# Isotactic polypropylene/hydrogenated oligo(cyclopentadiene) blends: phase diagram and dynamic–mechanical behaviour of extruded isotropic films

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The phase structure and the dynamic–mechanical properties of isotropic films of isotactic polypropylene (iPP)/hydrogenated oligocyclopentadiene (HOCP) blends are reported. It is found that the phase diagram presents both the lower critical solution temperature and the upper critical solution temperature. The dynamic–mechanical tests (performed at a frequency of 1 Hz and at a heating rate of $4°C\,min^{-1}$) show that the addition of HOCP > 20 wt% causes an increase of the storage modulus at low temperatures; the curves of storage modulus and loss modulus of the isotropic films containing HOCP > 20 wt% show the transition of the smectic form of iPP to the crystalline $\alpha$ form.

**(Keywords: phase structure; dynamic–mechanical properties; polypropylene)**

## INTRODUCTION

Isotropic films of isotactic polypropylene (iPP)/hydrogenated oligocyclopentadiene (HOCP) blends were introduced a few years ago into packaging. They were successful due to the fact that the films possess a reduced permeability to oxygen and to any aroma compared with that of the pure iPP film. Moreover the HOCP is a reinforcing agent and a heat-sealing promoter for the iPP. This system also had a scientific interest and several papers have been published concerning the blends[1–4] and the commercial isotropic films[5].

Among several results for the isothermally crystallized blends it is reported that iPP/HOCP mixtures presented only one glass transition temperature ($T_g$) as detected by d.s.c.[1]; the spherulite growth rate and the equilibrium melting point of iPP decreased by adding HOCP[1]; the HOCP did not interfere with the apparent size of iPP crystalline lamellae, whereas the long period increased with HOCP content[2]; the addition of HOCP improved the low-strain properties (modulus and yield stress), whereas it decreased the fracture toughness parameters[3]; by dynamic–mechanical testing a unique peak of the loss modulus was detected and the maximum shifted to higher temperatures with increasing HOCP content[4].

The above results were explained by assuming that iPP and HOCP are miscible in the amorphous state and that during crystallization they are mainly located in the interlamellar regions. For the isotropic films of iPP/HOCP blends obtained by quenching the melt mixture from 260 to 40°C it was found that the addition of HOCP induces the formation of the smectic phase at temperatures where the pure iPP crystallizes only in the monoclinic form[5]. Furthermore the relative content of smectic phase present in the film is dependent on blend composition. This phenomenon was explained by considering the effect of HOCP on $T_g$, on the equilibrium melting point and on the crystallization temperature and rate of crystallization of iPP.

So given that iPP and HOCP are miscible at ordinary temperatures and the isotropic films with HOCP > 20% contain iPP in the smectic form, the aim of this work is to study the limits (if any) of the miscibility and the dynamic–mechanical behaviour of extruded isotropic films of iPP/HOCP as a function of temperature and composition.

## EXPERIMENTAL

### *Isotropic film preparation*

The isotropic films of iPP/HOCP used in this work were supplied by FIAP SpA, Turate (MI), Italy. The materials used were a commercial iPP, Moplen T305 Montedison, with $M_w = 3.0 \times 10^5\,g\,mol^{-1}$, and the hydrogenated mixtures of isomers of oligocyclopentadiene (HOCP), Escorez, were obtained from Esso Chemical Co., with $M_w = 630\,g\,mol^{-1}$ and $T_g = 65 \pm 3°C$. The blends were prepared by extruding the two components with a twin-screw extruder at about 210°C. After extrusion the blend was cooled to room temperature and granulated.

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Finally, the films were prepared by extruding the chips with a screw extruder at about 240°C and the molten material was solidified as film on a moving roller placed in a water bath at 40°C.

The compositions of the films tested are: iPP/HOCP (wt/wt) 100/0, 95/5, 90/10, 80/20, 70/30, 65/35, and 30/70. Some data reported in this work are related to blends, i.e. to the material obtained after the first extrusion in the twin-screw extruder.

### *Optical microscopy*

The phase diagram was obtained by using an optical microscope fitted with an automatic hot stage. The films were sandwiched between a microscope slide and a coverglass and heated from room temperature to 270°C at a heating rate of 2°C $\mathrm{min}^{-1}$ in a nitrogen atmosphere.

### *Calorimetric measurement*

The calorimetric properties of the films were investigated with a differential scanning calorimeter (Mettler DSC-30). The samples were heated from $-100$ to 250°C at a scanning rate of 20°C $\mathrm{min}^{-1}$.

### *WAXS measurement*

WAXS measurements were carried out on a Phillips (PW1050 model) powder diffractometer (Cu Ni-filtered radiation).

### *Dynamic–mechanical test*

Dynamic–mechanical data were collected at 1 Hz and at a heating rate of 4°C $\mathrm{min}^{-1}$ from $-100$ to 130°C under a nitrogen purge with a DMTA-Polymer Laboratories apparatus configured for automatic data acquisition.

## RESULTS AND DISCUSSION

### *Phase diagram*

*Figure 1* shows the phase diagram of the iPP/HOCP system with the occurrence of both the lower critical solution temperature (*LCST*) and the upper critical solution temperature (*UCST*). The observed melting points and the $T_g$s are taken from reference 5. The sketched line was calculated by the Fox equation[6] assuming random mixing between the amorphous iPP and HOCP molecules, setting $T_g$ (iPP) = 0°C and $T_g$ (HOCP) = 65°C.

The shape of the experimental cloud point curves seems to indicate the existence of a closed-phase loop. The presence of the *LCST* and *UCST* indicate that the iPP and HOCP are miscible at temperatures higher than 240°C and lower than 90°C whereas the system undergoes phase separation in the range between these two temperatures.

At room temperature the iPP, 95/5 and 90/10 iPP/HOCP films are opaque because of the presence of iPP crystals. The films with HOCP content > 20 wt% are transparent as they do not contain crystals of iPP but iPP in the smectic form[5] and, of course, one amorphous phase constituted by amorphous iPP and HOCP. This explanation is supported by the WAXS diffractograms of *Figure 2*. In *Figure 2* it is shown that iPP film crystallizes mainly in the conventional α form, whereas for the 70/30 film the iPP assumes the smectic form.

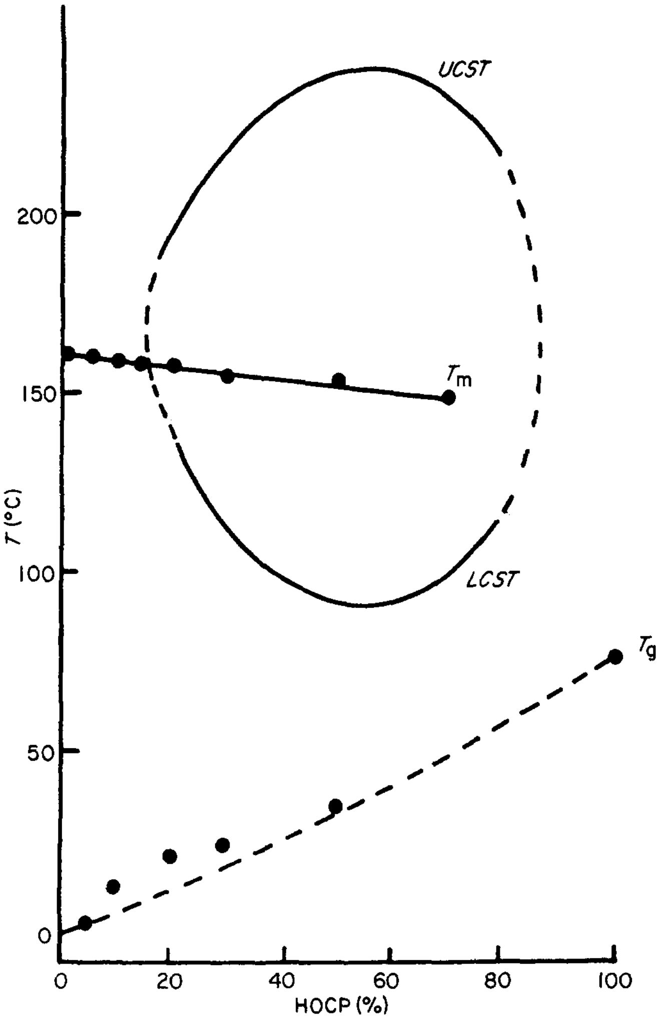

**Figure 1** A phase diagram of the iPP/HOCP system

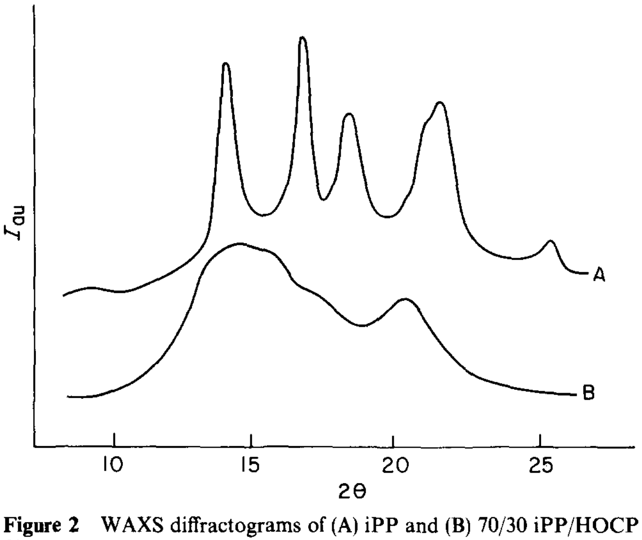

**Figure 2** WAXS diffractograms of (A) iPP and (B) 70/30 iPP/HOCP films

If we confine our analysis to the isotropic film 50/50 iPP/HOCP heated from 25 to 260°C; at room temperature (see *Figure 3a*) the isotropic film is constituted by iPP in the smectic form and one homogeneous phase containing amorphous iPP and HOCP; at about 50–70°C there is the change of iPP from the smectic form to the monoclinic α form that melts at about 160°C; this phenomenon is detected by the d.s.c. thermogram shown in *Figure 4* for 70/30 films: the first peak, at about 60°C, is due to the melting of the smectic phase of iPP, soon

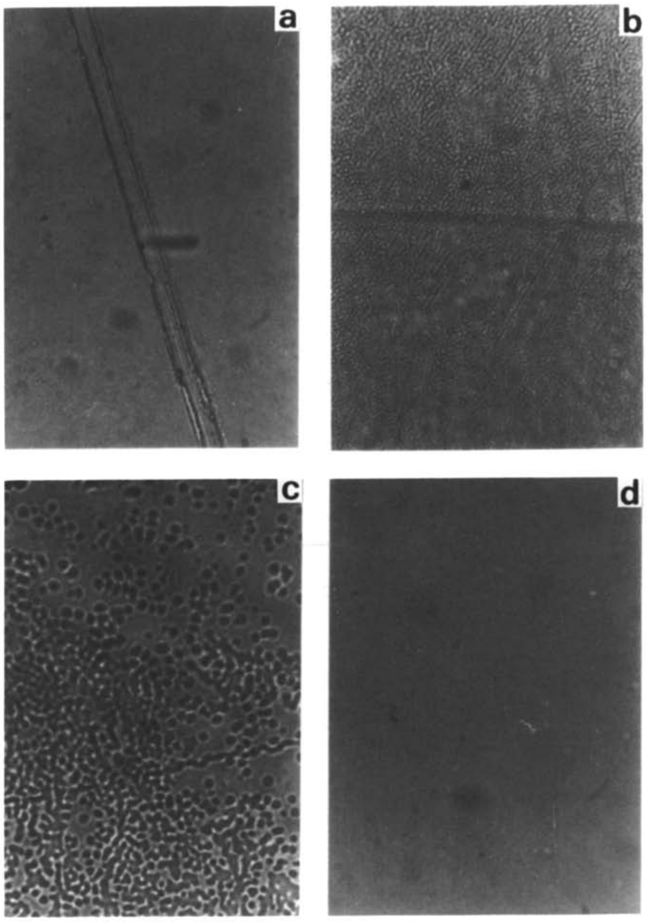

**Figure 3** Optical micrographs of 50/50 iPP/HOCP films: (a) 25°C (18 ×); (b) 100°C (18 ×); (c) 220°C (37 ×); (d) 250°C (18 ×)

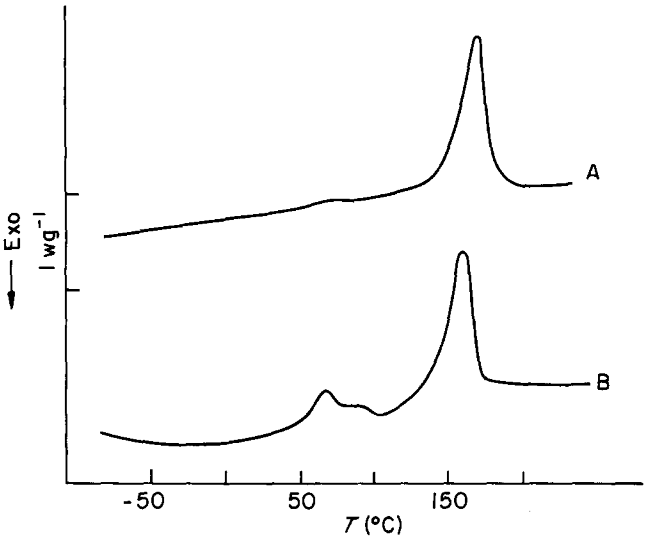

**Figure 4** D.s.c. thermograms of (A) iPP and (B) 70/30 iPP/HOCP films

followed by an exothermic peak due to recrystallization in the more stable monoclinic structure, and the third peak corresponds to the melting of the α form.

It is interesting to note that after the smectic–monoclinic transitions the film still appears homogeneous because the iPP crystals are not detectable by optical microscopy due to their small dimensions; when the film is heated to about 90°C there is the appearance of an interconnected two-phase morphology (or modulated structure), see *Figure 3b*. In the temperature range from 90 to the melting temperature (≈160°C) the film contains three phases; one crystalline phase and two amorphous phases. On increasing the temperature, the modulated structure remains up to 240°C, where a rapid dissolution of the interconnected two-phase morphology takes place and the film becomes homogeneous again (see *Figure 3d*).

We analyse now the path from 260°C to room temperature. When the film is quenched from 260 to 25°C the final film contains iPP in smectic form and one homogeneous amorphous phase. If the film is cooled slowly from 260°C, for example at 2°C min$^{-1}$, the modulated structure appears at 240°C indicating the formation of two phases; when the temperature is lowered to about 140°C a certain percentage of iPP is able to crystallize forming a spherulitic superstructure that hides the two amorphous phases (see *Figure 5*).

*Figure 6* shows the optical micrographs of the 80/20 iPP/HOCP film. For this isotropic film the phase separation starts at about 150°C and the phase dissolution takes place rapidly at about 190°C. *Figure 6c* shows the late aspect of the two phases at 190°C.

For the films of iPP/HOCP 95/5 and 90/10, whose starting morphology is spherulitic, no phase separation was observed after the melting of the crystals. The decrease of the observed melting points of the films with HOCP content up to 20 wt% could be attributed to thermodynamic and kinetic factors, whereas the decrease observed for the blends with HOCP content higher than 20 wt% should be only due to kinetic factors. Moreover

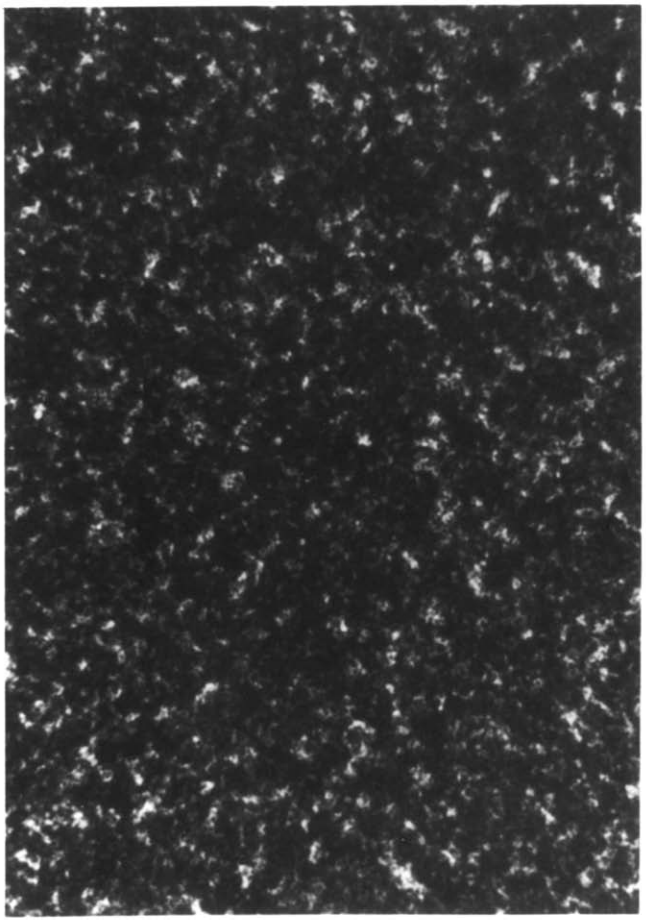

**Figure 5** Optical micrograph of 50/50 iPP/HOCP film crystallized at 130°C, after melting at 240°C and cooling at 2°C min$^{-1}$. Part of a large spherulite is shown

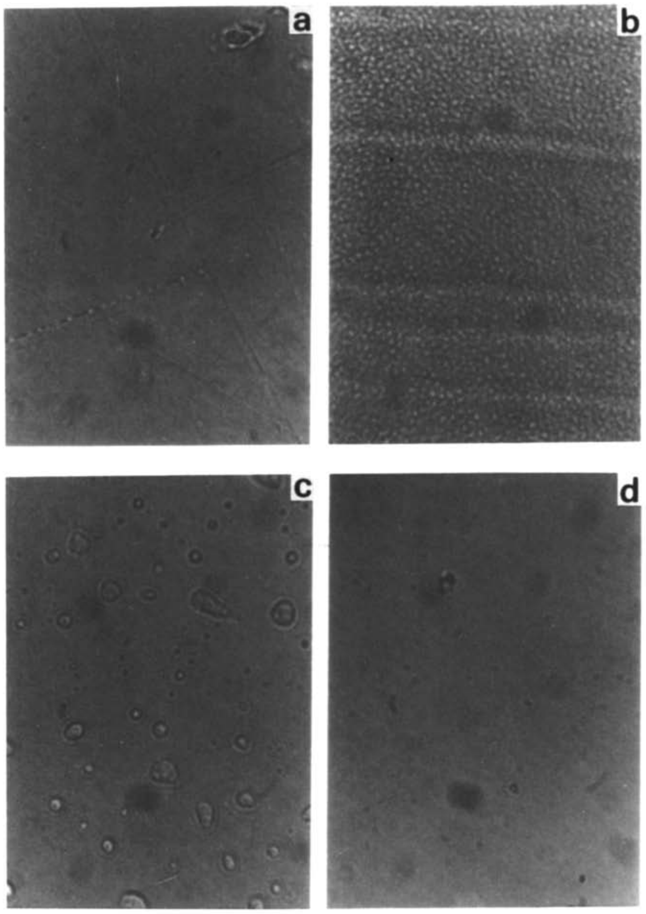

**Figure 6** Optical micrographs of 80/20 iPP/HOCP film: (a) 25°C; (b) 150°C; (c) 190°C; (d) 210°C

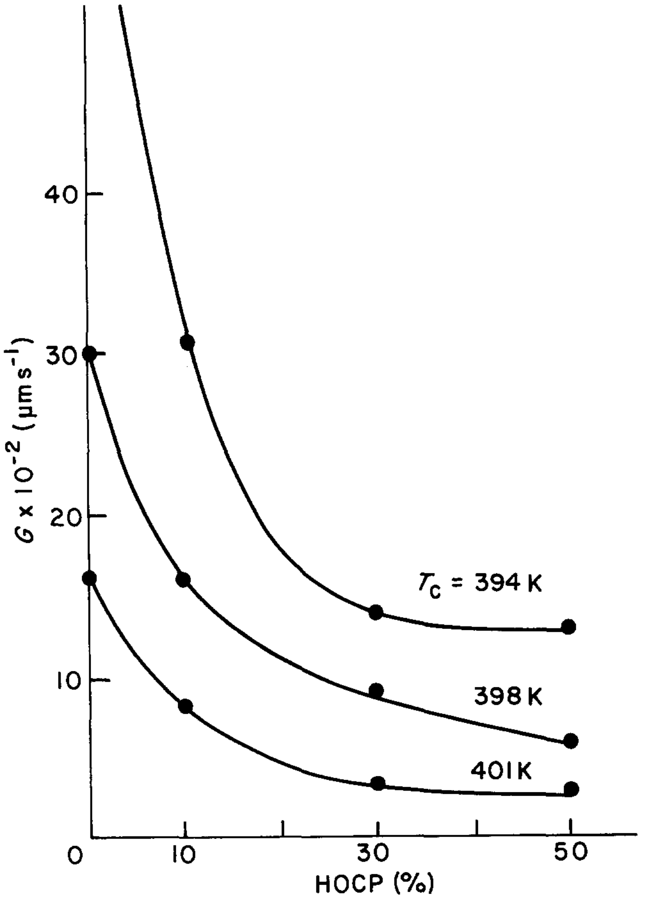

**Figure 7** Spherulite radial growth rate as a function of blend composition for iPP/HOCP blends

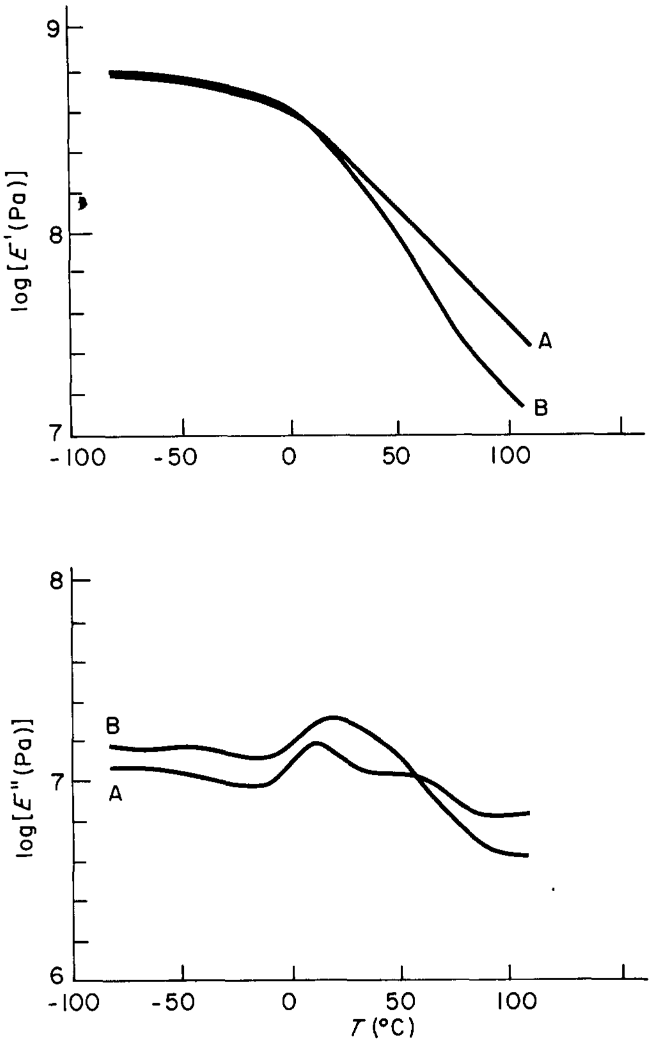

**Figure 8** $E'$ and $E''$ as a function of temperature, obtained at a frequency of 1 Hz, of (A) iPP and (B) 95/5 iPP/HOCP isotropic films

in *Figure 7*, taken from reference 1, we have reported the spherulite radial growth rate, $G$, as a function of composition at three crystallization temperatures.

The continuous decrease of $G$ from plain iPP to the 70/30 composition is observed, whereas $G$ for the 50/50 blend is almost the same as that of the 70/30 blend. This constancy of the values of $G$ for the two blends is in accordance with the phase diagram in *Figure 1*. In fact both the 70/30 and 50/50 blends, at fixed crystallization temperature, separate in the same two amorphous phases before isothermal crystallization takes place. Hence the spherulites grow from a melt phase that is the same for both blends even if the starting compositions of the blends were different.

### *Dynamic–mechanical tests*

The curves of the storage modulus ($E'$) and loss modulus ($E''$) of the iPP/HOCP films are reported in *Figures 8* and *9*. For the sake of clarity, the d.m.t.a. curves have been divided into two groups: the first relates to the iPP film and iPP/HOCP 95/5 film (*Figure 8*); the second relates to the 80/20, 65/35 and 50/50 iPP/HOCP films (*Figure 9*).

From an analysis of the figures it can be deduced that: for the iPP and 95/5 films (*Figure 8*), the curves of the loss modulus ($E''$) present a single peak with maxima at 10 and 19°C, respectively; the curves relate to $E'$

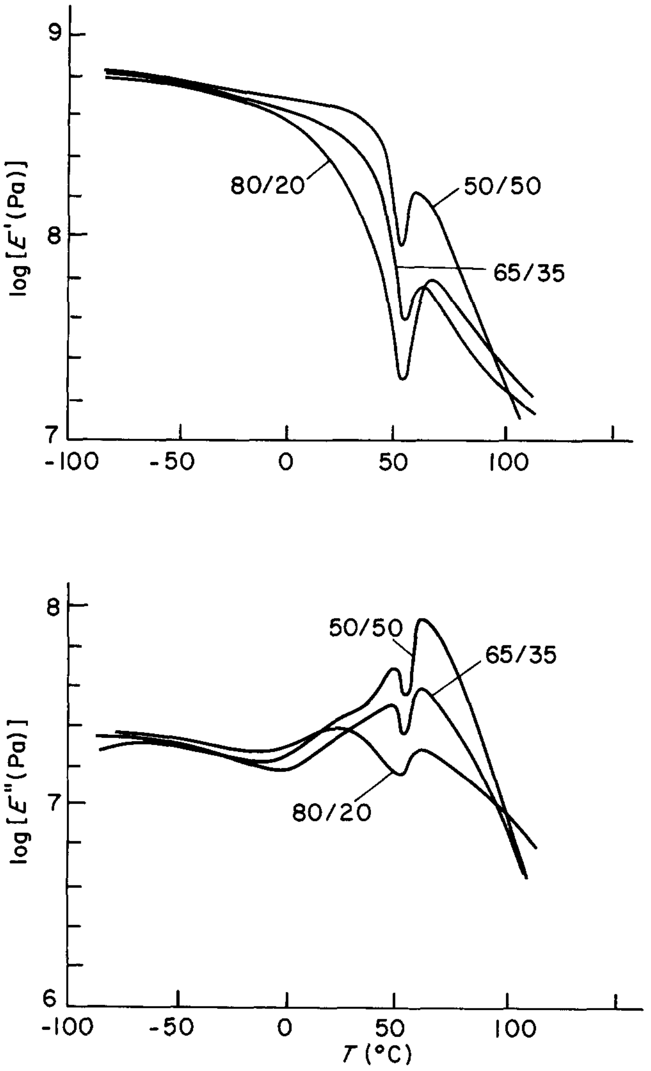

**Figure 9** $E'$ and $E''$ as a function of temperature, obtained at a frequency of 1 Hz, of iPP/HOCP isotropic films, as indicated

(*Figure 8a*), show that $E'$ is the same for both films up to 20°C. This indicates that an addition of 5 wt% of HOCP to iPP is not enough to modify the modulus at low temperatures. At higher temperatures, $E'$ decreases for both films more steeply for the 95/5 film than for the pure iPP film. The decrease of $E'$ with temperature is characteristic of semicrystalline polymer and the diverse slopes of the two curves are due to the fact that iPP film is more crystalline than the 95/5 film.

For the films of 80/20, 65/35 and 50/50 iPP/HOCP blends (*Figure 6a*), the curves of $E'$ present a plateau at low temperatures whose extension increases with HOCP content in the film. In fact for the 80/20 film, $E'$ keeps almost constant from −80 to 0°C, whereas for the 50/50 film it is constant up to 30°C. It is observed that $E'$ values increase slightly along the series from 80/20, 65/35 and 50/50. After the plateau, the $E'$ values decrease swiftly with a minimum at about 55°C for all three films; the curves then increase again and finally there is a definitive decrease. This behaviour of $E'$ is obviously reflected in the shape of the $E''$ curves that present two distinct peaks.

The behaviours of $E'$ and $E''$ could be explained by considering that the amorphous iPP and the HOCP are miscible in the temperature range of the dynamic–mechanical experiment and that the $T_g$ of the film increases with the HOCP content: so $E'$ is constant up to $T_g$ and then decreases at temperatures higher than $T_g$; the rapid decrease observed for the $E'$ curves is due to the fact that the films contain iPP in smectic form that melts at about 55°C and then crystallizes inducing the transient increase of the modulus. The smectic–monoclinic transition affects the shape of the $E''$ curve with the formation of two peaks.

## CONCLUSIONS

This work reports the results of a study of miscibility and an analysis of the dynamic–mechanical behaviour of iPP/HOCP isotropic films. It is found that the iPP/HOCP system is a complex polymer system. In fact, depending on temperature, blend composition and cooling rate from the melt it is possible to obtain one or two amorphous phases together with or without iPP in smectic or monoclinic form.

The dynamic–mechanical thermal analysis shows that $E'$ increases with HOCP content; the plateau at low temperatures (glassy state) increases significantly with HOCP content indicating clearly the increase of the $T_g$ at higher temperatures.

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