Isotactic polypropylene/hydrogenated oligo(cyclopentadiene) blends: 1. Thermal and dynamic-mechanical behaviour of annealed samples

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(Received 1 November 1990; revised 21 December 1990; accepted 14 March 1991)

Blends of isotactic polypropylene and hydrogenated oligo(cyclopentadiene) were prepared by melting-mixing in a Brabender-like apparatus. Sheets of such blends were moulded under pressure, quenched in water and then annealed for 24 h at 140°C. Wide angle X-ray scattering was used to examine the effect of the annealing treatment on the quenched specimens. Thermal properties were analysed using a differential scanning calorimeter. Melting points and overall crystallinity content decreased linearly up to a content of 50% in water of HOCP. Beyond such a value a further decrease was observed. Dynamic-mechanical tests were performed at various frequencies (in the range 1×10^{-2}–75 Hz) and at different temperatures (from −40°C to 120°C). The two components appeared to be compatible in the amorphous regions of the system, as already suggested in the literature. In fact a unique peak of the loss modulus *versus* temperature (which is representative of the glass transition temperature), was always present. Moreover the maximum of the peak was shifted to higher temperatures with increasing oligomer content. The most interesting feature, however, was the change in shape of the whole curve. In fact the peak broadened more and more whereas the height increased only slightly as the oligomer percentage was increased. A tentative explanation is given in the present paper in terms of particular features of the blend morphology, and of a phase inversion at high HOCP content in the blends.

(Keywords: polypropylene; oligo(cyclopentadiene); blend; compatibility; dynamic-mechanical)

INTRODUCTION

Isotactic polypropylene (iPP) has become a high tonnage polymer since the Ziegler–Natta discovery in 1955[1,2]. It is presently used as virgin material as well as in blends and composites. In particular, some rubbers have been added to it to improve its impact strength at room temperature or below, or to study the influence that elastomers, such as polyisobutylene or ethylene–propylene random copolymers, have on its crystallization behaviour and mechanical properties[3–9].

Generally the two components in these blends are incompatible in the melt. Therefore the system consists of a semicrystalline matrix and a rubbery dispersed phase. The latter represents the reinforcing agent with respect to the low impact performance of the iPP below room temperature.

In order to increase iPP rigidity, inorganic fillers such as calcium carbonate, talc or glass fibres are generally added to obtain a composite material.

In the present paper a different type of additive is used to enhance the iPP modulus. This is a non-crystalline oligomer, a hydrogenated oligo(cyclopentadiene) (HOCP), whose glass transition temperature, T_g, is higher than that of iPP. Furthermore the HOCP is compatible with iPP in the melt as well as in the amorphous regions of the polyolefin, in the composition range from 0 to 50% HOCP content in weight, as already shown in previous work at our Institute[10–12].

Analysis of the crystallization and of the thermal behaviour of thin films showed that the overall rate of crystallization, the spherulite growth rate and the equilibrium melting point of iPP were all decreased by the addition of HOCP[10]. Mechanical and impact tests, performed on specimens obtained under different crystallization conditions from the previous one, some of them being annealed, showed an increase of rigidity in the system, due to the addition of HOCP[11]. Finally, X-ray diffraction patterns, obtained at wide and low angles, showed increased length spacings but no changes in the lamellar dimension with increasing HOCP content of isothermally crystallized samples. Extraction of HOCP by a solvent from such specimens created interesting superstructures[12].

From the above quoted papers the compatibility between amorphous regions of iPP and HOCP seemed to be clear evidence in the concentration range investigated.

In the present paper thermal characterization and dynamic-mechanical tests were performed on specimens first quenched in water at room temperature and then annealed at 140°C for 24 h. The aim was to gain more insight about the compatibility of iPP and HOCP by analysing mainly the viscoelastic behaviour encompassing

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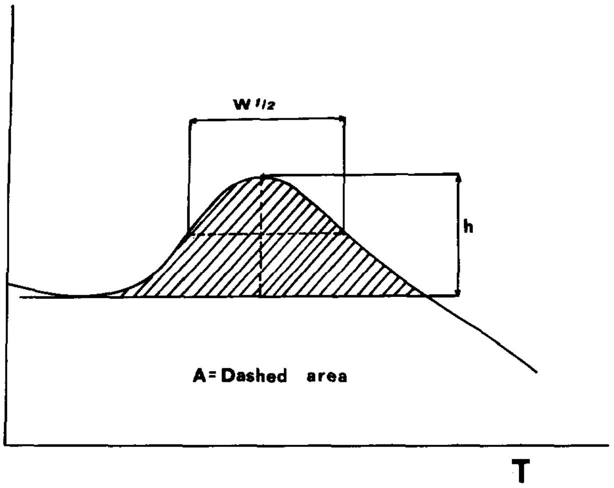

Figure 1 Schematic representation of the G'' *versus* T peak, and graphic definition of the parameters of *Table 2* and *Figure 6*

the glass transition phenomenon, and the thermal properties of the system over a composition range (0–70% HOCP in weight) more extended than that used in the previous papers[10–12].

EXPERIMENTAL

Materials and blends

The isotactic polypropylene (iPP) used was a commercial sample (Moplen T305) produced by Montedison ($M_w = 3 \times 10^5$); the hydrogenated oligo(cyclopentadiene) (HOCP) was a commercial sample (Escorer 5120) produced by Esso Chemical Co. ($M_w = 630$). Blends of the following composition (iPP/HOCP in weight) were prepared by melt mixing in a Brabender-like apparatus (Mixer 600, Haake Inc.) at 200°C: 100/0; 95/5; 90/10; 80/20; 70/30; 50/50; 40/60; 30/70.

Specimen preparation

The blend samples were first pressure moulded as described elsewhere[12], then quenched in water at room temperature and finally annealed at 140°C in an oven for 24 h. The annealing was made to avoid changes of the material structures during the temperature scanning from −40°C to 120°C. Sheets 3.15 mm thick so obtained were cut into a parallelepiped shape ($3 \times 12.7 \times 60\ \text{mm}^3$) to perform dynamic-mechanical tests.

Thermal analysis

Differential scanning calorimetry tests were performed on the blends to measure the crystallinity content and the melting point at a scanning rate of $10°\text{C min}^{-1}$ using a Mettler DSC 3000.

Wide angle X-ray scattering

Wide angle X-ray scattering (WAXS) profiles were obtained using a PW 1050/71 Philips powder diffractometer (Cu Kα, nickel filtered radiation) in the reflection mode scanning 2θ angle in continuous mode.

Dynamic-mechanical tests

Dynamic-mechanical tests were made on parallelepiped specimens in a torsional mode by a 7700 spectrometer from Rheometrics Inc. The nominal frequencies used were 0.01 Hz, 0.1 Hz, 1 Hz, 10 Hz and 75 Hz. The test temperature ranged from −40°C to 120°C. The storage modulus (G') and the loss modulus (G'') were automatically calculated, as a function of frequency and temperature for each blend.

The glass transition temperature (T_g) was measured at the maximum of the G'' peak. On the same peak the width at half height ($w_{1/2}$), the height (h) and the area (A) were calculated. The base line was taken as the horizontal straight-line tangent to the right-hand side minimum, preceding the G'' peak, as typically sketched in *Figure 1*.

RESULTS AND DISCUSSION

Wide angle scattering

The diffraction intensity of WAXS tests as a function of the scattered angle 2θ is shown in *Figure 2* for several iPP/HOCP blends. For up to 30% of HOCP the spectrum shows iPP crystallization in the α form (monoclinic) for both quenched and annealed specimens. Annealing of course increases the amount of crystallinity and the crystal perfection and therefore peak sharpness. From the blend containing 50% in weight of HOCP the quenched samples are in smectic form, which in turn is transformed into the α form after annealing. With a further increase of HOCP content (iPP/HOCP 40/60) the quenched material is still in the smectic form. The annealed samples show, instead, a crystalline iPP whose peaks are sharper than in the case of the 50/50 blend.

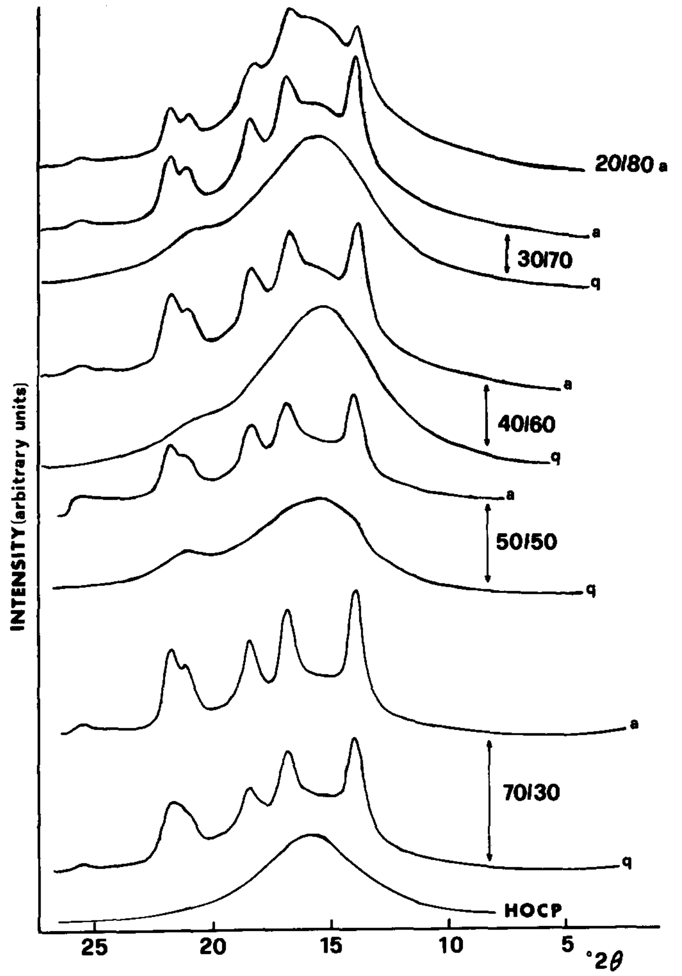

Figure 2 Wide angle X-ray spectra for HOCP and several blends as indicated: q, quenched specimens; a, annealed specimens

Table 1 Thermal properties as a function of HOCP content

HOCP	X_c $iPP_c/(iPP_a + iPP_c + HOCP)$	X'_c $iPP/(iPP_c + iPP_a)$	X_a (Amorph.) $(iPP_a + HOCP)$	T_m (°C)
0	47.5	47.5	52.5	166
5	46	48	54	165
10	44	49	56	165
20	40	50	60	163
30	33	47	67	163
50	26	52	74	160
60	19	47	81	151
70	13	43	87	148

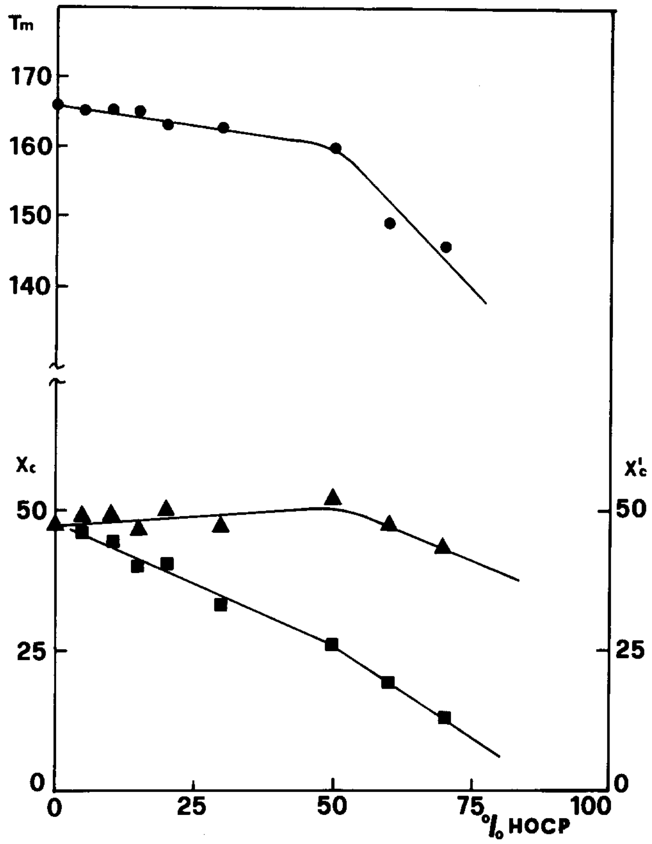

Figure 3 Thermal behaviour of pure iPP and iPP/HOCP blends as a function of the HOCP percentage: ● T_m, melting points; ▲ X'_c, overall blend crystallinity percentage; ■, X_c, crystallinity percentage referred to pure iPP

Even the (iPP/HOCP) 20/80 blend exhibits quite sharp peaks on top of the broad amorphous halo of pure HOCP.

This effect could be due to the fact that at high HOCP contents the annealing treatment at 140°C makes the iPP crystallize in a wholly liquid environment of HOCP. In other words the iPP molecules, diluted in the HOCP solvent, are easily able to migrate towards the growing crystals. In this sense at high iPP content (high iPP melting points) the system is able only to partially recrystallize, improving the crystal perfection, whereas at low iPP content (low iPP T_m) a quasi-total recrystallization takes place. However, the further T_m decrease indicates that the crystal perfection is lower in such a case than for blends with high iPP content (see thermal properties). This could be due to the iPP–HOCP compatibility in the amorphous regions of the solidified materials whose long lamellar spacing increases with HOCP addition[12].

Thermal properties

In *Table 1* from left to right the following parameters are reported as a function of HOCP content (first column):

(a) the overall crystallinity content of the blend, X_c
(b) the crystallinity content referred to iPP, X'_c
(c) the total amorphous content, X_a
(d) the melting point, T_m.

The data for a, b and d are also shown in *Figure 3*.

The trend for all three variables is linear (T_m slightly decreases; X_c decreases and X'_c slightly increases) up to 50% of HOCP in the blends. Beyond this value there is a further diminution in all three parameters. This probably indicates that there has been a phase inversion with a different morphology formed.

Dynamic-mechanical tests

Data, calculated on a linear scale from the curve of loss modulus (G'') *versus* temperature, are reported in *Table 2*, as a function of the frequency f and the iPP/HOCP weight ratio. At each frequency the glass transition temperature, T_g, the width at half height, $w_{1/2}$, the peak height, h, and the area under the peak, A, are reported. They were calculated as explained in the experimental section.

Behaviour at a given frequency. Typical curves, for iPP and blends of varying HOCP content, of G' and G'' as a function of temperature obtained at 1 Hz are reported in *Figures 4* and *5*. The curves relative to blends containing up to 30% in weight of HOCP (*Figure 4*) show a T_g peak shift to higher temperatures and peak broadening with increasing HOCP in the G'' curve (encompassing a temperature range on the base line of about 40°C).

The storage modulus G' is constant at low temperatures and then gradually starts to decrease at temperatures where G'' starts to increase; then an inflection point is present around the G'' maximum followed by a pseudo-plateau which is less and less evident the higher the HOCP content. For HOCP percentages greater than 30% such a pseudo-plateau is no longer distinguishable and the G'' peak broadens considerably, encompassing a temperature range of more than 80°C. The latter behaviour resembles that for a

Table 2 Various parameters calculated from the G'' *versus* T curves for iPP and iPP/HOCP blends

	100/0				95/5				90/10			
f (Hz)	T_g (°C)	$W_{1/2}$ (°C)	h (dyn cm^{-2})	A (dyn cm^{-2} °C^{-1})	T_g	$W_{1/2}$	h	A	T_g	$W_{1/2}$	h	A
10^{-2}	−9	20	298	1.43	2	24	180	1.04	7	23	222	1.17
10^{-1}	−5	21	252	1.17	7	20	172	0.78	13	25	210	1.17
1	−3	20	254	1.08	10	17	164	0.69	18	25	172	1
10	3	21	282	1.38	14	21.5	188	0.87	19	25.5	202	1.17
75	8	25	328	1.82	18	25	246	1.14	24	32	228	1.56
	80/20				70/30				50/50			
10^{-2}	15	30	226	1.51	25	43	296	2.77	43	51	250	2.47
10^{-1}	20	32	166	1.17	31	36	312	2.47	47	45	298	2.81
1	24	32	150	1.0	38	40	268	2.38	51	53	256	2.68
10	30	33.5	160	1.17	44	41	292	2.73	57	59	270	3.2
75	36	37	174	1.34	47	48	340	3.88	64	65	296	3.98
	40/60				30/70							
10^{-2}	46	53	320	3.51	55	51	330	3.55				
10^{-1}	52	54	306	3.33	59	55	322	3.9				
1	60	59	300	3.55	70	57	334	3.85				
10	69	60	312	3.9	75	60	344	4.2				
75	78	72	252	3.64	89	60	410	5.2				

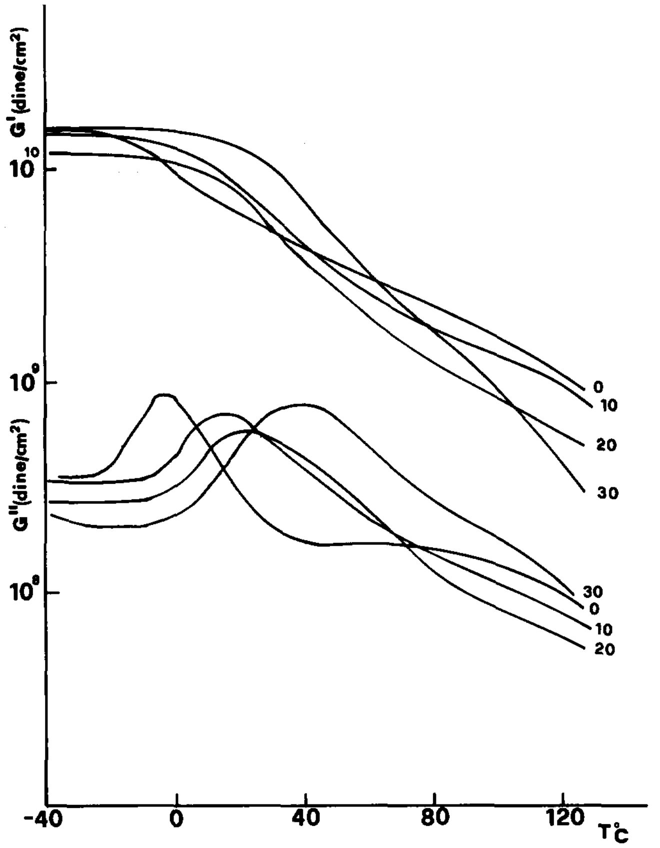

Figure 4 G' and G'' as a function of temperature obtained at a frequency of 1 Hz, in a semilog plot for iPP and blends of HOCP% up to 30% as indicated

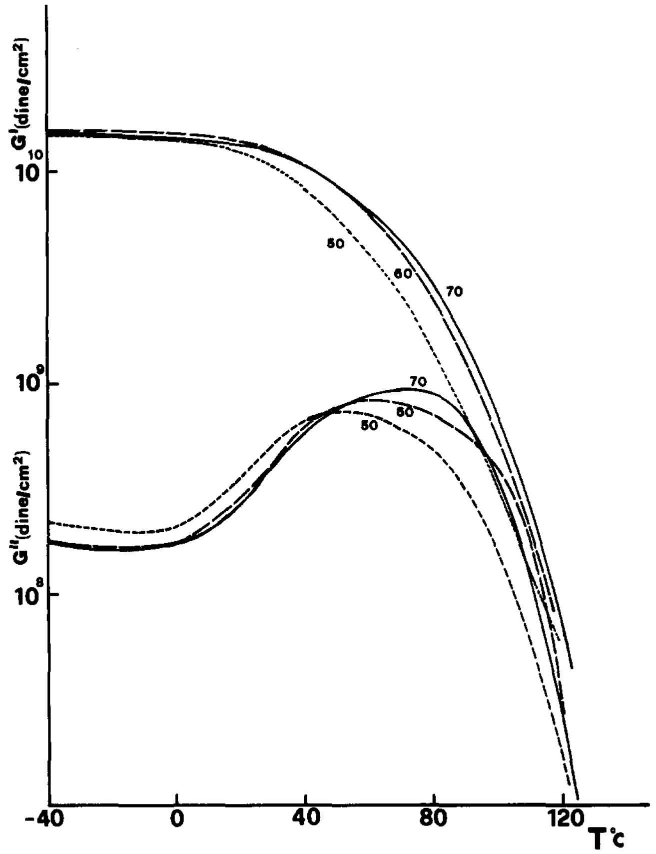

Figure 5 G' and G'' as a function of temperature obtained at a frequency of 1 Hz, in a semilog plot for blends of HOCP% from 50% up to 70% as indicated

quasi-amorphous system having a relatively low average molecular weight. In fact after T_g, G' drops continuously and the pseudo-plateau corresponding to entanglements and/or to the semicrystalline network seems to disappear.

The parameters T_g, $W_{1/2}$, h and A at 1 Hz, given in *Table 2*, are also shown in *Figure 6*, as a function of total amorphous content, X_a, respectively, for a typical but more quantitative comparison among the different blends.

T_g (*Figure 6*) increases monotonically with increasing amorphous content in the system and the trend depends on the frequency used as well. In particular, with increasing frequency T_g increases and the G'' peak

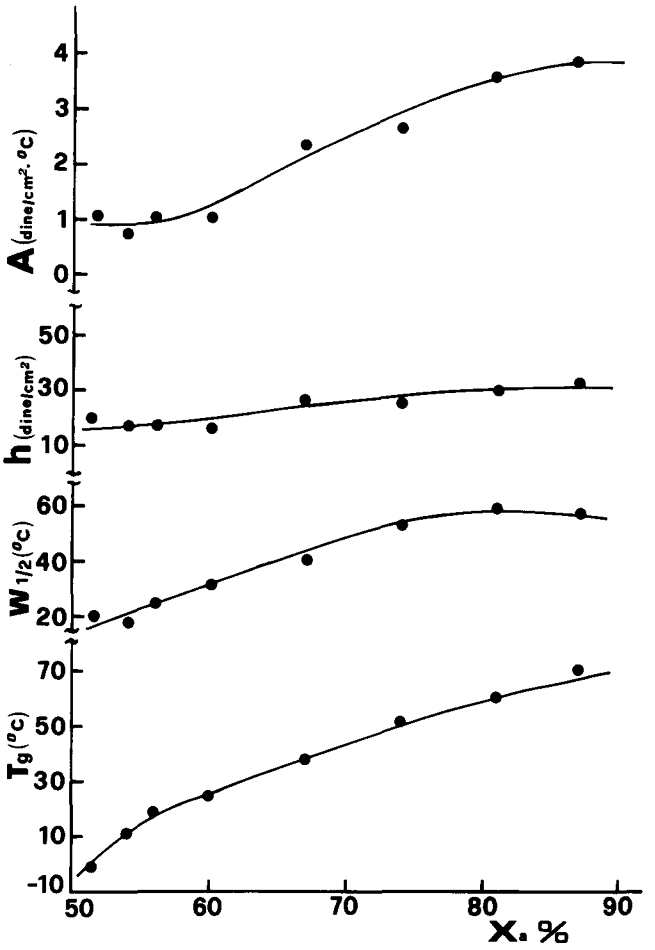

Figure 6 Various parameters derived by G'' *versus* T curves as a function of total amorphous content X_a at 1 Hz: (a) T_g; (b) $w_{1/2}$; (c) h; (d) A

broadens, as will be discussed later. It is to be noted that the highest percentage for which the dynamic-mechanical tests could be performed is 70% of HOCP. Beyond such a value the specimens were too brittle, and a T_g value for pure HOCP could be obtained only by d.s.c. measurements. Hence, since this value is not directly comparable with the other data obtained by dynamic mechanical tests, no comparison could be made with theoretical curves, such as Fox's law.

The increase of the unique blend T_g and its intermediate values between those of pure iPP and HOCP are further confirmation that the two components iPP and HOCP are compatible in the melt and in the amorphous regions of the system.

Analysing the shape of the peak one can make interesting observations. It is well known that in a semicrystalline polymer, the peak height is much lower than in the same fully amorphous polymer[2,13]. The peak width is, instead, broadened due to the more numerous species present in the amorphous regions. In fact the mobility of the various chains depends not only on the way they are entangled in the amorphous zones but also on how they are linked to the crystals (loops, cilia, etc.). This concept was developed by Boyer several years ago, who proposed the existence of a multiple glass transition in the case of semicrystalline polymers[14].

Adding HOCP up to 20% to iPP, the height h (*Figure 6c*) slightly decreases, whereas the width at half height $w_{1/2}$ (*Figure 6b*) starts to increase. The effect is balanced in the area A subtended by the peak (*Figure 6d*).

With further addition of HOCP h slightly increases while $w_{1/2}$ and A increase more markedly. This behaviour is quite different from that for a semicrystalline homopolymer. In fact h changes very slightly in spite of the large increase of the amorphous content due to the HOCP addition. However, this is compensated for by the marked increase in $w_{1/2}$ and consequently A strongly increases at high HOCP content. In other words the number of resonant species at that frequency and at the various temperatures is considerably enhanced. Since iPP and HOCP are compatible in the amorphous regions, the latter mixes in the interlamellar zones with iPP (see increase of long spacing at constant lamellar thickness[12]). Therefore the concentration cannot be constant in the interlamellar zones, giving rise to a gradient going from pure iPP in the vicinity of the crystallites to a high HOCP content mixture in the middle of the interlamellar zones. This increase of the number of species having a different mobility in the blend with increasing T_g values can explain the observed large peak broadening as the HOCP content increases. This qualitative model could be typical of all binary blends consisting of a semicrystalline polymer and a compatible amorphous oligomer (or polymer).

Behaviour at varying frequency. By changing the externally imposed frequency the shapes of the G' and G'' curves as functions of temperature change as well. This is a well known effect particularly for T_g, which increases with increasing frequency, f (*Figure 7*). This interpretation is based on the fact that by increasing f, the molecular species, whose relaxation or retardation

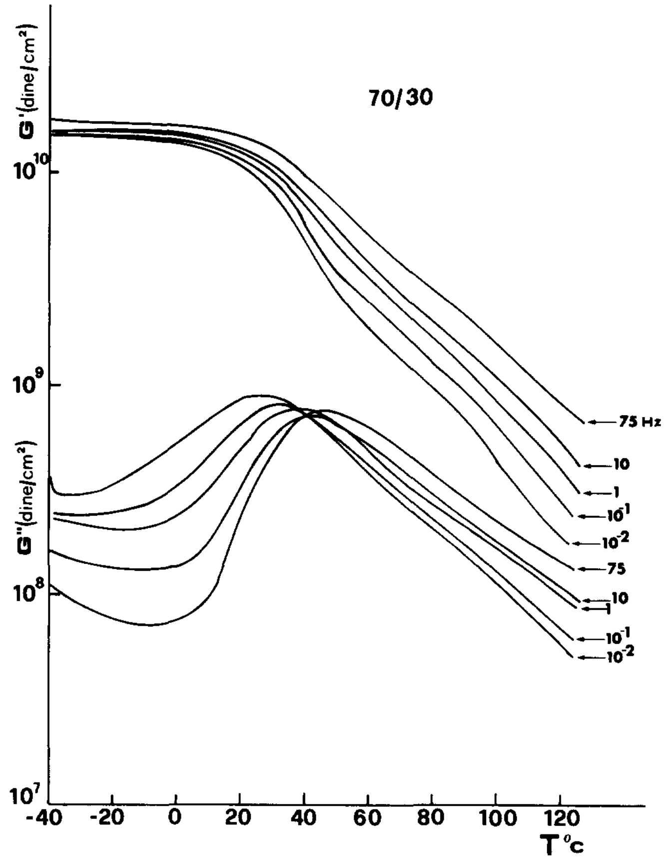

Figure 7 G' and G'' as a function of temperature for a blend of a given composition (iPP/HOCP = 70/30) at various frequencies as indicated

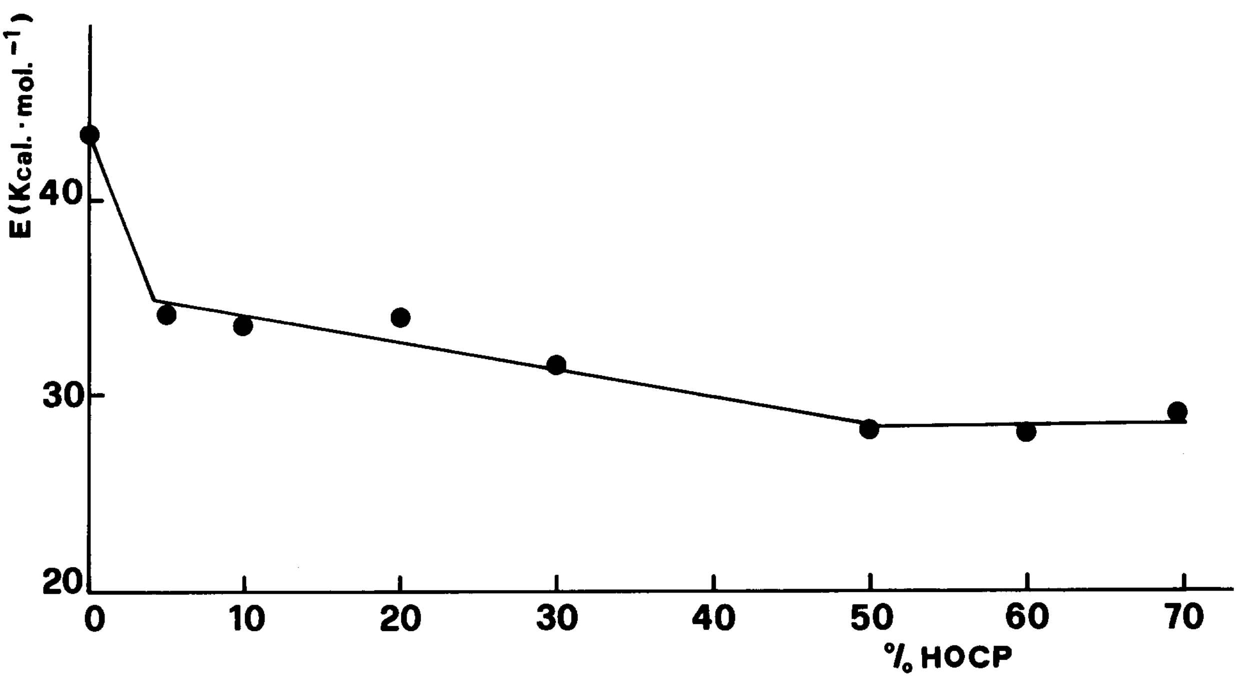

Figure 8 Apparent activation energy E of the glass transition as a function of HOCP content

times depend on the temperature, have less time to respond. Therefore the system behaves as though it were more rigid and therefore shows higher T_g the greater the frequency. It is also possible to observe that no curve superposition can be obtained by simple horizontal translation, since the whole curve shapes change with varying frequency. This effect, as clearly explained by Ferry[15], is due to the non-linear temperature dependence of the shift factor, a_T. In other words, the shapes of the G' *versus* T curves at a given point P (G', T) are different at different frequencies. They depend, in fact, on both the local derivative of $G'(\omega)$ at the given temperature and on that at a_T (T) at the particular temperature.

Other observations are that the higher the curve frequency the higher the G' values prior to the transition and the lower the G'' maximum and the G'' values in the low temperature range. These effects are also a consequence of an increased material rigidity in response to the increased external strain frequency.

Plotting $\log f$ against reciprocal temperature on a linear scale, one can calculate an activation energy, E, of the transition. In fact an Arrhenius-type law holds in such a case. Such a parameter E takes into account the way in which the molecular species change their response with frequency by a temperature variation. It is to be emphasized, however, that the shapes of the peak change with frequency and that a limited range of frequencies and temperatures has been explored. Therefore E is to be considered only an apparent activation energy, useful, however, for comparison of the behaviour of different blends.

In *Figure 8*, E is shown as a function of HOCP content. There is a small sharp decrease of E from the value of pure iPP (43 kcal mol^{-1}) down to a value of about 35 kcal mol^{-1} with an addition of only 5% of HOCP. Then there is a slight linear decrease up to 50% HOCP down to a value of about 30 kcal mol^{-1}, which remains constant at higher HOCP content.

This last effect could be related to the phase inversion at high HOCP content between iPP and HOCP having a different blend morphology.

CONCLUDING REMARKS

In this paper a new insight was gained about the properties and the possible morphological features of iPP/HOCP blends, whose constituents were confirmed to be compatible in the amorphous regions of the system.

WAXS patterns showed the effect of the quenching and of the successive annealing of the specimens on the crystalline and amorphous phases. Some different features were observed when a phase inversion at high HOCP made the iPP recrystallize during annealing in the presence of liquid matrix HOCP. In particular thermal properties showed that the annealing treatment yielded the same crystallinity content on the iPP basis in all the blends up to 50% of HOCP content. Beyond such a value the crystallization behaviour was different due to a phase inversion between the two components.

In the dynamic-mechanical analysis it was proposed that the HOCP, contained among the iPP lamellae (as already shown elsewhere[12]), formed a gradient of concentration with amorphous iPP chains. This model is a reasonable interpretation of the T_g shift and particularly of the peak broadening in the loss modulus *versus* temperature curve. This finding and interpretation could possibly be extended to other blends consisting of a semicrystalline polymer and an oligomer or a polymer compatible with it.

Work is in progress on the same samples to further confirm and enhance the insight into the morphology and properties of such a system by complementary techniques.

ACKNOWLEDGEMENT

This work was partially supported by Progetto Finalizzato 'Chimica Fine II' of CNR.

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