

The influence of HOCP oligomer on the crystallization and morphology of iPP/HDPE blends

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Summary

Ternary mixtures of isotactic polypropylene (iPP), high density polyethylene (HDPE) and hydrogenated oligo(cyclopentadiene) (HOCP) commercial products were prepared by melt mixing. The crystallization behaviour of iPP/HDPE and (iPP/HDPE)/HOCP systems were compared. It was shown that the ternary system separated in two binary systems. The presence of HOCP modified the morphology of iPP and HDPE phases. The polyolefins nucleation and crystal growth rates decreased due to the diluent effect of the oligomer. HDPE showed higher compatibility with HOCP than iPP.

Introduction

The formation of supermolecular structures in homopolymers usually depends on chemical constitution, configuration, molecular weight, polydispersity and crystallization conditions (1-7). The ductile or brittle behaviour in high crystalline polymers is affected by these characteristics. When the bulk in crystallization consists of polymer blends, instead of homopolymers, special aspects need to be focused. The mixture properties are dependent on the reciprocal degree of dispersion between the components, the degree of crystallinity and the crystal shape. All components can induce changing on the rate of crystallization and on the morphology of each phase(8,9). The low cost, good properties and versatility make the polyolefins the main plastics commodities. These qualities make the polyhydrocarbon blends very attractive materials. There is a vast literature on iPP/HDPE blends. The main results indicate that system is immiscible, segregates in two phases and cocrystallization does not occur(10-13). The papers in the literature are in disagreement as far as mechanical properties are concerned(14,15). The blend of iPP and HDPE with oligomers is less investigated. Only iPP/HOCP (commercial product) and HDPE/HOCP system were reported previously (16-21). The iPP/HDPE/HOCP ternary system have not been mentioned yet. Thus, the aim of this work was to verify the effect of the oligomer (HOCP) addition on the crystallization of the polyolefin binary system (iPP/HDPE).

Experimental

Materials

-High Density Polyethylene (HDPE), Eltex A 1050P produced by Exxon Co., $M_w = 3.15 \times 10^5$, $M_n = 3.3 \times 10^4$, density = 0.95 g/cm³, crystallinity index = 0.65 (by DSC) and degree of methyl branching = 1.7 (CH₃/1000 C); MFI = 4.8 g/10min.

-Isotactic Polypropylene (iPP), S30S, produced by Himont Italy, $M_w = 2.7 \times 10^5$, $M_n = 4.5 \times 10^4$, density = 0.90 g/cm³, crystallinity index = 0.45 (by DSC), isotacticity index = 82%, MFI = 0.85 g/10min.

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-Hydrogenated mixtures of isomers of Oligo(Cyclopentadiene) (HOCP), Escorez 5120 produced by Esso Chemical Co., with $M_w = 630$, density = 1.07 g/cm^3 .

Sample preparation and analysis

The blends were mixed in a Brabender like apparatus (Rheocord EC of Haake Inc.) at 210°C and 32 rpm for 10 minutes. The compositions of the binary system iPP/HDPE were: 100/0, 87.5/12.5, 75/25, 50/50, 25/75, 12.5/87.5 and 0/100. In the ternary system (iPP/HDPE)/HOCP the binary polyolefin mixture was considered like one component, changing the content of HOCP in the range of 10 to 40 weight percent. The optical observations were carried out on a Zeiss Axioscop polarizing optical microscope, equipped with a Linkham TH 600 hot stage. Thin slices were cut from the compression moulded samples, inserted between two microscope cover-glasses, melted and squeezed in order to obtain thin films with homogeneous thickness. The films were put on the hot stage microscope, heated from room temperature until 220°C , at 20°C/min and kept for 10 minutes to eliminate the thermal history. Then, the material was cooled up to 125°C , at 20°C/min and kept for a time long enough to crystallize. Photographies were taken in specified time intervals using polarized and non polarized light, in order to follow the crystallization evolution.

The degree of crystallinity was determined in a differential scanning calorimeter (Mettler DSC30).

Results and discussion

iPP/HDPE system

After 10 minutes at 220°C the melting bulk of the iPP/HDPE blends was homogeneous. A typical micrograph is shown in Figure 1. When the blends were cooled until 125°C to allow isothermal crystallization the materials crystallized very quickly, after few minutes. Only the 50/50 iPP/HDPE mixture permitted to notice that the HDPE crystallized firstly, because the birefringent species melted at HDPE melting temperature. It was not possible to observe that behavior in another composition because iPP and HDPE crystallized very quickly as microspherulites, as shown in Figure 2. The component in higher proportion represented the dominant phase in all studied blends. The regularity and shape of iPP spherulites were influenced by the second component, HDPE. The dimension of iPP spherulites was reduced in the iPP/HDPE blend compared to iPP, as observed in Figures 3 and 4, respectively.

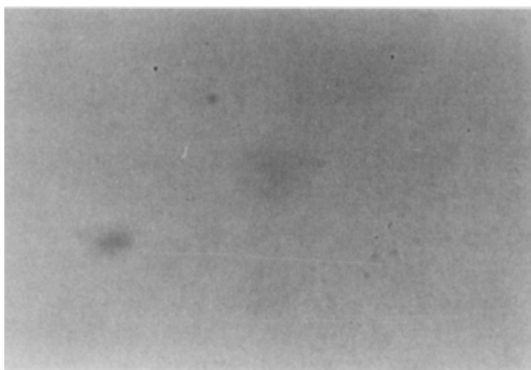


Figure 1. Photomicrograph of the 25/75 iPP/HDPE blend, melting bulk at 220°C .

20 μm

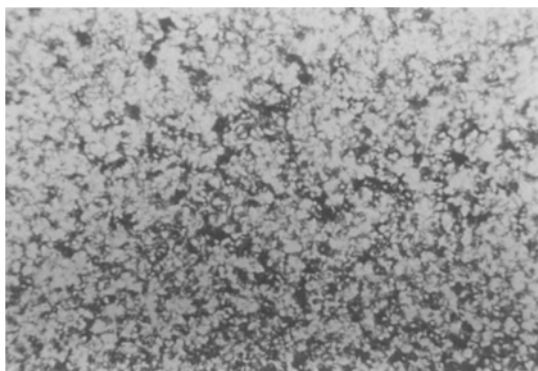



Figure 2. Photomicrograph of the 25/75 iPP/HDPE blend, isothermally crystallized for 1 min. at 125°C (polarized light).

20µm

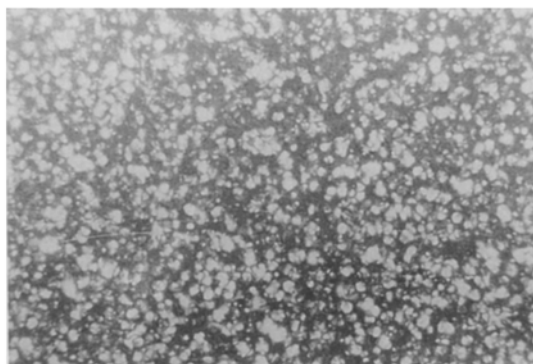


Figure 3. Photomicrograph of the 25/75 iPP/HDPE blend, isothermally crystallized for 1 min. at 125°C, after HDPE melting (polarized light).

20µm



Figure 4. Photomicrograph of the 100/0 iPP/HDPE blend, isothermally crystallized for 3 min. at 125°C (polarized light).

20µm

iPP/HDPE/HOCP system

The optical micrograph of the melting bulk after 10 minutes at 220°C was quite different when the oligomer, HOCP, was added to the binary system. In all cases was observed that the mixtures were inhomogeneous. With 10% of HOCP, phase separation was observed even in the melting bulk (Figure 5).

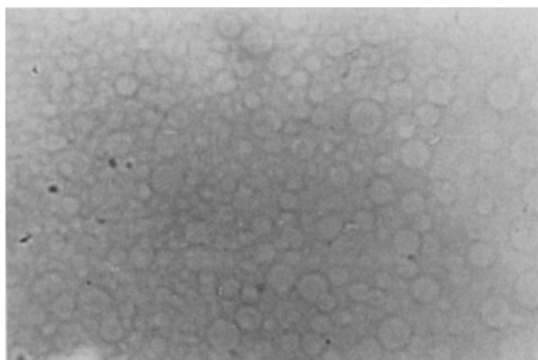


Figure 5. Photomicrograph of the (25/75)/10 (iPP/HDPE)/HOCP blend, melting bulk at 220°C.

20μm

The mixture with 40% of HOCP showed a more intense phase separation (Figure 6). It seems that the melting bulk of iPP/HDPE blend was homogeneous because in the experimental conditions the mixture was optically miscible. Maybe the refractive index of both components is too close at 220°C or the size of the domains is smaller than the incident light wave length. The presence of HOCP disturbs the apparent miscibility of iPP/HDPE system. It is interesting to notice that iPP/HOCP and HDPE/HOCP were homogeneous systems at 220°C.

The (25/75) iPP/HDPE blends with 10 and 40% of HOCP showed that the HDPE crystallized firstly as the dominant phase. The birefringent species formed melted at HDPE melting temperature (Figure 7a). The iPP domain, segregated as small drops, was the dispersed phase and acted as substrate for crystallization of HDPE. The crystallization occurred on the boundary of the two phases, as shown in Figure 7b. The dimension of HDPE spherulites was increased as the proportion of HOCP in the blend was raised (Figure 8) while the plain HDPE crystallized as microspherulites.

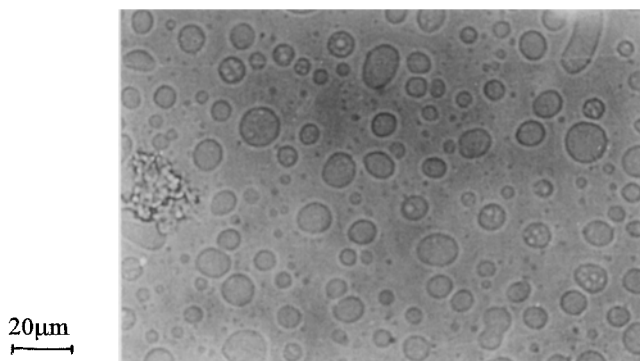


Figure 6. Photomicrograph of the (25/75)/40 (iPP/HDPE)/HOCP blend, melting bulk at 220°C.

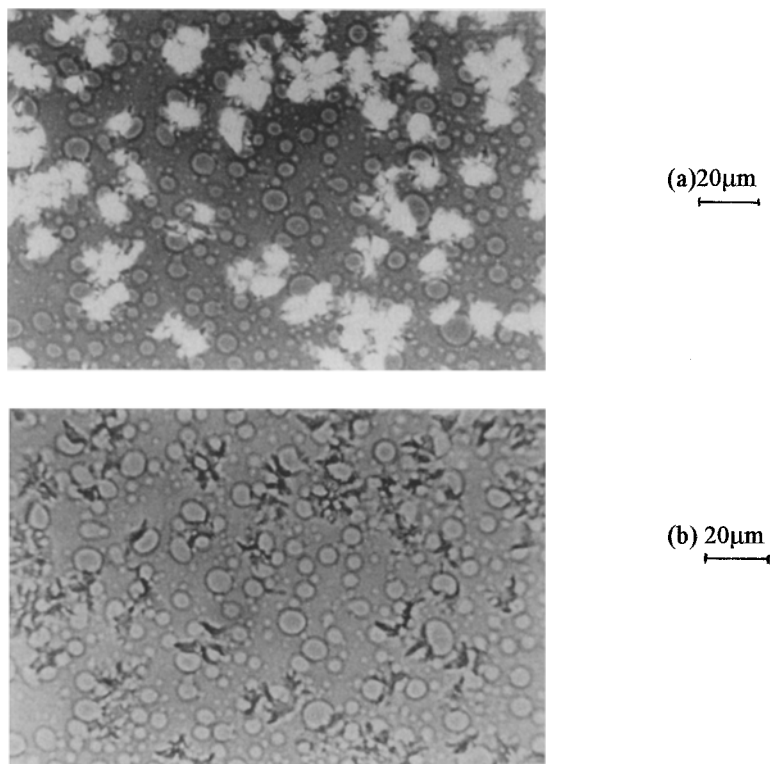


Figure 7. Photomicrograph of the (25/75)/40 (iPP/HDPE)/HOCP blend, isothermally crystallized for 100 min. at 125°C. a) polarized light; b) non polarized light.



Figure 8. Photomicrograph of the (25/75)/40 (iPP/HDPE)/HOCP blend, isothermally crystallized for 900 min. at 125°C (polarized light).

The nucleation and crystal growth rates of both components decreased by the presence of the oligomer. When HOCP was added to iPP/HDPE blend two binary systems were formed: iPP/HOCP and HDPE/HOCP.

The 50/50 (iPP/HDPE) blends with 10 and 40% of HOCP showed iPP as the dominant phase and HDPE as the dispersed one.

Similarly, in the same HOCP content range the 75/25 iPP/HDPE blend showed also the effect of the oligomer in both constituents. The crystallinity development appeared after a long time, as presented in Figure 9. The size of iPP spherulites increased and HDPE dispersed phase had the crystallization rate affected when the content of HOCP was raised. In both cases the oligomer acted as a diluent and this effect was more clearly noticed in HDPE phase. The HDPE degree of crystallinity was influenced more accentuatedly than iPP one by the presence of HOCP oligomer as presented in Figure 10, suggesting that HDPE is more compatible with HOCP than iPP.

The results indicated the ternary system was separated in two binary systems - iPP/HOCP and HDPE/HOCP. The crystallizable components crystallized individually and the oligomer induced a strong effect on the polyolefin crystallization.

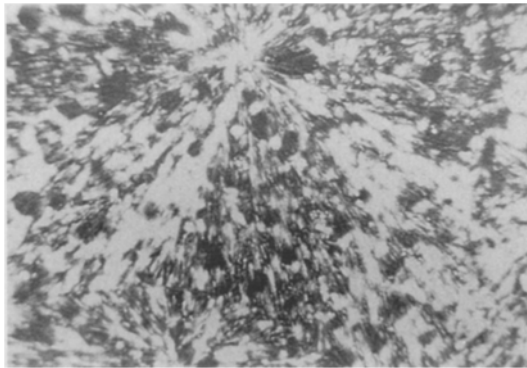


Figure 9. Photomicrography of the (75/25)/40(iPP/HDPE)/HOCP blend isothermally crystallized for 315 min. at 125°C (polarized light).

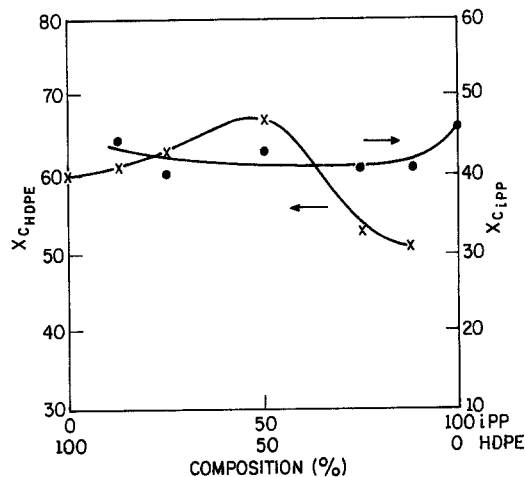


Figure 10. Changing of the degree of crystallinity (X_c) of iPP and HDPE in (iPP/HDPE)/HOCP system with 10% of HOCP.

Acknowledgements

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