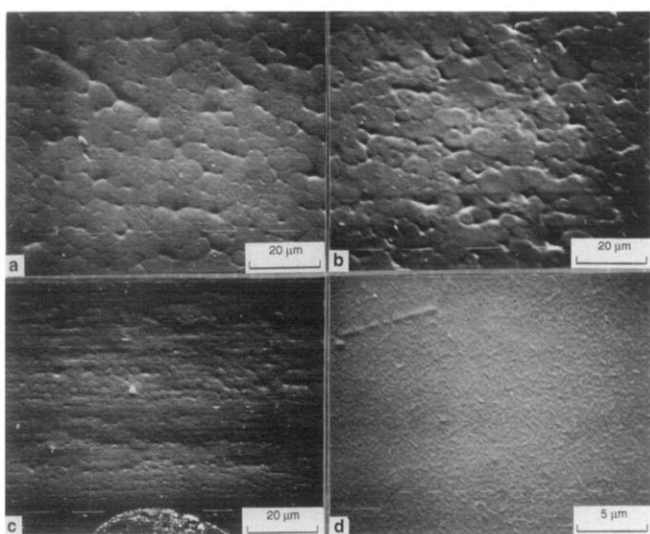


Figure 1 Electron micrographs of surface films of (a) pure iPP, (b) iPP/HOCP 95/5, (c) iPP/HOCP 90/10 and (d) iPP/HOCP 50/50

isotactic polypropylene (iPP), Moplen T 305 from Montedison with $M_w = 300\,000\text{ g mol}^{-1}$, and a hydrogenated mixture of isomers of oligocyclopentadiene (HOCP), Escorez obtained from Esso Chemical with $M_w = 630\text{ g mol}^{-1}$.

The blends were prepared by extruding the two components with a double-screw extruder at about 210°C . After extrusion, the blend was cooled to room temperature and granulated to chips. The films were prepared by extruding the chips with a screw extruder at about 240°C . After extrusion the molten material was solidified on a moving roller, placed in a water bath at 40°C .

Electron microscopy

The morphology of the unoriented films was investigated by scanning electron microscopy (SEM). Before observation the surfaces of the films were coated with gold-palladium.

WAXS measurements

Wide-angle X-ray scattering (WAXS) measurements were carried out on a Philips (PW1050 model) powder diffractometer (Cu Ni-filtered radiation). WAXS patterns were also collected by a flat camera (sample-film distance = 50 mm).

Calorimetric measurements

In order to investigate the calorimetric properties of the films, a differential scanning calorimeter (Mettler DSC-30) was employed. Each sample underwent the following thermal treatment: the film (about 10 mg) was heated from -100 to 250°C at a scanning rate of $20^\circ\text{C min}^{-1}$.

The weight crystallinity indices of the iPP phase, $X_c(\text{iPP})$, and of the overall blend, $X_c(\text{blend})$, were calculated from:

$$X_c(\text{iPP}) = \Delta H^*(\text{iPP}) / \Delta H^\circ(\text{iPP}) \quad (1)$$

$$X_c(\text{blend}) = \Delta H^*(\text{blend}) / \Delta H^\circ(\text{iPP}) \quad (2)$$

where $\Delta H^\circ(\text{iPP})$ is the heat of melting per gram of 100% crystalline iPP. This was taken to be 210 J g^{-1} . In

equations (1) and (2) $\Delta H^*(\text{iPP})$ and $\Delta H^*(\text{blend})$ are the apparent enthalpies of melting per gram of iPP and blend, respectively. The melting point (T'_m) was taken as the temperature corresponding to the maximum of the endothermic peak, and the glass transition temperature (T_g) was read as the temperature corresponding to the maximum of the peak obtained by the first-order derivative of the transition trace.

RESULTS AND DISCUSSION

Morphology and structure analysis

Scanning electron micrographs of films of pure iPP and iPP/HOCP blends obtained by extrusion are reported in Figure 1. The iPP and iPP/HOCP 95/5 blend films are spherulitic with dimensions of about $10\ \mu\text{m}$. At the junctions where the spherulites meet, some voids are present. These voids are probably caused by contraction of volume (Figures 1a and 1b) on crystallization.

In the blends with more HOCP the morphology is dependent on the blend composition. For the iPP/HOCP 90/10 blend the morphology is still spherulitic, but the size of the spherulites drastically decreases, whereas their number increases (see Figure 1c). This result indicates that HOCP influences the apparent nucleation density of iPP and could be due to the fact that the growth rate of iPP in the blends is strongly depressed with respect

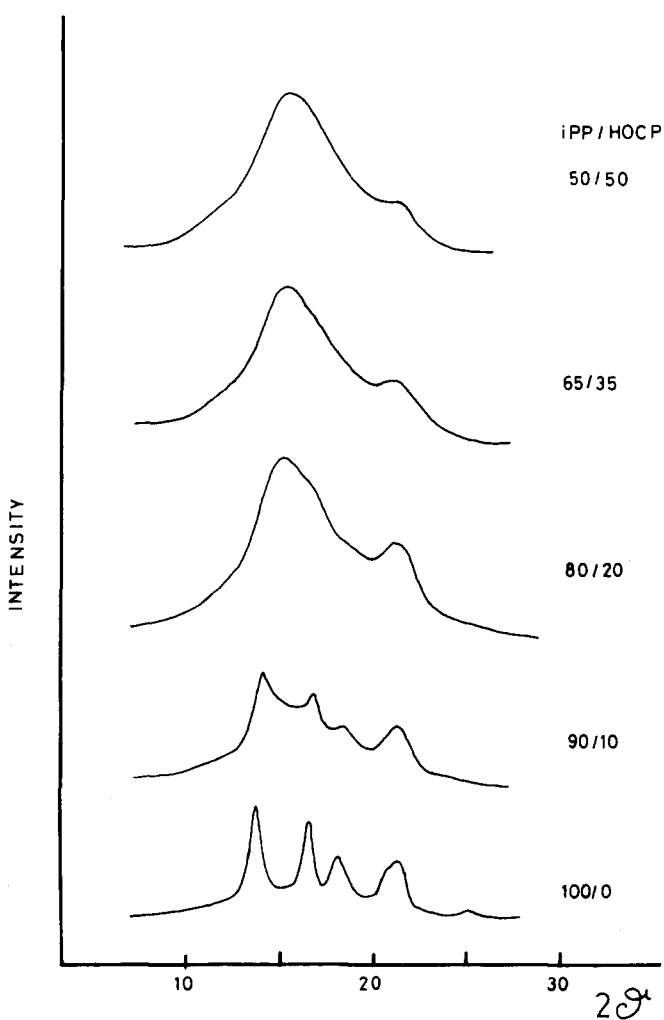


Figure 2 WAXS diffractograms of iPP and iPP/HOCP blends

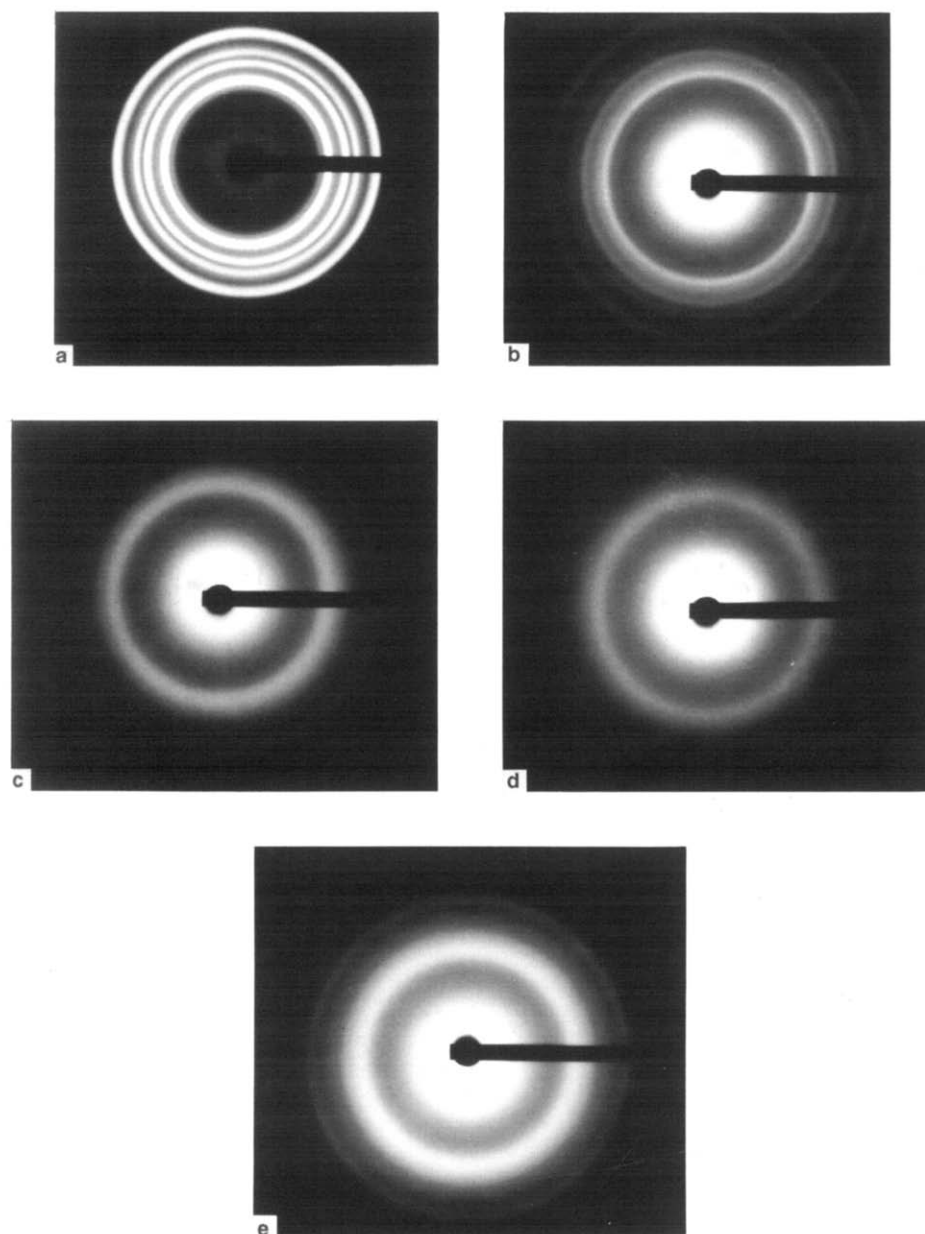


Figure 3 WAXS spectra of iPP and iPP/HOCP blends: (a) pure iPP; (b) iPP/HOCP 90/10; (c) iPP/HOCP 80/20; (d) iPP/HOCP 65/35 and (e) iPP/HOCP 50/50

to that of pure iPP¹. Therefore, in the molten blend during crystallization there is a larger uncrystallized volume in which the nuclei can develop, giving rise to an increase of the nucleation density, by analogy to what happens in the case of poly(ethylene oxide)/atactic poly(methyl methacrylate) blends¹¹. It should be noted that nucleation effects of HOCP on iPP spherulites cannot be excluded *a priori*.

In blends with even higher content of HOCP the morphology changes completely, the surface of the film is smoother and there are no spherulites visible (*Figure 1d*).

The wide-angle X-ray diffractograms and spectra of pure iPP and iPP/HOCP blends are shown in *Figures 2 and 3*. Both figures show isotropic patterns, indicating that film preparation does not orientate the samples. The diffractograms of pure iPP indicate that iPP crystallizes predominantly in the conventional α form.

The addition of HOCP to iPP modifies the diffractograms and spectra of iPP (see *Figures 2 and 3*).

For 90/10 and 80/20 iPP/HOCP blends, the peaks and rings related to the α form of iPP become broader and more diffuse, indicating the presence in the samples of the smectic modification, and the amount of this phase increases with composition. In fact the diffraction patterns show the peak shapes usually reported in the literature when iPP is present in the α form together with the smectic phase.

For blends containing more than 20% of HOCP, only two broad peaks are observed, which are due to the presence of only the smectic modification of iPP together with the amorphous phase. In this case, the diffraction patterns show the shape usually reported in the literature for the smectic form of iPP.

According to literature data^{4,8}, the smectic form of iPP is obtained only on fast quenching of pure iPP from the melt below 0°C and its content is dependent on quenching temperature and sample geometry. The addition of HOCP to iPP also causes the formation of the smectic phase on iPP on rapid cooling from the melt

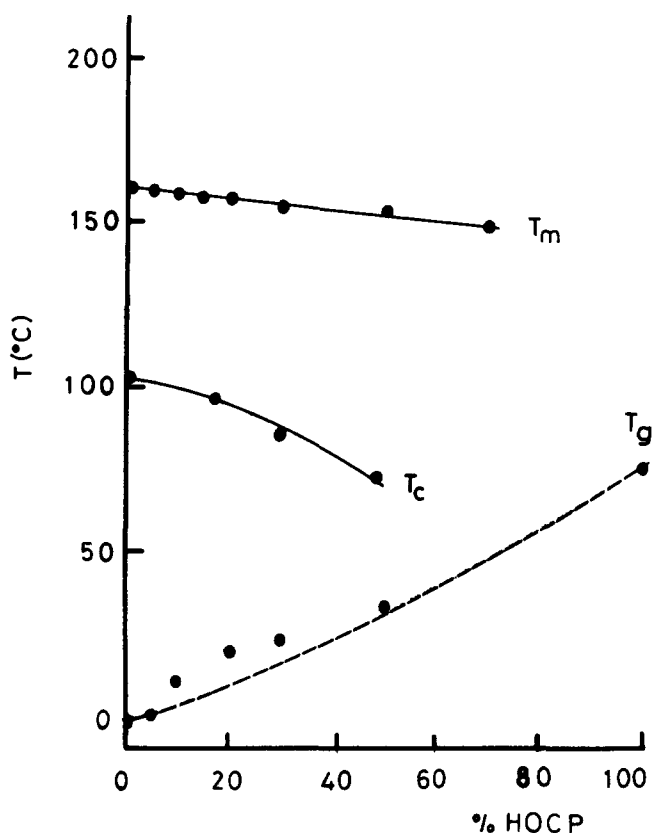


Figure 4 Phase diagram of the iPP/HOCP system, showing as functions of blend composition the glass transition temperature T_g , the melting temperature T_m and the crystallization temperature T_c for crystallization during cooling at $V_c = 50^\circ\text{C min}^{-1}$

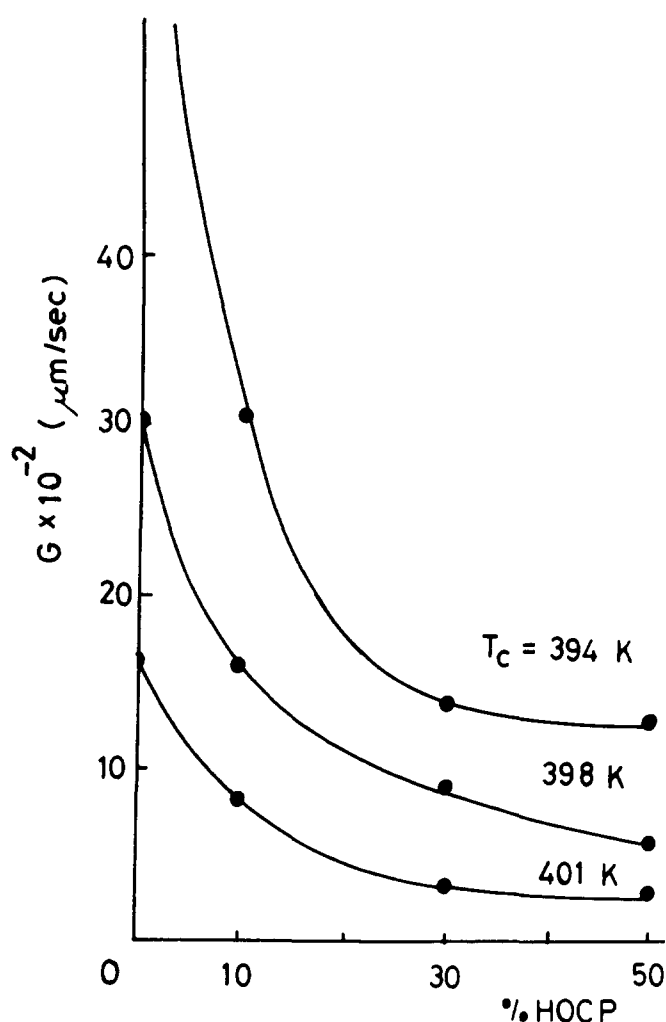


Figure 5 Spherulite radial growth rate as a function of blend composition for iPP/HOCP blends

at 40°C , whereas, as we have already pointed out (see Figure 2), neat iPP under the same conditions crystallizes predominantly in the monoclinic α form.

The formation of the smectic phase in the blend could be attributed to the increase of the glass transition temperature and to the decrease of the equilibrium melting temperature, the crystallization rate and the crystallization temperature^{1,2,12}. These phenomena, reported elsewhere^{1,2,12}, are illustrated in Figures 4, 5 and 6. Figure 4 reports the phase diagram of the iPP/HOCP blend system, Figure 5 the influence of composition on the radial growth rate and Figure 6 the d.s.c. crystallization peak during the cooling of iPP and iPP/HOCP blends. From these figures it is clear that the addition of HOCP to iPP causes:

- (1) a narrowing of the crystallization window, measured by $T_c - T_g$ (Figure 4),
- (2) a depression in the rate of crystallization, at a given T_c (Figure 5), and
- (3) a shift of the crystallization peak to lower temperatures, for crystallization occurring during cooling (Figure 6).

All these phenomena inhibit the crystallization of iPP and permit the necessary conditions for the formation of the smectic phase of polypropylene.

In fact, during cooling from 250 to 40°C , all the material or part of it, depending on composition and T_g , could reach a temperature close to the glass transition temperature, before crystallization of iPP in the α form can occur. At this temperature, owing to the high viscosity, the iPP molecules cannot organize themselves

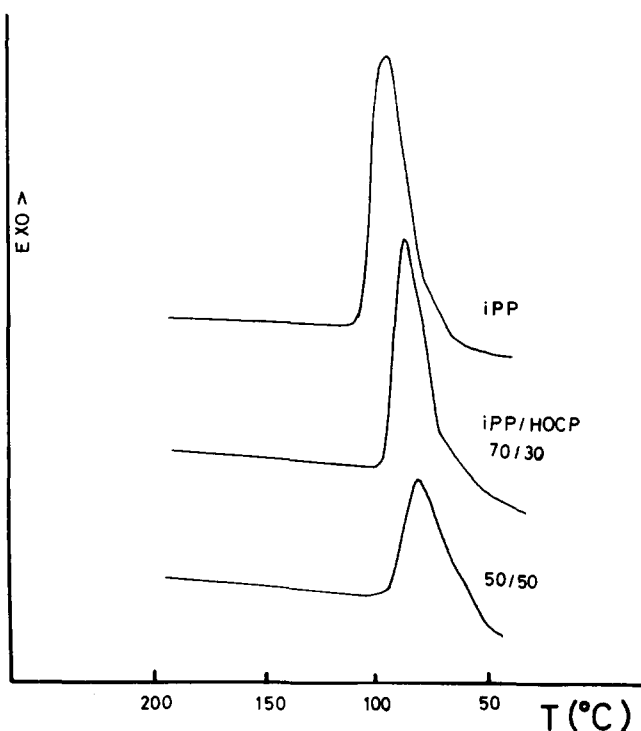


Figure 6 D.s.c. thermograms of non-isothermal crystallization of iPP and iPP/HOCP blends during cooling at $V_c = 50^\circ\text{C min}^{-1}$

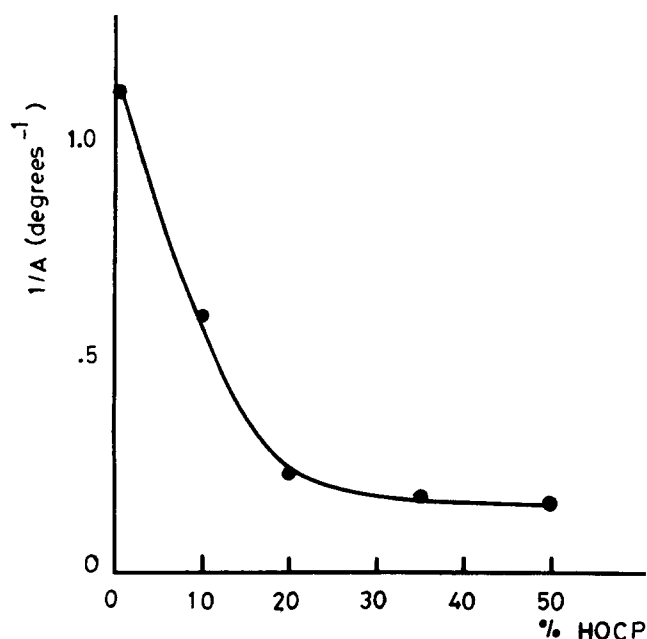


Figure 7 Reciprocal of the width at half-height ($1/A$) for the (1 1 0) reflection of isotactic polypropylene as a function of blend composition

in the monoclinic structure but only in the smectic modification. In order to investigate the level of order attained by the iPP crystallites as a function of composition, the variation of the reciprocal of the width at half-height of the 1 1 0 diffraction peak ($1/A$) with composition has been evaluated. The parameter $1/A$ is an index of the degree of order^{5,7}. The values of $1/A$ as a function of blend composition are shown in Figure 7. There is a dramatic decrease of $1/A$ with composition, indicating a decrease in the degree of crystalline order in the iPP crystallites with blend composition. Moreover, because the first-order wide-angle X-ray diffraction peak has a width largely determined by the inverse of the crystallite size¹³⁻¹⁵, the experimental data could also indicate the decrease of the dimension of iPP crystallites with the increase of HOCP content in the blends, measured in a direction normal to the {1 1 0} crystallographic planes.

Thermal behaviour

The d.s.c. thermograms of films of iPP and iPP/HOCP blends are shown in Figure 8. The thermogram for pure iPP film presents only one endothermic transition due to the melting of iPP crystallized in the monoclinic α form.

The iPP film is found to contain about 38% of crystalline phase with a melting peak centred at about 173°C. The thermograms of the blends (see Figure 8) are significantly different from that of the bulk iPP film. Three peaks are always detected—the first and the third centred at about 60°C and 160°C are endothermic peaks, whereas the second one centred at about 110°C is an exothermic peak. The first peak is related to the melting of the smectic phase of iPP, whereas the exothermic peak is due to the recrystallization of this material in the more stable monoclinic structure. Finally the peak at 160°C corresponds to the melting of iPP crystallized in the monoclinic form. A similar thermogram has already been reported in the literature^{6,7}.

It is interesting to note that the areas under the first

endothermic peak and the exothermic peak increase on increasing the HOCP content in the blends, confirming that the formation of the smectic phase depends on blend composition, in agreement with the X-ray results.

Therefore, comparing these results with those obtained by X-ray and morphological investigations, it can be concluded that for blends containing less than 20% of HOCP the iPP crystallizes mainly in the monoclinic crystal structure, but part of it gives rise to the formation of the smectic and of course amorphous phases. In the case of blends having a higher HOCP content, films are characterized by the fact that the iPP is present as smectic and amorphous phases. No crystalline iPP has been detected by X-ray.

CONCLUSIONS

In this paper we have studied the structure, morphology and thermal behaviour of extruded isotropic films of neat iPP and iPP/HOCP blends as functions of blend composition. The results of the X-ray and d.s.c. analyses show that in the case of unblended iPP the molecules crystallize in the monoclinic α form, whereas the smectic form is observed in the blend films. The amount of the smectic form depends on blend composition. Since all the films were obtained with the same procedure, the smectic form of the iPP crystallized from the blends was not expected. In fact, such a form is possible only by quenching iPP at a temperature below 0°C. These results demonstrate that the presence of HOCP molecules in the film influences the packing of iPP chains, giving rise to the formation of the smectic form also at temperatures where pure iPP chains would normally crystallize in the monoclinic α form. These phenomena are due to the effect of HOCP on the glass transition temperature, equilibrium melting temperature, crystallization temperature and rate of crystallization of iPP. In particular, the addition of HOCP to iPP increases the T_g and decreases the crystallization rate as well as T_c . These effects seem to inhibit the crystallization process of iPP in the monoclinic form, permitting a rapid quenching of the material, which is a necessary condition for the formation of the smectic phase.

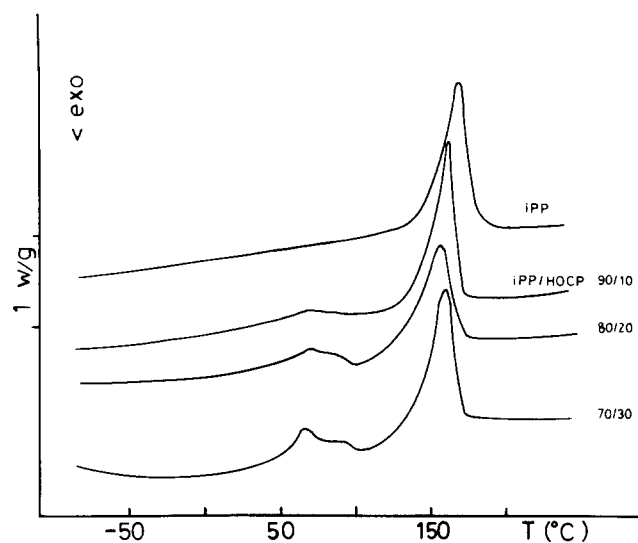


Figure 8 D.s.c. thermograms of films of iPP/HOCP blends for different blend compositions

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