

Morphology and Supermolecular Structure of Polypropylene–Poly(1-butene)–Hydrogenated Oligo(Cyclopentadiene) Ternary Blends

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Received 15 April 1997; accepted 18 October 1997

ABSTRACT: Ternary blends containing polypropylene, poly(1-butene), and hydrogenated oligo(cyclopentadiene) have been studied using microscopic, calorimetric, and X-ray diffraction techniques. While no phase separation was found to occur in the melt for all the considered compositions, demixing phenomena were observed by scanning electron microscopy in the ternary blends after crystallization of both polyolefins. On the other hand, a homogeneous surface without the presence of separate domains was observed for blends quenched avoiding the crystallization of polypropylene. The composition has been found to affect the crystallization and the melting properties of the ternary blends and the crystal modification of polypropylene. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1877–1882, 1998

Key words: polypropylene; poly(1-butene); hydrogenated oligo(cyclopentadiene); ternary blends; characterization

INTRODUCTION

In previous works,^{1,2} we reported studies concerning the thermal behavior of polypropylene (PP)–poly(1-butene) (PB)–hydrogenated oligo(cyclopentadiene) (HOCP) ternary blends. These ternary blends, cooled from the melt up to a temperature allowing the crystallization of the PP component, then quenched to avoid the crystallization of the PB component, showed a single glass transition temperature depending on composition. On the other hand, two separate T_g values were observed after the crystallization of both polyolefins. This revealed that the crystallization of the PB component produces demixing phenomena. An influence of the blend composition on the

isothermal bulk crystallization kinetics of the PP component was observed. For all the examined blends, the melting temperature of the PP component was found to linearly increase with the crystallization temperature, and the equilibrium melting temperature was influenced by blend composition. These results suggested the occurrence of miscibility in the melt of the three components in the considered ratios. The miscibility in the melt of binary blends prepared from every couple of the above components was evidenced previously.^{3–5}

Studies on the crystallization from the melt of PB–HOCP binary blends, rich in PB component, showed that PB crystallizes in the tetragonal crystal modification (form II) and then transforms in the hexagonal crystal modification (form I).⁶ This transformation changes the thermal, mechanical, and physical properties of the polymer.^{7–13}

In the present work, the morphology and the

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structure of PP–PB–HOCP ternary blends have been investigated by using microscopy techniques, differential scanning calorimetry (DSC), and wide angle X-ray diffraction (WAXD). Some preliminary results have been already given.¹⁴

EXPERIMENTAL

Materials

Ternary blends of isotactic PP (Moplen T 30 S, \bar{M}_w 300,000, from Montedison), PB (PB 8340, \bar{M}_w 700,000, from Shell), and HOCP (Escorez, \bar{M}_w 630, from Esso Chemical) were prepared by melt-mixing the components at 195°C for 15 min in a Brabender electronic plasticorder PLE 330 mixer, in the following weight ratios.

PP	80	70	70	60	60	60	50	50	50	50
PB	10	10	20	10	20	30	10	20	30	40
HOCP	10	20	10	30	20	10	40	30	20	10

Optical Microscopy

The microscopic analyses were carried out on thin films of the blends by employing an optical polarizing Wild microscope with an automatic hot-stage Mettler model FP 82 controlled by a Mettler FP 80 Control Processor. Thin films of blend samples were sandwiched between microscope cover glasses and melted at 260°C for 5 min and then cooled to 90°C at 2°C min⁻¹.

Scanning Electron Microscopy

The blends, fractured under liquid nitrogen, were observed after gold-coating with a scanning electron microscope, Philips model 515, operated at 9.4 kV. Morphological analysis by scanning electron microscopy (SEM) was carried out on blends prepared in the following two different ways:

1. Crystallization from the melt, by cooling the samples from 200°C to room temperature; and
2. isothermal crystallization of the only PP component obtained by quick cooling the samples from 200 to 120°C. After the complete crystallization of the PP component, the blends were quenched in liquid nitrogen to avoid the crystallization of the PB component.

Differential Scanning Calorimetry

The ternary blends and the pure components were analyzed by a Perkin–Elmer DSC-4/Thermal Analysis Data Station. About 7 mg of sample were melted at 200°C for 10 min, then cooled to 0°C at the constant rate of 5°C min⁻¹. The same pan was heated again from 0 to 200°C at a scanning rate of 20°C min⁻¹. The crystallization and melting temperatures were obtained from the maximum of the exothermic and endothermic peaks, respectively. An indium standard sample was used to calibrate the instrument.

Wide-Angle X-ray Diffraction

The WAXD data were obtained at 20°C using a Siemens D-500 diffractometer equipped with a Siemens FK 60-10, 2000W Cu tube (Cu K_α radiation, $\lambda = 1.54 \text{ \AA}$). The operating voltage and current were 45 kV and 25 mA, respectively. The data were collected (0.02 2 θ° intervals) and treated by the Diffract-AT V 3.2 software controlling the system. The degree of crystallinity of the blends was calculated from diffracted intensity data in the range of 2 θ° 7.5–30.5 by using the area integration method.¹⁵ For the WAXD analysis, the samples were crystallized under the same thermal conditions adopted in the first DSC scan, as follows: thin films of pure PP, pure PB, and blends were melted at 200°C for 10 min, then cooled to 0°C at the constant rate of 5°C min⁻¹, in the automatic hot-stage Mettler FP-82. Every sample was analyzed immediately after crystallization. A nickel standard sample was employed to determine the instrumental calibration.

RESULTS AND DISCUSSION

Optical Microscopy

When thin films of PP–PB–HOCP ternary blends were cooled from 260 to 90°C at 2°C min⁻¹, no melt phase separation was observed for all the examined compositions. At temperatures lower than 140°C, PP crystallized, showing a birefringent spherulitic structure. In every case, when PP crystallization was complete, no separate domains were observed either in the intraspherulitic region or in the interspherulitic contact zones. Cimmino et al.¹⁶ found that the industrial films produced by using binary blends of PP and HOCP, when cooled from 260°C to lower temperatures, showed at the optical microscopy a modulated structure, indicating the formation of two

phases. This fact led the authors to carefully study the morphology of the ternary blends by SEM.

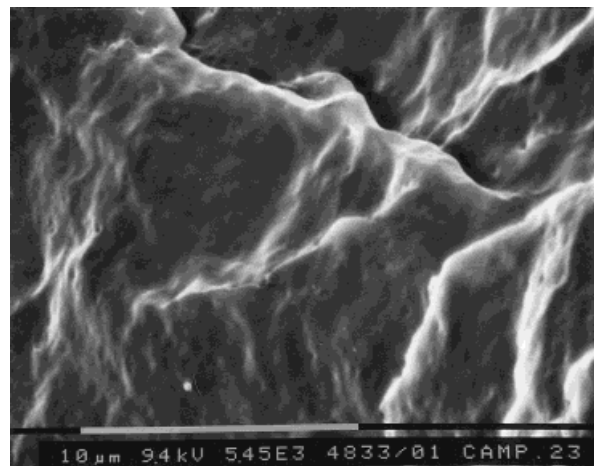
Scanning Electron Microscopy

Examination by SEM of blends crystallized from the melt at room temperature revealed a homogeneous surface without domains of separate phases for 70/20/10 and 50/20/30 PP-PB-HOCP ternary blends and for all the ternary blends containing 10% of PB (Fig. 1A). In the case of the remaining blends, 60/20/20, 60/30/10, 50/30/20, and 50/40/10, the SEM micrographs showed the presence of bubbles as a separate phase having a diameter generally lower than $2\ \mu\text{m}$ (Fig. 1B). On the other hand, when those last blends were cooled from the melt at 120°C , kept under isothermal conditions for a sufficient time to completely crystallize the PP component and eventually quenched in liquid nitrogen to avoid the PB crystallization, they showed a homogeneous surface without the presence of bubbles or other separate domains (Fig. 1C). This suggests that the formation of bubbles can be reasonably attributed to the phase separation that occurs during the crystallization of the PB component. For all the examined compositions, the above results indicate compatibility between the three components before PB crystallization. The demixing phenomena observed after PB crystallization were dependent on blend composition. These results are in agreement with the detection of one or two T_g 's revealed by dynamic mechanical thermal analysis (DMTA) on quenched or crystallized blends.²

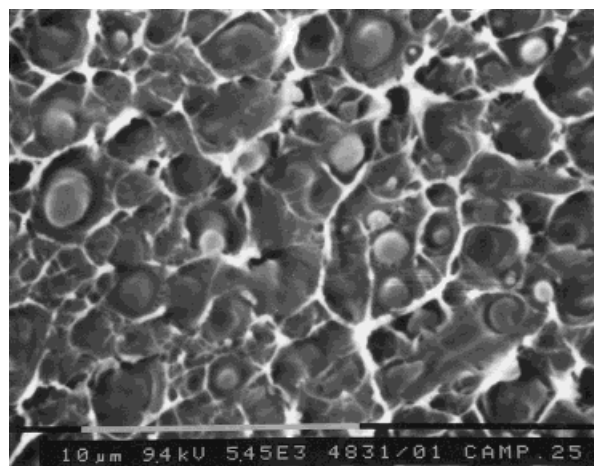
Differential Scanning Calorimetry

The ternary blends cooled from the melt in DSC measurements showed two exothermic peaks due to the PP and PB crystallization, respectively (Fig. 2). The increase of the HOCP fraction in the ternary blends produced a decrease of the T_c values for both polyolefins (Table I).

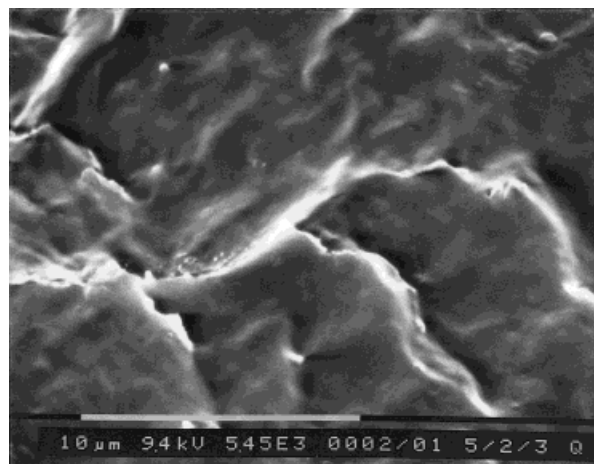
After crystallization, the ternary blends were heated to 200°C at a constant rate. In Figure 3, the DSC scans observed for ternary blends prepared with 60% of PP are reported. Besides the melting peak of the PP component, the thermograms of all the ternary blends exhibit two endothermic peaks centering at $82\text{--}91^\circ\text{C}$ and $104\text{--}111^\circ\text{C}$, respectively, and an exothermic peak centering at $91\text{--}100^\circ\text{C}$. The two endothermic peaks correspond to the melting of PB crystallized in forms I' and II, respectively. As suggested by Boor and Youngman,⁸ we define I' as the crystalline



(A)



(B)



(C)

Figure 1 SEM micrographs of PP-PB-HOCP ternary blends: (A) 50/10/40, crystallized from the melt at room temperature; (B) 50/30/20, crystallized from the melt at room temperature; (C) 50/30/20, crystallized under isothermal conditions up to complete crystallization of the PP component and eventually quenched in liquid nitrogen.

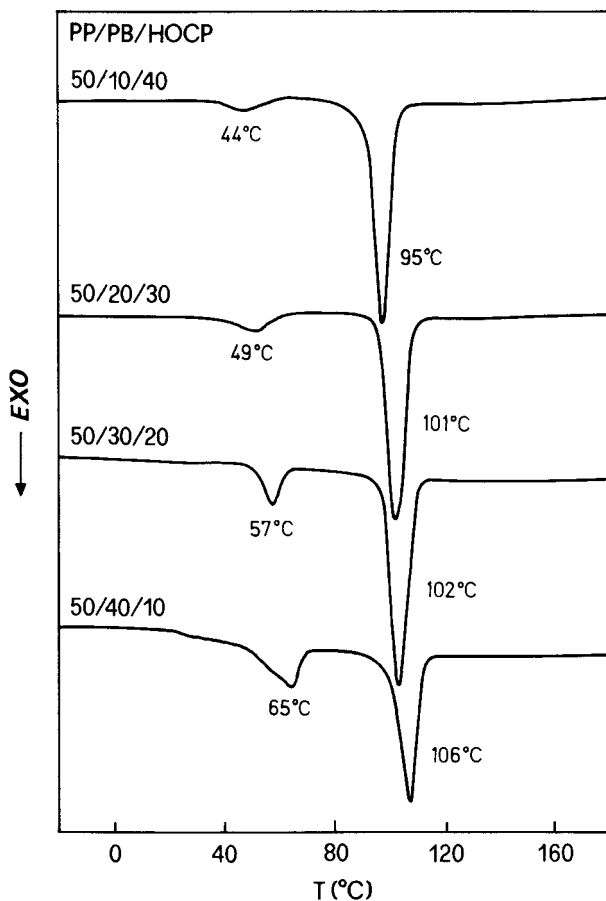


Figure 2 DSC seams for the crystallization from the melt of ternary blends prepared with 50% of PP. The samples were cooled from 200 to -20°C with a constant rate of $-5^{\circ}\text{C min}^{-1}$.

form of PB that shows the crystalline X-ray profile of form I (see below), but it melts at a considerably lower temperature than that ($130\text{--}140^{\circ}\text{C}$) of the material spontaneously deriving from form II. The melting of form I' is immediately followed by PB recrystallization in form II and by its melting (including the crystalline form II possibly present in the blend at the origin).

Generally, for blends prepared with a constant fraction of PB, the melting point of the two forms decreased with the increase of the HOCP fraction in the blend (Table I). The tendency of PB to crystallize in form I' rather than in form II appeared to be strongly influenced by blend composition. The melting point of PP slightly decreased with the decrease of its fraction in the blend or with the increase of the fraction of HOCP.

Wide-Angle X-ray Diffraction

In Figure 4, the WAXD profiles of two ternary blends containing 60% of PP are reported. The

Table I Crystallization and Melting Temperatures ($^{\circ}\text{C}$) Measured by DSC on PP-PB-HOCP Ternary Blends

PP-PB-HOCP	80/10/10	70/10/20	70/20/10	60/10/30	60/20/20	60/30/10	50/10/40	50/20/30	50/30/20	50/40/10	100/0/0	0/100/0
T_c , PP	107	103	107	99	103	107	95	101	102	106	107	—
T_c , PB	58	55	59	50	54	64	44	49	57	65	—	57
T_m , PP	166	164	165	162	162	164	160	161	163	163	170	—
T_m , PB _I	94	90	91	87	88	91	82	84	88	88	—	—
T_m , PB _{II}	111	110	111	108	108	110	104	105	108	109	—	114

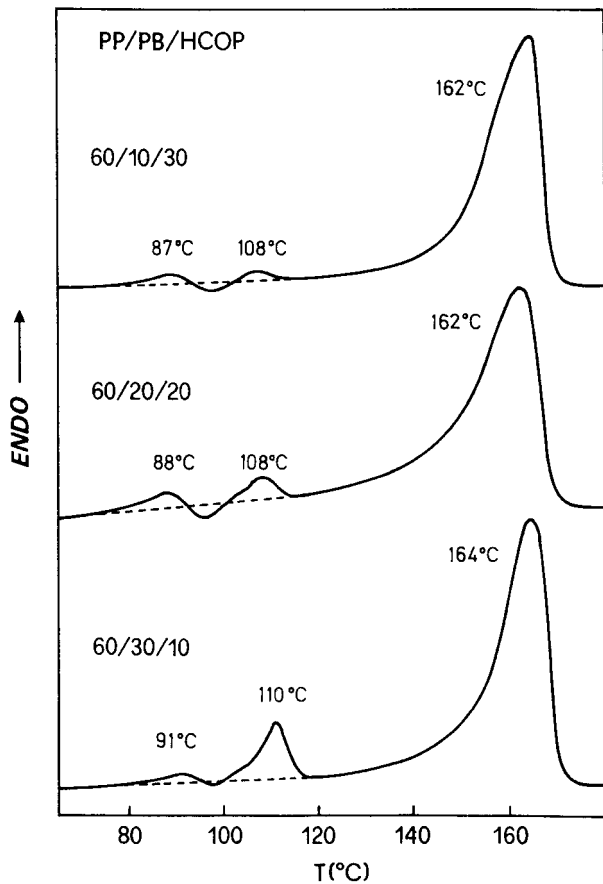


Figure 3 DSC scans for the melting of ternary blends prepared with 60% of PP. The samples were heated from -20 to 200°C with a constant rate of $20^{\circ}\text{C min}^{-1}$.

X-ray diffraction due to the amorphous phase increased with the increase of the HOCP fraction in the blend. The crystalline index of the blend (ω_b) decreased with the increase of the HOCP fraction (Table II). The diffractograms of the blends showed that PP crystallizes in the α -form for the whole range of the compositions analyzed, while the crystalline forms of PB were strongly influenced by blend composition. In Figure 5, the WAXD profiles of blends containing different amounts of PB (and a constant fraction of PP) show different intensity diffraction relative to the crystalline forms I' and II.

The contribution to the total crystallinity of the blend (ω_b) of the three different crystalline phases (α -form of PP, forms I' and II of PB) possibly present in the ternary blends were calculated by the following equations:

$$\omega_{\text{PB,I}'} = \frac{I_{\text{PB,I}'}a}{I_{\text{PB,I}'}a + I_{\text{PB,II}}b + I_{\text{PP},\alpha}c} \omega_b \quad (1)$$

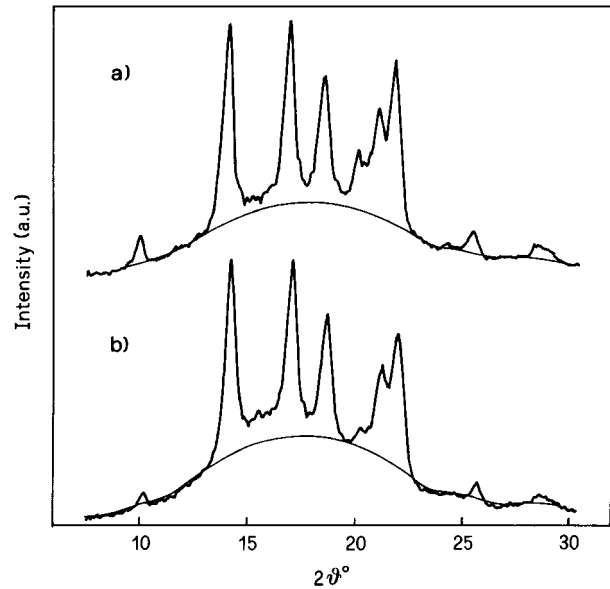


Figure 4 WAXD profiles of PP-PB-HOCP ternary blends: (a) 60/20/20; (b) 60/10/30.

$$\omega_{\text{PB,II}} = \frac{I_{\text{PB,II}}b}{I_{\text{PB,I}'}a + I_{\text{PB,II}}b + I_{\text{PP},\alpha}c} \omega_b \quad (2)$$

$$\omega_{\text{PP},\alpha} = \omega_b - (\omega_{\text{PB,I}'} + \omega_{\text{PB,II}}) \quad (3)$$

where $\omega_{\text{PB,I}'}$ and $\omega_{\text{PB,II}}$ are the weight fraction of forms I' and II of PB, respectively, and $\omega_{\text{PP},\alpha}$ is the weight fraction of the crystalline PP. $I_{\text{PB,I}'}$ and $I_{\text{PB,II}}$ are the diffraction intensities of the peaks at 9.8 and at 11.8 $2\theta^{\circ}$ relative to the PB crystallized in forms I and II, respectively, and $I_{\text{PP},\alpha}$ is the diffraction intensity of the peak at 14.1 $2\theta^{\circ}$ rela-

Table II Total Blend Crystallinity (ω_b), PP Crystalline Fraction ($\omega_{\text{PP},\alpha}$), and Form I' Fraction of the Crystallized PB ($f_{\text{I}'}$)

PP-PB-HOCP	ω_b	$\omega_{\text{PP},\alpha}$	$f_{\text{I}'}$
100/0/0	—	0.66	—
0/100/0	—	(0.43) ^a	0.00
80/10/10	0.56	0.53	1.00
70/10/20	0.48	0.45	1.00
70/20/10	0.50	0.43	0.82
60/10/30	0.42	0.39	1.00
60/20/20	0.50	0.43	0.91
60/30/10	0.51	0.40	0.23
50/10/40	0.37	0.34	0.88
50/20/30	0.41	0.35	0.41
50/30/20	0.47	0.36	0.32
50/40/10	0.48	0.34	0.04

^a Crystallinity index of PB crystallized in form II.

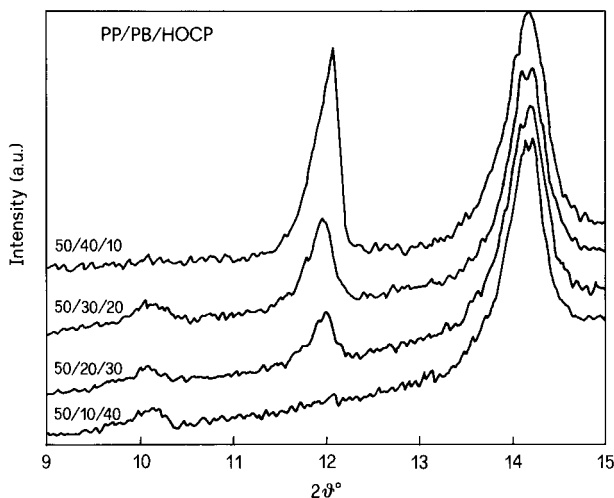


Figure 5 WAXD profiles of ternary blends containing 50% of PP.

tive to the (110) crystallographic plane of PP crystallized in α -form; a , b , and c are the proportionality factors between the peaks calculated from the diffraction data of pure PB and pure PP; the form I of pure PB was obtained from the total spontaneous evolution at 20°C of the pure PB crystallized in form II.

The influence of blend composition on the PB crystalline forms was evidenced by calculating the $f_{I'}$ index, as follows:

$$f_{I'} = \frac{\omega_{PB,I'}}{\omega_{PB,I'} + \omega_{PB,II}} \quad (4)$$

The values of $f_{I'}$ reported in Table II show that the crystallization in form I' is the favorite for blends prepared with small fractions of PB; by increasing the PB content in the blends, the fraction crystallized in form II increased. These results are in good agreement with the trend observed for the thermal data obtained by DSC. PB–HOCP binary blends containing 30% max of HOCP showed that PB crystallizes from the melt completely in the form II.⁶ All the examined ternary blends showed the presence of PB in form I' as a consequence of the different crystallization conditions of PB occurring after PP crystallization. The results reported in Table II show a quite constant value of $\omega_{PP,\alpha}$ for blends prepared with the same content of PP.

CONCLUSIONS

The experimental data obtained by microscopy techniques, DSC, and WAXD have shown that the

demixing phenomena in the ternary blends occur during and/or after the crystallization of the PB component.

The possibility of preparing PP–PB–HOCP ternary blends where the PB component directly crystallizes in form I' could offer new opportunities about their application. Work is in progress with the aim to obtain further information about the crystallization of the PB component in PP–PB binary blends and to verify the phase transformation of the PB component in the annealed ternary blends.

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