Crystallization of Poly(1-butene)/Hydrogenated Oligocyclopentadiene Blends

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ABSTRACT: The crystallization process of poly(1-butene) and its blends with hydrogenated oligocyclopentadiene was analyzed in dependence on composition. Both isothermal and nonisothermal crystallization processes were studied, and the isothermal crystallization process was investigated starting from both the glass and the melt states. Results revealed that spherulite growth rate, overall crystallization rate, and morphology are strongly dependent on crystallization conditions and blend composition. Nonisothermal crystallization data were analyzed according to the theories of Ozawa and Ziabicki. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1677–1690, 1999

Key words: poly(1-butene); hydrogenated oligocyclopentadiene; blend; crystallization; nucleation; morphology

INTRODUCTION

In previous works, we studied the influence of the hydrogenated oligocyclopentadiene (HOCP) on the morphology, thermal, and mechanical properties of its blends with some polyolefins, namely isotactic polypropylene, high-density polyethylene, and poly(4-methylpentene-1).[1–6] In dependence on polyolefin, temperature, blend composition, and crystallization conditions, the systems can present one or two amorphous phases in the melt and glassy states. During cooling, a crystalline phase in equilibrium with the amorphous phases develops.

Recently, to complete the study of the influence of HOCP on the properties of polyolefins with different side groups, we started to analyze the behavior of poly(1-butene) (PB-1)/HOCP blends.[7] Observation of the morphology and results of the differential scanning calorimetric analysis and dynamic mechanical thermal analyzer analysis showed that, in the melt state, PB-1 and HOCP do not form a miscible system, but two conjugated phases: a PB-1-rich phase and a HOCP-rich phase. Moreover, after crystallization, the solidified samples contain a third phase composed by crystalline PB-1 in the tetragonal modification (form II) that, after a certain time, transforms into the hexagonal modification (form I). Study of the tensile stress-strain properties revealed that, at 25°C, the addition of HOCP to PB-1 arouses a noteworthy hardening of the samples, whereas at 80°C the blends show a decrease of Young's modulus. Different behavior of the mechanical properties has been attributed to differences of the physical states of the amorphous phases and to the amount of the crystalline phase.

Partial miscibility observed in the melt by us is not in agreement with the conclusions drawn on the same system by Bonfatti and colleagues.[8] In their article, the influence of HOCP on the isothermal crystallization from the melt and thermal behavior of thin films of PB-1/HOCP blends were described. Their results were accounted for by assuming that the two components were miscible in the amorphous state, and miscibility was

due to specific interactions between the two components. Miscibility between the two components was also claimed by Canetti and colleagues[9] in their study of the influence of HOCP resin on the kinetics of crystal transformation of PB-1 from form II to form I of isothermally crystallized blends.

On the basis of these results, we decided to investigate in detail morphology and the crystallization process of PB-1/HOCP blends as function of composition and crystallization conditions. The morphological and thermodynamic parameters connected to both isothermal and nonisothermal crystallization are presented herein. The isothermal crystallization process of PB-1/HOCP blends was followed starting from the melt and cold state, and the nonisothermal crystallization was studied as function of cooling rate.

EXPERIMENTAL

Materials

The following materials were used:

- isotactic PB-1, produced by Scientific Polymer Products, Inc. (Ontario, NY), with M_w = 1.85×10^5 g $\cdot$ mol^{-1}, density = 0.915 g $\cdot$ cm^{-3}, melt index = 20, T_g = $-24°C$, and T_m = $125°C$

- hydrogenated mixtures of isomers of oligo(cyclopentadiene) (HOCP), Escorez 512 produced by Esso Chemical Co. (Houston, TX), with M_w = 630 g $\cdot$ mol^{-1}, T_g = $85°C$, and density = 1.07 g $\cdot$ cm^{-3}.

Blend Preparation

PB-1 and HOCP components were mixed in a Brabender-like apparatus (Rheocord EC of Haake, Inc., Saddle Brook, NY) at 160°C for 10 min. Blends with weight ratios of PB-1/HOCP of 100/0, 90/10, 80/20, 60/40, and 40/60 were prepared.

Calorimetric Measurements

The overall isothermal kinetics of crystallization of the blends was investigated with a differential scanning calorimeter (Mettler DSC-30). Samples ($\sim 10 \div 15$ mg) were heated from 30°C to 160°C, melted at 160°C for 10 min, then rapidly cooled to the desired T_c, and allowed to crystallize. For cold

crystallization, samples were heated from room temperature to 160°C, kept at 160°C for 10 min, then quenched to $-50°C$, held at $-50°C$ for 5 min, and then rapidly heated to the desired T_c.

Nonisothermal crystallizations from the melt were performed for the blends with up to 40% HOCP: samples were melted at 160°C for 10 min and cooled to room temperature at different rates. Four different cooling rates were used: 0.5°, 1°, 2°, and 4°C min^{-1}. The heat evolved during the isothermal and nonisothermal crystallizations was recorded as a function of time. The fraction X_t of the material crystallized after a period of time t was calculated by the relation

$$X_t = \frac{\int_0^t \left(\frac{d\,H}{d\,t}\right) d\,t}{\int_0^\infty \left(\frac{d\,H}{d\,t}\right) d\,t} \tag{1}$$

where the first integral is the heat generated at time t and the second integral is the total heat when crystallization is complete.

Optical Microscopy

Morphology and isothermal spherulite growth rate were studied by using a Zeiss Axioscop polarizing optical microscope, fitted with a Linkam TH600 hot stage. A film of each blend was sandwiched between two microscope glasses and then subjected to the same thermal cycles used for the calorimetric measurements. For the study of the isothermal spherulite growth rate, the radius of a growing spherulite was measured as a function of time by taking photomicrographs at various times.

RESULTS AND DISCUSSION

Morphology

A series of optical and electron micrographs of samples of the PB-1/HOCP blends isothermally and nonisothermally crystallized from the melt are reported in Figures 1 and 2.

For the PB-1 samples isothermally crystallized from the melt, well-defined spherulites are obtained [see Fig. 1(a)]. At high crystallization temperatures, some crystallites lose part of the

spherulitic character (Maltese cross and spherical shape), and square crystallites are also observed, indicating that the crystallites have a hedritic character [Fig. 1(b)]. The formation of PB-1 hedrites has been reported by other authors,[10] and crystallites with hedritic character have been also observed for some other polymer systems, like polyethylene oxide,[11,12] isotactic polystyrene,[13] poly(4-methylpentene-1),[13] and poly(3-*d*-hydroxybutyrate).[14] Hedrites have been observed not only in neat PB-1 samples, but also in all blend compositions when samples are crystallized at high T_c [see, e.g., Fig. 1(c)]; therefore, HOCP seems to have no influence on the shape of the PB-1 crystallites.

As reported in the "Introduction," miscibility and phase structure of the PB-1/HOCP blends have been studied in a previous paper by Cimmino and colleagues.[7] They found, in particular, that PB-1 and HOCP are partially miscible. In the melt, two conjugated phases are present,

Figure 1 Optical micrographs of PB-1 superstructures isothermally crystallized at 80°C: (a) spherulite in a 100/0 sample; (b) hedrite in a 100/0 sample; and (c) hedrite in a 60/40 blend.

Figure 2 Optical micrographs of PB-1 spherulites, cooling from the melt at 4°C min^{-1}: (a) 57°C and (b) 30°C.

Table I   Temperature at Which Different Kinds of Nuclei Become Visible by Optical Microscopy During Cooling from 160°C at 4°C min^{-1}

% HOCP	First Nucleation Step	Second Nucleation Step
0	89	69
10	85	60
20	80	54
40	70	42
60	59	28

whereas after crystallization the system contains three phases: a crystalline phase formed by PB-1 crystals, an amorphous PB-1 rich phase, and an amorphous HOCP rich phase. For more details on the phase structure of this system, see ref. 7.

For the blends, during isothermal crystallization, small domains included in the intracrystallitic regions are observed [see, e.g., Fig. 1(c)]. These domains, according to ref. 7, are made of the HOCP rich phase.

For the samples crystallized during cooling from the melt (Fig. 2), morphology is characterized by the presence of large and small spherulites, nucleated at different times and temperatures. The time lag between the two nucleation processes is clearly indicated by the curvature of the common boundary between small and large spherulites.

Decreasing the temperature from the melting point, at a certain T that depends on composition, few nuclei start to grow, giving rise to large spherulites. At lower T, independently of the used cooling rate, suddenly many other nuclei appear and grow [Fig. 2(a)]. As their number is elevated, they impinge each other very quickly and hence they cannot grow into large spherulites [Fig. 2(b)]. The number of the nuclei and the temperature at which both kinds of nuclei become active are almost independent of premelting temperature. In fact, premelting the sample at a temperature ranging between 140° and 200°C does not induce any modification in the nucleation process. This result excludes the possibility of self-seeded nucleation. Therefore, the two kinds of spherulites could be attributed to the presence of heterogeneous nuclei having different activation energies. The temperatures at which these two different kinds of nuclei become visible are reported in Table I in dependence on blend composition.

There is clear evidence that the nucleation of both nuclei is delayed by the addition of HOCP, suggesting that, in the blends, the heterogeneous nuclei need a higher undercooling to become active. This phenomenon probably can be attributed to the presence of entanglements that interlace the phases and reduce the diffusion rate of chain segments and hence the rate of nucleation. Entanglements between the phases were also claimed to explain the relatively high elongation before rupture of the PB-1/HOCP blends.[7]

For the samples crystallized from the cold, the morphology is rather different. After crystallization, no birefringent objects are observable using polarized optical microscopy. The domains of the HOCP rich phase are still visible. Analysis of the morphology of these crystals by using a scanning electron microscope evidences no structure, indicating that the crystal dimension is below the resolution used.

The different morphology of the samples crystallized from the cold is probably related to the influence of the crystallization conditions on the nucleation process. In fact, before cold crystallization, samples are rapidly quenched from the melt at −50°C. With this quench, it is possible to reach the range of temperature where the homogeneous nuclei are active.[15] At T_c, a large number of nuclei are stable and grow quickly. Probably, as the nucleation density is very high, the crystals are unable to develop into large ones before termination of their growth due to impingement.

As PB-1 presents polymorphism phenomena,[10] wide-angle X-ray scattering analysis was performed as soon as the crystallization process was completed to establish the form assumed by the crystals in dependence on crystallization conditions and compositions. It was found that from both the cold and melt states the PB-1 crystallizes in form II, independently of the presence of HOCP.

Crystallization

Isothermal Crystallization

The isothermal spherulite growth rates as a function of temperature for the PB-1 and its blends with HOCP are reported in Figure 3. For pure PB-1 and the 90/10 and 80/20 blends, it is not possible to build the entire crystallization curve, because for these samples, at low temperatures (i.e., below 70°C), the crystallization process is not isothermal.

The addition of HOCP to PB-1 causes a decrease of the spherulite radial growth rate. Because the blends are constituted by two phases,[7] the decrease can be attributed to the diluent effect of the HOCP present in the PB-1 rich phase and to the presence of HOCP rich phase domains and entanglements between the phases. The diluent effect is constant with composition, because the composition of the PB-1 rich phase is independent of nominal composition.[7] The HOCP rich phase domains and the entanglements between the phases probably produce a composition-dependent increase of the energy related to the crystallization. The entanglements, as previously discussed, reduce the diffusion rate of chain segments and hence the crystallization rate. During crystallization, the HOCP rich phase domains are occluded in the spherulites. The energy to perform the occlusion is an energy barrier that opposes the crystallization process.

Half-time of the overall isothermal crystallization ($\tau_{1/2}$) as a function of temperature for samples crystallized from the melt and glass state is reported in Figure 4 for different blend compositions. From the figure, it is possible to

know that the crystallization process depends on temperature, composition, as well as on crystallization conditions. HOCP always delays the crystallization process of PB-1. For the same crystallization temperature and composition, samples crystallized from the glass state need a shorter time to crystallize in comparison with the samples crystallized from the melt. The reported results can be explained taking into account that the overall crystallization rate depends on the crystal growth rate, as well as on the nucleation rate and density. For the melt crystallized samples, the decrease observed with composition is mainly due to the decrease of the spherulites growth and nucleation rates, plus the dilution of the PB-1 nuclei following the addition of HOCP in the blends. For the samples crystallized from the cold, experimental crystal growth rate data are not available. Considering that the crystal dimensions are probably well below the dimensions of domains of the HOCP rich phase, it is expected that the PB-1 crystals in the PB-1 rich phase during the growth are almost not disturbed by the presence of the HOCP rich phase domains. Probably the decrease of the crystallization rate with

Figure 3 Spherulite radial growth rate (G) of PB-1/HOCP blends isothermally crystallized from the melt as a function of crystallization temperature for different blend compositions.

Figure 4   Half-time of crystallization ($\tau_{1/2}$) of PB-1/HOCP blends isothermally crystallized as a function of crystallization temperature for different blend compositions: (a) from the melt and (b) from the glass state.

composition can be attributed mainly to the decrease of the crystallizable material from which homogeneous nucleation can take place.

At this point, it seems interesting to summarize the observations made on the nucleation of PB-1 and PB-1/HOCP blends. Four distinct re-

gions can be recognized cooling the samples from the melting point:

1. Below the experimental melting point, there is a temperature gap (112°C–90°C) where nucleation does not take place.
2. Below 90°C, there is a temperature region of ~ 20°C where some of the heterogeneous nuclei become active. These nuclei are limited in number and appear sporadically, giving rise to large spherulites.
3. At even lower temperatures, an intense nucleation process takes place. This could be considered the region of activity of heterogeneous instantaneous nuclei. These nuclei, as their number is elevated, grow in small but well-defined spherulites.
4. Finally, at very low temperatures, reached by quenching the samples from the melt, there is probably the region of the homogeneous nucleation. A very high number of nuclei become active, from which very small crystals can be obtained, due to impingement of the crystals among each other.

The isothermal crystallization data were analyzed following the Avrami theory. Experimental data appear to fit Avrami's equation. In fact, for any composition, T_c and thermal treatment, plots of $\ln(-\ln(1 - X_t))$ versus $\ln t$ are linear. Values of the Avrami index, n, determined from the slope of the previously described straight lines, lie between 2 and 3 for the melt crystallized samples. For cold crystallized samples, a value of n close to 2 is obtained. Variation of the Avrami index between 2 and 3 could be caused by the different nucleation mechanisms and shapes of the crystals, in dependence on crystallization conditions.

Nonisothermal Crystallization

Theoretical Background. To study the kinetic parameters of nonisothermal crystallization processes, several methods have been developed, and the majority of the proposed formulations are based on the Avrami equation. The most used theory is the one proposed by Ozawa,[16] which can be used when crystallization occurs at a constant cooling rate and the nuclei grow as spherulites. The most interesting feature of Ozawa's method is the possibility to compare the continuous cooling results with the isothermal results obtained

by means of the Avrami equation. According to Ozawa's theory, the degree of conversion at temperature T is

$$-\ln[1 - X(T)] = \frac{K(T)}{\chi^n} \qquad (2)$$

where $X(T)$ is the relative crystallinity at temperature T, χ is the cooling rate, n is the Avrami exponent, and K is the cooling crystallization function. From eq. (2), it follows

$$\mathrm{Log}\{-\ln[1 - X(T)]\} = \mathrm{Log}\, K(T) - n\, \mathrm{Log}\, \chi \qquad (3)$$

By plotting the left term of eq. (3) against χ, a straight line should be obtained, and the kinetic parameters K and n can be derived from the slope and the intercept, respectively.

Another widely used theory is the one proposed by Ziabicki,[17–19] which is based on the assumption that the nonisothermal crystallization process can be treated as a sequence of isothermal steps. The equation that he proposed is a series expansion of the Avrami equation. In quasistatic conditions, provided that the nucleation and growth of the crystals are governed by a thermal mechanism only, their time dependence comes from a change in the external conditions, the Avrami exponent is constant throughout the whole process, and nonisothermal crystallization kinetics can be expressed in terms of an observable half-time of crystallization, $\tau_{1/2}$, as a function of time and history of external conditions.[20,21] The following equation was derived for the dependence of the total volume of the growing crystal, $E(t)$, with time:

$$E(t) = \ln 2 \left(\int_0^t \frac{ds}{\tau_{1/2}} \right)^n$$

$$\times \left[1 + a_1 \int_0^t \frac{ds}{\tau_{1/2}} + a_2 \left(\int_0^t \frac{ds}{\tau_{1/2}} \right)^2 + a_3 \ldots \right] \qquad (4)$$

where $a_1, a_2, \ldots, a_n$ are the coefficients of the series, and s is the time required for the nucleation of the crystals. When $a_1 = a_2 = \ldots = a_n = 0$, eq. (4) becomes

$$E(t) = \ln 2 \left(\int_0^t \frac{ds}{\tau_{1/2}} \right)^n \qquad (5)$$

Figure 5 Differential scanning calorimetric thermoanalytical curves of PB-1/HOCP blends; cooling rate $1°C \, min^{-1}$.

This equation can be used when the ratio between the nucleation and growth rates is constant with time and, therefore, the athermal nucleation is negligible (isokinetic approximation). Ziabicki's theory can be applied only in the range of temperatures where isothermal crystallization data can be obtained.

To analyze the nonisothermal crystallization process according to Ziabicki's theory, $\tau_{1/2}$ as a function of time must be derived. This can be done by the knowledge of the $\tau_{1/2}$ values obtained in isothermal conditions, presented in Figure 4(a), the times when crystallization starts and ends,

and cooling rate. Dependence of $\tau_{1/2}$ on time can be calculated by solving the following system:

$$\begin{cases} T = T(t) \\ \tau_{1/2}(t) = \tau_{1/2}(T(t)) \end{cases} \qquad (6)$$

The values of $E(t)$ can be obtained with eq. (5) and the theoretical values calculated with the equation

$$X(t) = 1 - e^{-E(t)} \qquad (7)$$

can be compared with experimental ones.

Experimental Results. DSC thermoanalytical curves of PB-1/HOCP blends crystallized during cooling from the melt state at $1°C \, min^{-1}$ are presented in Figure 5. A similar trend is obtained for other cooling rates. Crystallization peaks are shifted to lower temperatures, and their width increase with the HOCP content in the blend. From thermoanalytical curves, several parameters can be obtained: the induction time, t_i, the time required for the phase transition, Δt (i.e., the difference between the time required by the sample to crystallize completely and the induction time), and the temperature of the maximum of the peak, T_{max}. Behaviors of t_i, Δt, and T_{max} (with composition and cooling rate) are reported

Figure 6 Induction time (t_i) versus HOCP percentage for different cooling rates.

Figure 7 Plot of the time required to crystallize (Δt) as function of HOCP percentage for different cooling rates.

in Figures 6, 7, and 8, respectively. t_i and Δt increase with HOCP content and decrease with the cooling rate at a given composition. For a given cooling rate, T_{max} shifts to lower T upon addition of HOCP to PB-1 and, for a given composition, on increase of the cooling rate. Khanna[22]

Figure 8 Crystallization peak (T_{max}) against HOCP content for different cooling rates.

Figure 9   Cooling rate (χ) as a function of the crystallization peak (T_{max}) for different blend compositions.

suggested comparing the crystallization rate of different polymer systems by means of a crystallization rate coefficient (CRC), which can be measured from the slope of the plot of the cooling rate *vs.* T_{max}. According to Khanna, the CRC parameter can be used as a guide for ranking the polymers on a single scale of crystallization rates. The CRC values should be higher for faster crystallizing systems. Plotting the cooling rate as a function of T_{max}, straight lines were obtained (Fig. 9). From the slopes of the straight lines, the CRC values were derived. Values are reported in Table II. For pure PB-1, a value of 18 h^{-1} is found. For the blends, the CRC value decreases almost linearly with composition and becomes $\sim$ 6 h^{-1} for the blend containing 40% of HOCP, indicating that the presence of HOCP hinders the nonisothermal crystallization process of PB-1. All of

Table II   Crystallization Rate Coefficient of the Blends at Various Compositions

% HOCP	CRC (h^{-1})
0	18
10	15
20	11
40	6

these results suggest that HOCP lessens the crystallization rate of PB-1 not only in isothermal conditions, but also when the crystallization is performed during continuous cooling. Explanations given for the decrease of the overall isothermal crystallization rate hold also in the case of nonisothermal crystallization.

In Figure 10, following Ozawa's treatment,[16] the plot of Log{$-\ln[1-X(T)]$} versus Log χ for 90/10 and 80/20 blends is reported. Experimental data, as well as those (not shown) of the other blends, are fitted by straight lines, which show that Ozawa equation can be used to describe satisfactorily the nonisothermal crystallization of PB-1/HOCP blends.

The value of the Avrami exponent (calculated with the nonisothermal analysis applying Ozawa's theory) is 3, in quite good agreement with the value obtained in isothermal conditions.

Intercepts of the Ozawa plots give the cooling crystallization function, K. Plots of Log(K) as a function of temperature are reported in Figure 11. For all blend compositions, Log(K) is a decreasing linear function of T, as previously observed for other polymers.[23–25] As first proposed by López and Wilkes,[26] K is indicative of the rate of nonisothermal crystallization; for the PB-1/HOCP system, its value decreases with the increase of

Figure 10   Plot of Log{$-\ln[1 - X(T)]$} against Log χ for PB-1/HOCP blends: (a) 90/10 and (b) 80/20.

HOCP content, indicating that the crystallization rate decreases with composition.

In Figure 12, the experimental $X(t)$ values (broken curves) as a function of time for two cool-

ing rates are shown. On the same figure, the theoretical $X(t)$ values calculated by means of eqs. (5) and (7) are presented (full curves). In all cases, it can be seen that the zero-order approxi-

Figure 11   Plot of Log (K) versus T for PB-1/HOCP blends.

mation cannot be used to describe the nonisothermal crystallization process of PB-1 and its blends with HOCP, probably indicating that the athermal nucleation of PB-1 is not negligible for both pure PB-1 and the blends.

CONCLUSIONS

Study of morphology and the crystallization process of PB-1 and PB-1/HOCP blends leads to the following:

- Results of this article are in good agreement with those reported in ref. 7, where partial miscibility between PB-1 and HOCP was claimed. Results support the hypothesis that the amorphous material of blends is separated in two conjugated phases, at least in the range of composition (up to 30% of HOCP) and temperature investigated (−50° to 160°C).
- For the samples crystallized from the melt, the HOCP rich phase domains are enclosed in the intraspherulitic or intrahedritic regions. For the samples crystallized from the

cold, these domains are probably outside the crystals.
- Independent of HOCP content in the blend (for crystallization from the melt), at low crystallization temperatures, a spherulitic morphology is observed. At relatively high crystallization temperatures, both spherulites and hedrites are present. For crystallization from the cold, no birefringent crystals are detected.
- HOCP strongly reduces the crystallization rate of PB-1 both in isothermal and nonisothermal conditions. The decrease is attributed to a balance between the diluent effect of HOCP within the PB-1 rich phase and the presence of the HOCP rich phase domains, and the entanglements between the phases. In dependence on crystallization conditions, PB-1 crystals can grow from homogeneous or heterogeneous nuclei.
- In dependence on crystallization temperature and cooling rate, four different mechanisms of nucleation can be observed cooling the PB-1 from the melt.
- Nonisothermal crystallization data for neat

Figure 12 Relative crystallinity as a function of time for PB-1 and 80/20 blends: (a) PB-1 at 0.5°C min^{-1}; (b) PB-1 at 1°C min^{-1}; (c) 80/20 at 0.5°C min^{-1}; and (d) 80/20 at 1°C min^{-1}. Broken curves correspond to experimental results; full curves are obtained using Ziabicki's theoretical approach.

PB-1 and the blends are in good agreement with Ozawa's theory, whereas no agreement can be found by using Ziabicki's theoretical predictions.

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