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New Aspects of the Microstructure of PE/iPP Gel Blends As Revealed by Microhardness: Influence of Composition

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ABSTRACT: The microhardness of films of polyethylene/polypropylene blends prepared by gelation from semidilute solution by using ultrahigh molecular weight polyethylene (PE) (6×10^6) and isotactic polypropylene (iPP) (4.4×10^6) was determined. The morphological properties and the drawing behavior of these blended gel films were reported previously.[3] The PE/iPP compositions chosen were 75/25, 50/50, and 25/75. The microhardness of the films was markedly affected by the composition. It is shown that the large deviation of microhardness (H) from the additivity law of the single components is mainly due to the depression of the crystal hardness values of the PE and iPP lamellar crystals and to a minor extent to a decrease in the crystallinities of both polymer phases. Comparison of experimental and calculated H data and analysis of DSC results reveals that the surface free energy of the crystals increases with increasing concentration of the iPP component up to 75% iPP. Results are discussed in light of changes occurring in the defective surface boundary of the crystals.

Introduction

In a previous study[1] the microhardness (H) of a series of linear polyethylene samples, slowly crystallized from the melt with a wide range of molecular weights and investigated with reference to changes occurring in the defective surface boundary of the lamellar crystals.[1] The hardness-derived constant

$$b = l_c(H_0/H_c - 1) \tag{1}$$

(where H_c is the crystal hardness and l_c is the crystal thickness) was shown to measure the hardness depression from the value $H_0 = 170$ MPa for an infinite crystal, due to the finite thickness of lamellar crystals. It was further shown that the increase in b with molecular weight is parallel to the concurrent increase in the surface free energy (σ) derived from DSC experiments. The increase in σ was interpreted in terms of an increase in the number of defects and molecular entanglements segregated onto the surface boundary of the lamellar crystals. The analysis of results, in light of the concept of thermodynamically stable nonhomogeneous microphases,[2] showed that, above a critical molecular weight, $M_c \approx 2 \times 10^5$, the defective surface layer of the crystal was saturated with defects (entanglements, chain-folded loops). It was pointed out that, for molecular weights beyond M_c, the total number of entanglements transferred from the melt into the solid state could not be accepted anymore into the crystal defective surface. As a result these defects were thought to be excluded into the amorphous phase of the solidified material. Since the b parameter is equal to the ratio of 2σ to the enthalpy (Δh) required for crystal destruction[1] and, furthermore, as the σ value seems to depend on the level of defects at the crystal surface, one may speculate that a polymer material with no entanglements or with a very low density of them may give rise to very small b values, which will, in turn, lead to an enhanced crystal hardness value. In a separate study Sawatari, Shimogiri, and Matsuo[3] have suggested that the easy drawability of PE/iPP blend films prepared by gelation/crystallization from semidilute solutions, yielding draw ratios larger than 50, is due to the existence of a relatively low level of molecular entanglements between the PE and iPP lamellar crystals. Thus, PE/iPP blend gel films may offer an interesting model system with presumably a low density of surface defects, which can be tested by the microhardness technique. The aim of the present work in relation with this contention is to stuy the microhardness of ultrahigh molecular weight polyethylene (PE)/polypropylene (PP) blend films and examine whether the hardness-derived constant b depends on PE/iPP composition. In addition, the variations of crystallinity of the blends with composition will be analyzed with reference to the deviation of H from the additivity behavior of the single components.

Experimental Section

Polyethylene/polypropylene blend films were prepared by gelation/crystallization from semidilute decalin solution as reported in ref 3, using ultrahigh molecular weight PE ($M_2 = 6 \times 10^6$) and iPP ($M_w = 4.4 \times 10^6$). In addition to the individual PE and iPP homopolymer dry gels, the PE/iPP compositions chosen were 75/25, 50/50, and 25/75. For all compositions a concentration of about 0.45 g/100 mL was shown to be most convenient to assure the maximum draw ratio of each blend film. For further details concerning the preparation of the dry gel films see ref 3.

WAXS and SAXS patterns of the 300-μm-thick films indicate that the structure of the blended gel films and homopolymers is similar to that of single-crystal mats; i.e., the crystal c axes within the laminar crystals of the gel are oriented perpendicular to the large flat faces. Thus, the lamellar crystals are oriented parallel to the film surface.[3] The long periods, L, of the original PE and iPP films and the blended dry gels are estimated to be 119 and 105 Å, respectively, from the SAXS intensity distribution with a position-sensitive proportional counter (PSPC). These maxima have been ascribed to the average scattering from the random stacking of lamellae of the individual homopolymers.[3] DSC measurements were carried out by using a Perkin-Elmer DSC-4 differential scanning calorimeter to derive the crystallinity content from both components. DSC scans were carried out in the temperature range of 50–200 °C. A heating rate of 10 °C/min was used. Crystallinity of each phase within the blend gels was derived from the ratio of the heat of fusion measured for each sample to the corresponding heat of fusion for infinite crystals,[7] Δh_f. (For PE, $\Delta h_f = 2.8 \times 10^9$ erg/cm^3; for iPP $\Delta h_f = 1.96 \times 10^9$ erg/cm^3.)

The microhardness was measured at room temperature of using a Vickers square-based-pyramid indenter. Loads of 0.15, 0.25,

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Table I
Experimental Values of Microhardness and Crystallinity of Polyethylene and Polypropylene Blended Gel Films as a Function of Composition

PE/iPP	H, MPa	α_{PE}	α_{PP}
100/0	105	0.80	
75/25	90	0.77	0.39
50/50	82	0.74	0.43
25/75	94	0.71	0.45
0/100	116		0.49

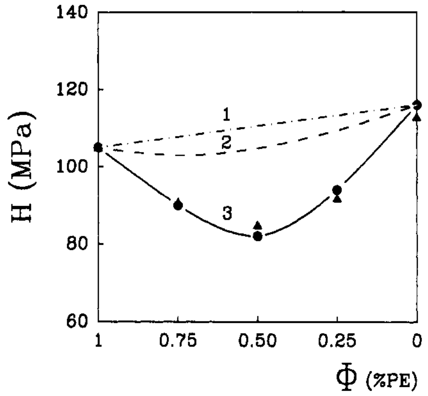

Figure 1. Microhardness of ultrahigh molecular weight PE/iPP blended gel films as a function of the weight concentration of the first component. (1) Additivity behavior from eq 5 with use of crystallinity values of the individual homopolymers. (2) H values from eq 5 using α_{PE} and α_{PP} data (Table I) for each blend. (3) Circles, experimental data; triangles, calculated values from Table II (see text).

0.5, and 1 N to correct for instant elastic recovery were employed. A loading cycle of 0.1 min was used. For further experimental details on the microhardness technique, see refs 4 and 5. It is noteworthy that, owing to the specific morphology of the blended gel films investigated (the lamellar crystals are parallel to the film surface), the mechanical test essentially furnishes a H value parallel ($H_{\parallel}$) to the chain direction. In a different study we have shown that the microhardness of mats of single crystals grown from diluted solution does not differ appreciably from the H value for the same melt-crystallized material having a similar crystal thickness.[6]

Results and Discussion

The microhardness of the blended gel films and the crystallinity values derived from calorimetry of the PE and iPP components within each blend are collected as a function of composition (Φ) in Table I. This table shows that the crystallinity of the polyethylene homopolymer measured by DSC is consistent with the value previously measured by density.[8] However, the crystallinity value of the polypropylene homopolymer derived from DSC in Table I is lower than the value measured by density.[9] The origin of this discrepancy is not clarified at present. Figure 1 illustrates the experimentally obtained variation of H as a function of Φ (curve 3). It is seen that the H values for the PE and iPP starting gel films (H^{PE} = 105 MPa and H^{PP} = 116 MPa) do not differ substantially from each other. In spite of the fact that the gel films (especially the homopolymers) show a porous microstructure, the H values are much larger (~50%) than those obtained for conventionally crystallized samples.[4,11] This implies that microhardness in these materials is not substantially affected by the presence of a few microns large microvoids.[10] Furthermore, a very conspicuous deviation from the additivity law (straight line 1)

$$H = \Phi H^{PE} + (1 - \Phi)H^{PP} \tag{2}$$

where Φ and 1 − Φ are, respectively, the weight fractions of PE and iPP with increasing Φ, is detected. Since the glass transition temperature (T_g) for PE is much lower than room temperature, the hardness contribution of the amorphous phase is $H_a^{PE} \approx 0$. Hence, for PE using the parallel model,[4] we may write

$$H^{PE} = \alpha_{PE}H_c^{PE} \tag{3}$$

On the other hand, for iPP $T_g \approx 0$ °C[7] and $H_a^{PP} \neq 0$. Consequently, for iPP

$$H^{PP} = \alpha_{PP}H_c^{PP} + (1 - \alpha_{PP})H_a^{PP} \tag{4}$$

By combination of eqs 2–4 we are led to the expression

$$H = \Phi\alpha_{PE}H_c^{PE} + (1 - \Phi)\alpha_{PP}H_c^{PP} + (1 - \Phi)(1 - \alpha_{PP})H_a^{PP} \tag{5}$$

which describes the microhardness of the blended gel films in terms of the hardness values of the independent crystalline and amorphous components. From Table I one sees that the iPP component hampers the crystallization capability of PE and, therefore, α_{PE} decreases with increasing iPP concentration. On the other hand, the presence of PE crystals also inhibits the crystallization level of iPP and α_{PP} likewise diminishes with PE concentration. If we take into account the crystallinity depression measured for the PE and iPP components in eq 5, use H_c^{PE} = 130 MPa and H_c^{PP} = 145 MPa, and let H_a^{PP} = 90 MPa, we are, then, led to curve 2 in Figure 1. In a previous investigation we had shown that a decrease in crystallinity of PE/iPP blends crystallized from the melt also led to a clear deviation of H from the additivity law.[11] However, in the case of the present blended gel films the crystallinity depression is insufficient to account for the enormous deviation of the experimental H values from the additivity law (Figure 1). Hence, according to eq 5, the only possibility left to explain the conspicuous hardness depression found is that the crystal hardness values themselves, H_c^{PE} and H_c^{PP} decrease, as a consequence of the coexistence of PE and iPP components. At this stage one may enquire as to what the origin for such H_c^{PE} and H_c^{PP} depression can be. If one rewrites eq 1 as

$$H_c = H_0/(1 + b/l_c) \tag{6}$$

then one immediately sees that, for crystals with given thicknesses l_c ($l_c^{PE} = \alpha_{PE}L_{PE}$ and $l_c^{PP} = \alpha_{PP}L_{PP}$, where L_{PE} = 119 Å and L_{PP} = 105 Å are the X-ray long periods of the individual homopolymers[3]), H_c only depends on the parameter $b = 2\sigma/\Delta h$, which furnishes a measure of the surface free energy of the laminar crystals. The latter depends on the level of defects located on the surface boundary of the crystals. We have previously shown that eq 6 is very similar to the well-known Thomson–Gibbs equation[1]

$$T_m = T_m°(1 - b^*/l_c) \tag{7}$$

where $b^* = 2\sigma/\Delta h_f$ and Δh_f is now the equilibrium enthalpy of fusion.

If we use H_0^{PE} = 170 MPa[12] and H_0^{PP} ~ 150 MPa[13] and let H_a^{PP} = 90 MPa, by adjusting the b value in eq 6 for PE and iPP, from eq 5, we can obtain the H_c values, for the different compositions to give the best fit between experimental and calculated H values (see Table II). It is to be noted that the derived H_a^{PP} value is larger than that quoted previously[11] for melt-crystallized iPP. This is probably due to the fact that in the present case we have used an iPP sample of very high molecular weight, which may shift the T_g value to even higher temperatures. The b values for PE and iPP that give the best fit between

Table II
Calculated Data, Using Equations 1–5, as a Function of Composition

PE/iPP	b_{PE}, Å	b_{PP}, Å	H_c^{PE}, MPa	H_c^{PP}, MPa	H^{cal}, MPa
100/0	28		131		105
75/25	40	35	118	81	90
50/50	57	30	103	90	83
25/75	61	14	99	116	94
0/100		5		137	113

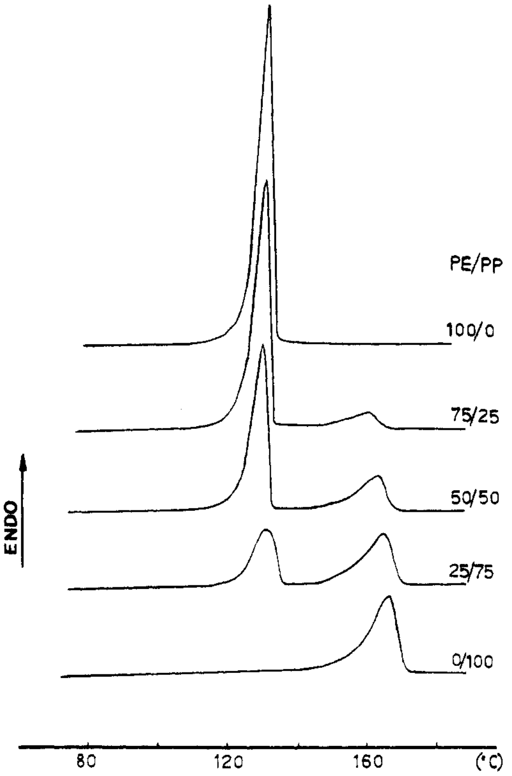

Figure 2. DSC curves of PE/iPP blend films investigated.

H-calculated and H-experimental in Figure 1 are collected in Table II. These data show, first, that the b_{PE} parameter at least for blended gel films of PE and for the individual PE homopolymer is 4–9 times smaller than that for conventionally melt-crystallized polyethylene (ref 1) and second, that the b_{PE} and b_{PP} values for the blended gel films gradually increase with the content of iPP and PE crystals, respectively. These results could tentatively be explained in light of Sawatari et al.'s[3] findings as due to an increase in the number of molecular entanglements between PE and the neighboring iPP crystals with increasing iPP content up to 75%. Here it should be noted that b is a parameter that characterizes the formation of a multitude of shearing planes at the crystals surface under the indenter.[1] Thus, it turns out that gel crystals apparently having a very low density of surface defects[3] give rise to lower b values (b_{PE} = 28–60 Å) and a much higher yield point (larger H values) than conventionally melt-crystallized PE crystals containing a large amount of surface defects ($b_{PE} \sim$ 180–260 Å).

To substantiate this viewpoint, we have additionally analyzed the melting endotherms of the series of blended gel materials. Figure 2 illustrates the melting enthalpy of the PE/iPP blended gel films for the various compositions used. Table III collects the thermodynamically derived $b^* = 2\sigma/\Delta h_f$ values with use of eq 7 for the PE and iPP gel crystals as a function of blend composition. Most interesting is the fact that, in each case, b^* for one component—similarly as b_{PE} or b_{PP} in Table II—clearly increases with increasing content of the other component and vice versa. It is to be noted that the difference found between b^* and b for each sample must be ascribed to the different values of Δh and Δh_f for both of them.[1] Table III also collects the σ values for both components, as derived from b^*, with use of eq 7. According to Kilian's concept of the nonhomogeneous microphase,[2] the surface free energy of a crystalline lamellae containing surface defects can be expressed as a sum of two terms:

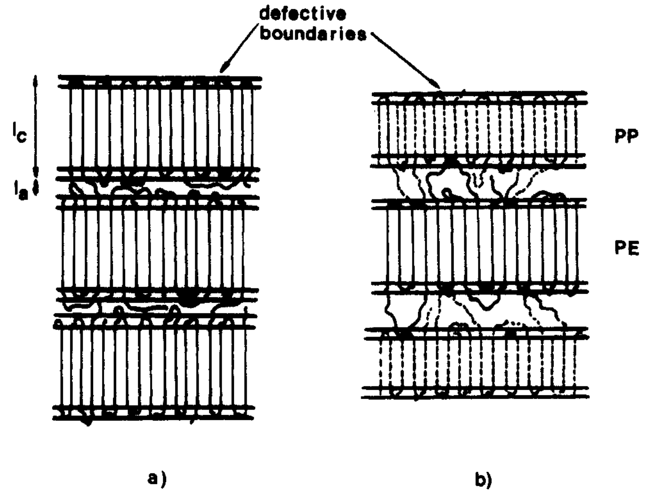

Figure 3. Schematics of dry gel lamellae for: (a) PE homopolymer with chain folds at the surface boundaries; (b) PE/iPP blend showing a number of PP entanglements segregated on the defective surface of PE lamellae. The rest of PP molecules in the amorphous phase are not drawn for simplicity.

Table III
Experimental Values of Melting Temperature, b^* Parameter, and Surface Free Energy, σ, Derived from DSC as a Function of Composition

PE/iPP	T_m^{PE}, K	T_m^{PP}, K	b^*_{PE}, Å	b^*_{PP}, Å	σ_{PE},[a] erg/cm^2	σ_{PP},[b] erg/cm^2
100/0	405		3.0		41.2	
75/25	404	434	3.2	3.0	44.5	28.8
50/50	403	436	3.4	2.7	47.4	26.6
25/75	401	438	3.9	2.5	54.4	24.3
0.100		439		2.2		21

[a] Values derived from eq 7 by using $\Delta h_f = 2.8 \times 10^9$ erg/cm^3. [b] Values derived from eq 7 by using $\Delta h_f = 1.96 \times 10^9$ erg/cm^3.

$$\sigma = \sigma_{core} + \sigma_s \qquad (8)$$

The first one, σ_{core}, denotes the surface free energy contribution of the crystal core with a sharp interface, and the second one represents the excess energy due to the presence of the surface defects and entanglements.[2] In polyethylene[2] σ_{core} for the crystal core has been shown to be a constant value[2] equal to 38 erg/cm^2. Inspection of the σ_{PE} data of Table III suggests that for the pure PE gel film the defect excess energy, σ_s, term is negligible ($\sim$3 erg/cm^2). This is consistent with the view that the PE homopolymer gel lamellae are similar structures to solution-crystallized chain-folded PE with practically no entanglements (Figure 3a). However, with increasing iPP concentration the increase in σ from 41 up to 54 erg/cm^2 indicates that the defect excess energy term, σ_s, gradually increases up to values of about 16.4 erg/cm^2. One could speculate that this result is in accordance with an increase in the number of entanglements formed by neighboring iPP chains on the surface of PE lamellae (Figure 3b). Most interesting is the fact that a symmetrical increase in the surface free energy of the iPP gel crystals with increasing PE concentration (maybe due to entanglements of the PE chains onto the iPP crystals) is also obtained (Table III). In other words, the analysis of the melting peaks of PE crystals within the blended gels seems to give information on the influence of the iPP neighboring molecules on the defective PE crystal surface and, vice versa, the study of the iPP thermograms apparently yields a qualitative view of the influence of PE neighboring chains on the iPP crystal surface.

Finally, from Table III it is noteworthy that the largest value of the sum $\sigma_{PE} + \sigma_{PP} = 78.7$ erg/cm^2 is found for the 25/75 gel blend, suggesting that this is the system containing the highest level of surface defects at the crystal boundary. This result is in good agreement with the SAXS and scanning electron microscope studies by Sawatari et al.,[3] which, indeed, indicate that mixing of PE and iPP molecules is most intimate in the 25/75 component and that, probably, the level of entanglements is expected to reach here a maximum value.

In conclusion, the deviation shown in Figure 1 from the hardness additivity law (straight line 1) can be explained in terms of two distinct contributions: (a) a crystallinity depression caused by the coexistence of the PE and iPP phases, which yields curve 2, and (b) a substantial decrease of the crystal hardness of the PE and iPP components provoked by an increase of the surface free energy (σ) with composition, which leads to curve 3. It is suggested that the σ rise is a consequence of the increase in the level of surface defects including entanglements.

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