Colloid Polym Sci 280:358–364 (2002)
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ORIGINAL CONTRIBUTION

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Microhardness of compatibilized blends of polypropylene with a semiflexible liquid-crystalline polymer

Received: 18 June 2001
Accepted: 4 October 2001

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Abstract The Vickers microhardness of blends of isotactic polypropylene and a semiflexible liquid-crystalline polymer (iPP/LCP 90/10 and 80/20 w/w), compatibilized with 2.5, 5 or 10 wt% PP-*g*-LCP copolymers with different composition has been studied. It has been shown that the microhardness values of uncompatibilized blends are close to the additive ones, while for compatibilized blends a strong positive deviation from additivity has been established. This result is interpreted by the increase in the degree of crystallinity of PP, by the decrease in the surface free energy of PP crystals and by the decrease in the surface free energy of the LC domains when the PP-*g*-LCP compatibilizer is present. The effect of the composition and concentration of the compatibilizer on the experimental hardness values has also been studied. The values of the microhardness/modulus of elasticity of some of the materials have been obtained. It is demonstrated that according to these values the compatibilized blends take a position closer to the elastic material in the elastic–plastic spectrum than the uncompatibilized blends. The results are interpreted by the compatibilizing efficiency of PP-*g*-LCP copolymers towards iPP/LCP blends.

Keywords Isotactic polypropylene/liquid-crystalline polymer blends · Compatibilization · Microhardness

Introduction

Compatibilization of blends of isotactic polypropylene (iPP) and liquid-crystalline polymer (LCP) has recently been attempted using different compatibilizing agents in order to enhance the adhesion and improve the blend properties. It has been shown that among compatibilizing agents, block or graft copolymers made up of segments with chemical structure and solubility parameters identical to those of the blending polymers are most suitable for the purpose. Our previous article [1] reports the successful synthesis of a PP-*g*-LCP copolymer by polycondensation of LCP monomers carried out in the presence of acrylic acid functionalized PP (PPAA). The new PP-*g*-LCP copolymers are constructed from relatively long PP and LCP segments, preserving the crystalline structure of the neat components [1]. The compatibilizing effect of these copolymers upon PP/LCP blends has been evaluated by investigation of the morphology, crystal structure, thermal properties and crystallization behavior of the compatibilized blends [2, 3]. A strong reduction in the size of the dispersed LCP domains and a drastic increase in the nucleation rate and crystallization rate of the iPP matrix in the compatibilized blends have been observed [1–3]. The compatibilized iPP/LCP blends display improved crystallization kinetics, enhanced degree of crystallinity and improved interphase adhesion [1–3]. Consequently, an improvement in the mechanical properties should be expected for these blends.

In the last two decades the value of microhardness as a technique capable of detecting a variety of morphological and textural changes in crystalline polymers has been amply emphasized, leading to extensive research [4–7]. Microindentation hardness is based on plastic straining and consequently is directly correlated to the mechanisms of molecular and supermolecular deformations occurring locally at the polymer surface. These mechanisms crucially depend on the specific morphology of the material. The fact that crystalline polymers are multiphase materials has prompted a new route to the identification of their internal structure and relating it to the resistance against local deformation (microhardness) [6–10]. In the case of polymer blends, microhardness is a helpful tool for the assessment of the degree of interpenetration of the blend components [11]. It has been shown that for blends of low- and high-density polyethylene [12] and for blends of poly(ethylene terephthalate) and poly(ethylene naphthalate) [5] microhardness is an additive function of the microhardness values of the individual components of the blend; however, in blends of polyethylene/PP or poly(butylene terephthalate)/polycarbonate a deviation from the additivity law is detected [13, 14] owing to the changes in crystallinity and to the thickness of the crystals of the components in the blend. The negative deviation from the hardness additivity law for polyethylene/PP gel blends has been explained by a crystallinity depression and by an increase in the surface free energy with composition [11].

In the present work the microhardness of PP/LCP blends, compatibilized with 2.5, 5 and 10 wt% of PP-*g*-LCP copolymers with different composition, was investigated. The aim was to estimate how the microhardness values are affected by the change in the blend morphology, caused by the addition of compatibilizer. The effect of the composition and concentration of the compatibilizer upon the experimental hardness values was also studied.

Experimental

iPP was a commercial pelletized material, Moplen F30S, produced by Himont. The LCP was a semiflexible copolyester synthesized as described before [15, 16] from sebacic acid, 4,4′-dihydroxybiphenyl and 4-hydroxybenzoic acid, supplied by Eniricerche SpA, Milan. In the following the LCP is indicated as SBH. The inherent viscosity, measured in 50/50 v/v 4-chlorophenol/1,2-dichloroethane solution (25 °C, 0.1 g/l), was 0.88 dl/g. This LCP has a crystalline-to-nematic phase-transition temperature of 230 °C and a nematic-to-crystalline transition temperature of 217 °C involving low enthalpy changes (about 6 J/g). Graft copolymers of PPAA with a semiflexible LC polyester (SBH 1:1:2) (PP-*g*-SBH copolymers) were prepared by melt polycondensation of SBH monomers carried out in the presence of PPAA [1]. The synthesized polycondensation products COPP50 and COPP70 contain a theoretical amount of PPAA of 50 and 70 wt% [1].

Binary and ternary blends of iPP, SBH and COPP (if any) were prepared in a PL330 Brabender Plasticorder apparatus, equipped with a 50-ml mixing unit at 245 °C and 50 rpm. The weight-to-weight ratio of iPP to SBH was held constant at 90/10 or 80/20 composition; these blends were compatibilized by the addition of 0, 2.5, 5 and 10 wt% of COPP50 or COPP70. The total SBH content within a given blend (SBH bulk plus SBH grafts of the copolymers) was always 10 or 20 wt%. The addition of 10 wt% of COPP50 (the composition of this graft PP/SBH copolymer is 50/50 w/w) to 80/20 iPP/SBH blend led to a ternary blend iPP/COPP50/SBH 75/10/15 w/w/w, i.e. the PP/SBH ratio was kept at 80/20 w/w. The neat components were subjected to the same treatment.

The microhardness of the blends was measured using a standard Vickers mhp-160 microhardness tester for an NU-2 (Germany) light microscope. The indentor was a square-shaped diamond pyramid, with top angle of 136°. Loads of 0.4, 0.8, 1.0 and 1.2 N to correct for instant elastic recovery were employed. A loading cycle of 0.1 min was used. The standard Vickers microhardness (H) was determined by the equation [4, 8, 17]

$$H = kP/d^2 \, , \tag{1}$$

where P is the applied load, k is a geometric factor equal to 1.854 and d is the mean diagonal length of the imprint after removing the indenter.

At least ten imprints were made under each load. H was determined within $\Delta H/H = 0.05$. Under the loads applied the mean diagonal length of the imprints varied in the range 100–200 μm.

Results and discussion

The materials investigated consisted of an iPP matrix in which the SBH component was dispersed in the form of predominantly spherical particles [1]. In order to provide reliable hardness values corresponding to the total hardness of the blends, the imprints under each load should be larger in size than the dimensions of the dispersed SBH particles. The dependence of the mean dimensions of the dispersed SBH particles, measured from scanning electron microscope micrographs of the fracture surfaces of the blends [1], are shown in Fig. 1 versus blend composition in uncompatibilized and compatibilized blends. In all the blends these dimensions are in the range 3–45 μm, i.e. they are smaller than the mean diagonal length of the imprints. That means that the imprints correspond to the total microhardness of the materials. Moreover, it should be noted that the iPP/SBH blends to which PP-*g*-SBH copolymer was added, can also be considered as a biphasic system because the PP and SBH segments of the copolymer are completely miscible with the corresponding bulk phases [2]. Schemes of imprints over an uncompatibilized iPP/SBH blend and a compatibilized iPP/COPP/SBH blend are presented in Fig. 2. PP-*g*-SBH copolymer, located on the interphase boundary, is also presented.

The microhardness data of iPP, SBH, uncompatibilized and compatibilized blends, and the values of the degree of crystallinity of neat iPP and the PP component within each blend derived from wide-angle X-ray scattering [2] are collected in Table 1. As seen H for the LCP is much lower that that of iPP. This is probably due to the LC structure of the polymer characterized by lateral packing of parallelly oriented macromolecules having cylindrical symmetry and longitudinal disorder [16]. The experimentally obtained variation of H as a function of SBH content is displayed in Fig. 3. The dashed line in Fig. 3 was obtained by following the additivity law according to the equation [11]

$$H = wH^{\mathrm{PP}} + (1 - w)H^{\mathrm{SBH}} , \tag{2}$$

where w and $(1-w)$ are the weight fractions of PP and SBH, respectively. It should be mentioned that the compatibilized blends form a two-phase system because the PP segments of PP-*g*-SBH copolymers contribute to the iPP phase, while the SBH grafts remain in the LCP phase.

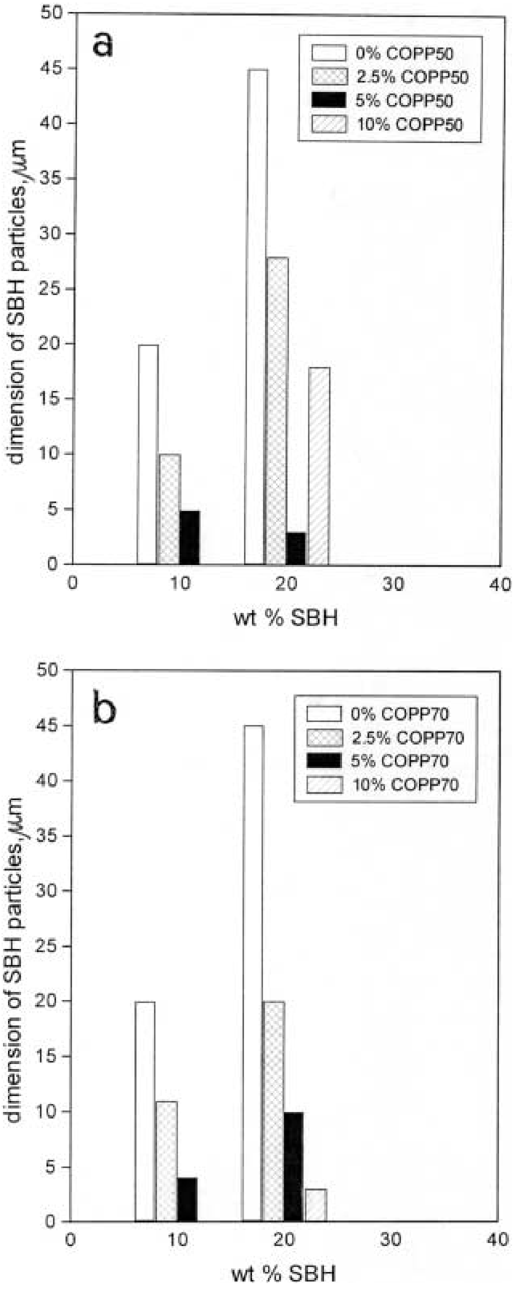

Fig. 1 Dimensions of sebacic acid/4,4′-dihydroxybiphenyl/4-hydroxybenzoic acid (*SBH*) copolymer particles versus weight percent of SBH in isotatic polypropylene (*iPP*)/SBH 90/10 and 80/20 blends, compatibilized with **a** COPP50 or **b** COPP70

The experimentally obtained H values for uncompatibilized blends are close to the additive ones, while for compatibilized blends a strong positive deviation from additivity is demonstrated (Fig. 3). In order to explain this hardness behavior of the blends the following dependencies should be considered: As shown [11, 18] the microhardness of the PP phase depends on the crystallinity, α, according to the equation

$$H^{\mathrm{PP}}{=}\alpha_{\mathrm{PP}}H_{\mathrm{c}}^{\mathrm{PP}}{+}(1 - \alpha_{\mathrm{PP}})H_{\mathrm{a}}^{\mathrm{PP}} , \tag{3}$$

where $H_{\mathrm{c}}^{\mathrm{PP}}$ and $H_{\mathrm{a}}^{\mathrm{PP}}$ are the hardness values for the crystalline and amorphous phases respectively.

Thus the expression for the total microhardness of the materials is obtained:

$$H = w\alpha_{\mathrm{PP}}H_{\mathrm{c}}^{\mathrm{PP}} + w(1 - \alpha_{\mathrm{PP}})H_{\mathrm{a}}^{\mathrm{PP}} + (1 - w)H^{\mathrm{SBH}} . \tag{4}$$

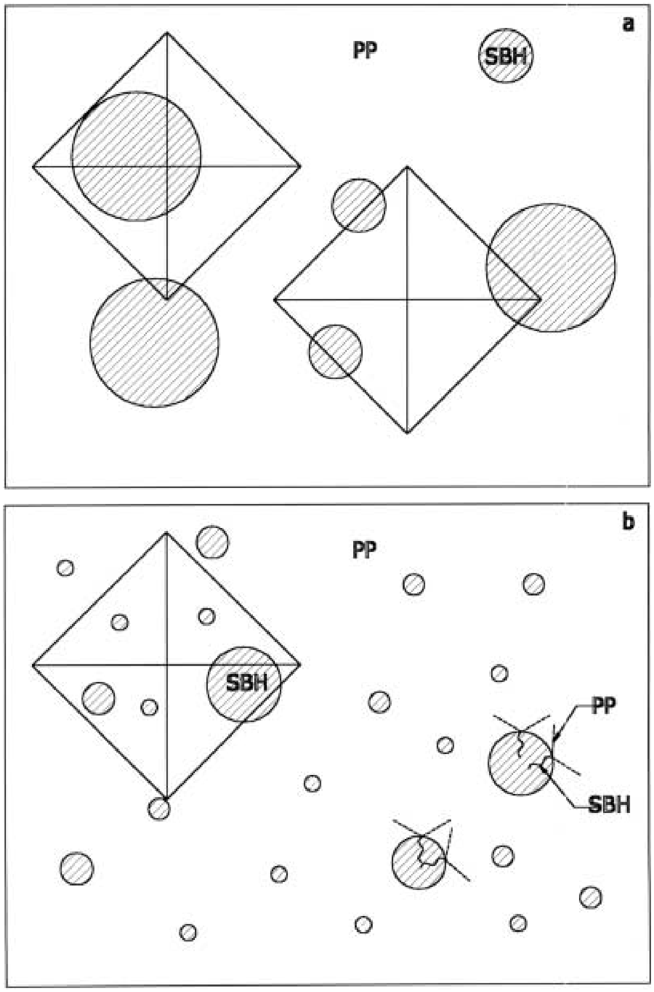

Fig. 2 Scheme of imprints over **a** an uncompatibilized iPP/SBH blend and **b** a compatibilized iPP/COPP/SBH blend. PP-*g*-SBH copolymer, located on the interphase boundary, is also presented

Table 1 The experimental microhardness values (H_{exp}), the microhardness values calculated according to Eq. (4) (H_{cal}) and the degree of crystallinity of polypropylene (*PP*) derived from wide-angle X-ray scattering [2] of the samples

PP-*g*-SBH copolymer	Composition of blends iPP/COPP/SBH	H_{cal} (MPa)	H_{exp} (MPa)	α
	0/0/100	–	27	–
	90/0/10	85	83	0.52
COPP70	88.2/2.5/9.2	87	92	0.54
COPP70	86.5/5/8.5	88	96	0.55
COPP50	87.5/5/7.5	89	95	0.56
	80/0/20	76	78	0.49
COPP70	78.2/2.5/19.2	–	89	–
COPP70	76.5/5/18.5	–	92	–
COPP70	73/10/17	–	92	–
COPP50	78.7/2.5/18.7	79	88	0.53
COPP50	77.5/5/17.5	82	94	0.55
COPP50	75/10/15	82	89	0.55

Table 1 reveals that the degree of crystallinity of PP increases in the compatibilized blends. Taking into account the increase in crystallinity for each blend and following Eq. (4) the H values can be calculated, using for $H_{\mathrm{c}}^{\mathrm{PP}} = 145$ MPa (this value is in a perfect agreement with that in Ref. [11]) and for $H_{\mathrm{a}}^{\mathrm{PP}} = 33$ MPa [18]. The calculated hardness values (H_{cal}) are also included in Table 1 and Fig. 3. Notably for uncompatibilized blends the experimental hardness values (H_{exp}) appear close or even lower than the calculated H values. In contrast, the increase in the degree of crystallinity of PP in the presence of a compatibilizer is still insufficient to induce the positive deviation of the experimental H values from the additivity law (Fig. 3). Hence, according to Eq. (4) one of the possibilities to explain the increase in the hardness when a compatibilizer is present is that $H_{\mathrm{c}}^{\mathrm{PP}}$ itself increases, as a consequence of interactions between both components [11]. In order to interpret the possible increase in $H_{\mathrm{c}}^{\mathrm{PP}}$ the morphology of the blends and the compatibilizing mechanism should be discussed. As shown [2, 3] PP segments of PP-*g*-SBH compatibilizer cocrystallize completely with bulk iPP, while the SBH grafts of the copolymer cocrystallize with the bulk SBH or enter the amorphous phase of the blends. This leads to a reduction in the interfacial tension and in the surface free energy of SBH domains, which in turn causes a strong reduction in the dimensions of the dispersed SBH phase. As a result the interphase adhesion is strongly enhanced. Moreover, it has been shown [2] that the PP matrix of the uncompatibilized blends crystallizes mainly into big monoclinic α spherulites (Fig. 4a). In contrast, in the compatibilized blends the dimensions of the iPP spherulites are remarkably reduced (Fig. 4b). The strong decrease in the dimensions of the PP spherulites in the compatibilized blends is in agreement with the increase in the PP nucleation and crystallization rates determined by differential scanning calorimetry [2, 3]. In compatibilized blends the size of the SBH LC domains is much smaller than that in the uncompatibilized blends (Fig. 4). The morphology of the compatibilized blends is almost homogeneous, consisting of tiny SBH domains and PP spherulites which are almost indistinguishable. This homogeneous morphology of compatibilized blends is characterized by higher degrees of crystallinity and melting temperatures of PP crystals [2] and by a lower surface free energy of SBH domains. All these parameters are connected directly to the microhardness of the blends.

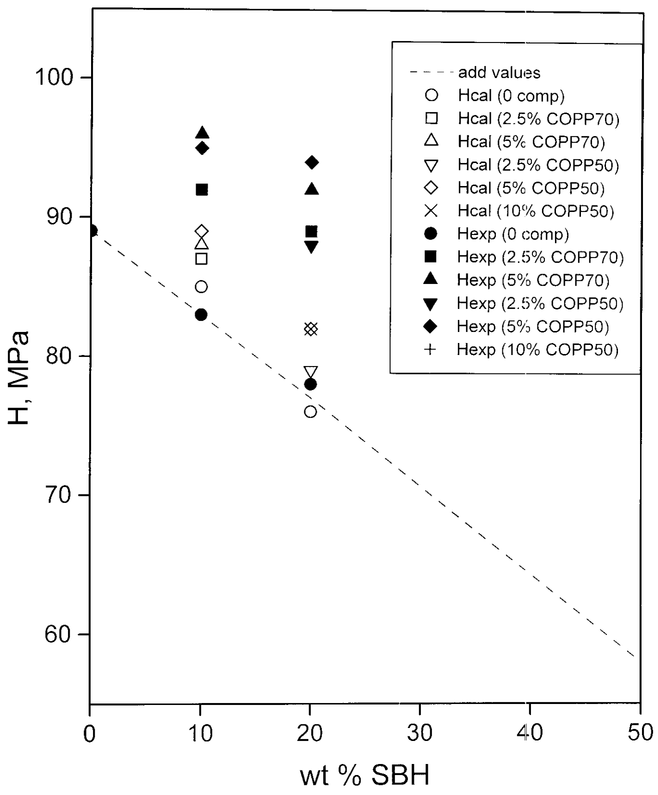

Fig. 3 Experimentally obtained values of microhardness (H_{exp}) and calculated microhardness values according to Eq. (4) (H_{cal}) as a function of the weight percent of SBH in the blends. The *dashed line* represents the additive values of microhardness, calculated according to Eq. (2)

Evidently, these effects resulting from the addition of the compatibilizer influence the hardness values measured. It is known that [11]

$$H_{\mathrm{c}} = H_0/(1 + b/l_{\mathrm{c}})\;, \qquad (5)$$

where l_{c} is the crystal thickness, H_0 is the hardness for an infinite crystal and b is a hardness-derived constant. For crystals with given thickness, l_{c}, H_{c} depends only on the parameter $b = 2\sigma/\Delta h$, which is 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. It could be assumed that l_{c} of PP crystals

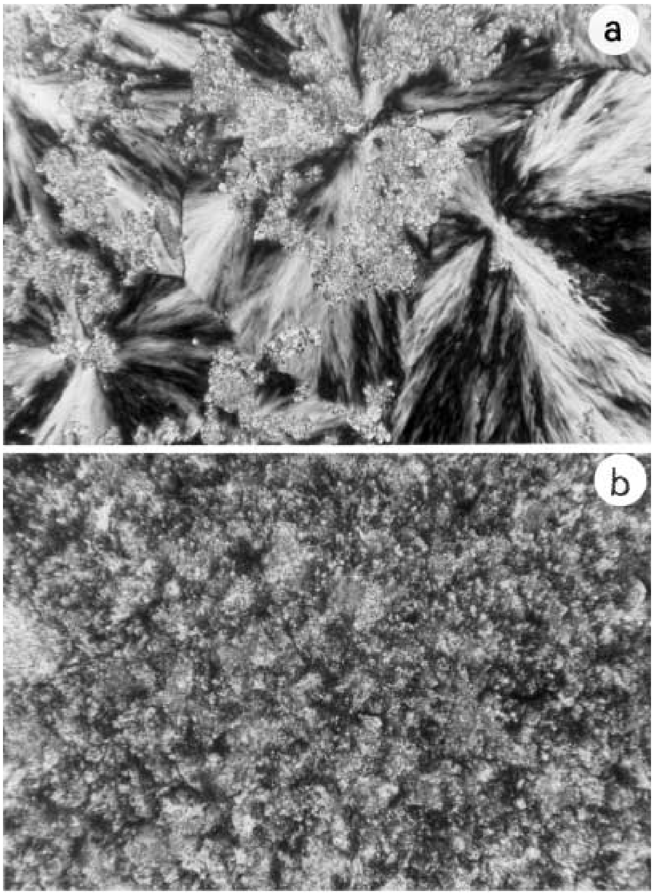

Fig. 4 Optical micrographs of **a** uncompatibilized iPP/SBH 80/20 blend and **b** compatibilized iPP/COPP50/SBH 77.5/5/17.5 blend. Magnification 200×

does not change significantly with the addition of a compatibilizer for the following reasons. Our previous investigations have shown that the PP crystallization mechanism does not change with the addition of compatibilizer [2, 3]. Moreover the compatibilized blends are prepared under similar experimental conditions as the uncompatibilized blends. Thus, for $H_0^{PP} = \text{constant}$, the increase in H_c^{PP} can be due only to the decrease in b and to the decrease in σ, respectively. In order to confirm this, the melting behavior of the blends should be also taken into account. It has been shown that Eq. (5) is very similar to the well known Thomson–Gibbs equation:

$$T_m = T_m^0(1 - b*/l_c), \tag{6}$$

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

The experimental values of the melting temperatures [2], b^*, and surface free energy, σ, of the neat iPP and PP components in uncompatibilized and compatibilized blends are presented in Table 2. The following data were used for the calculation of b^* and σ: $l_c = 125$ Å [19], $T_m^0 = 460.7$ K [20], $\Delta h_f = 1.96 \times 109$ erg/cm^3 [21]. The data in Table 2 show clearly that b^* and σ are lower in compatibilized blends than in uncompatibilized ones. The decrease in the surface free energy of PP crystals in the presence of a compatibilizer means that the level of defects on the crystal surface decreases.

Evidently, in compatibilized blends the PP crystals having a low density of surface defects give rise to lower b values and higher H_c values than those resulting from the PP crystals in the uncompatibilized blends. It could be assumed that H_c^{PP} increases up to the maximal value of 150 MPa (a value determined [22] for the hardness of an infinite PP crystal, obtained by extrapolation of H to $\alpha = 1$ in a H versus α plot). Recently the value $H_0^{PP} = 230$ MPa was obtained as a consequence of an increase in both the degree of crystallinity and the crystalline lamella thickness [23]. As in iPP/SBH blends, l_c of PP crystals does not change significantly with the addition of a compatibilizer; the value of 150 MPa should be taken as more adequate. Thus, the calculated H values for the compatibilized blends according to Eq. (4) are still lower than the experimental H values of the blends. Thus, analyzing Eq. (4) the only possibility to explain the experimental H values of compatibilized blends is that the H^{SBH} increases in the presence of a compatibilizer. The latter may be due to the decreased surface free energy of LC domains. As H_{exp} of the compatibilized blends varies from 88 to 96 MPa, that means the H^{SBH} values should be in the range 60–84 MPa, assuming that $H_c^{PP} = 150$ MPa. Evidently, the hardness of small SBH domains strongly increases in the presence of a compatibilizer.

So, the positive deviation of the experimentally obtained hardness values for compatibilized blends from the additive ones can be interpreted by the increase in the degree of crystallinity of PP, the decrease in the surface free energy of PP crystals, and the decrease in the surface free energy of LC domains. The lower hardness

Table 2 The experimental values of the melting temperatures [2], b^* and the surface free energy of neat PP and PP components in uncompatibilized and compatibilized blends

PP-*g*-SBH copolymer	Composition of blends iPP/COPP/SBH	T_m (K)	b^* (Å)	σ^{PP} (erg/cm^2)
	100/0/0	431.0	8.1	79.6
	90/0/10	430.6	8.1	79.6
COPP70	88.2/2.5/9.2	433.4	7.5	73.5
COPP70	86.5/5/8.5	433.4	7.5	73.5
COPP50	87.5/5/7.5	434.3	7.1	70.0
	80/0/20	430.8	8.1	79.6
COPP70	78.2/2.5/19.2	431.8	7.8	77.2
COPP70	76.5/5/18.5	432.8	7.6	74.7
COPP70	73/10/17	431.2	8.0	78.4
COPP50	78.7/2.5/18.7	433.3	7.5	73.5
COPP50	77.5/5/17.5	432.2	7.7	75.9
COPP50	75/10/15	432.8	7.6	74.7

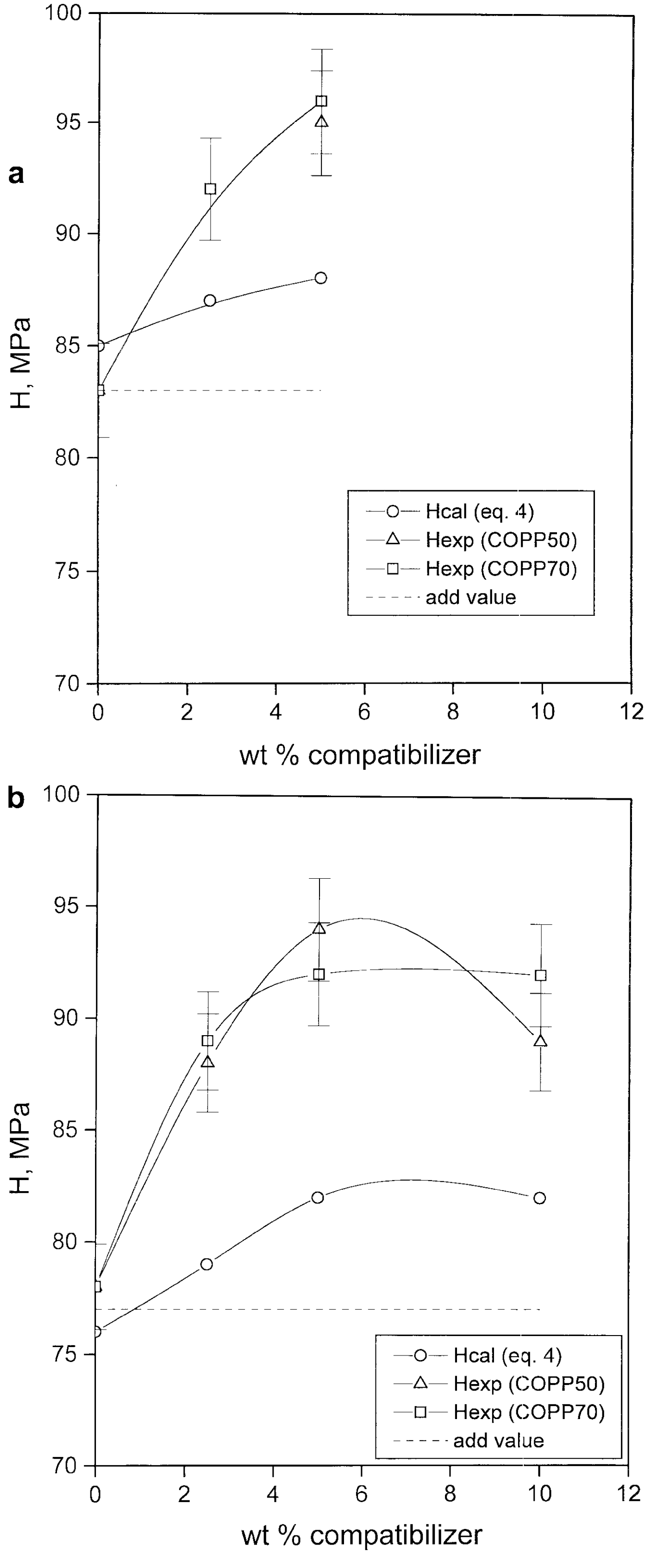

Fig. 5 Dependence of H_{exp} and H_{cal} on the concentration of COPP50 and COPP70 **a** for iPP/SBH 90/10 blends and **b** for iPP/SBH 80/20 blends. The *dashed line* represents the additive values of microhardness, calculated according to Eq. (2)

values for uncompatibilized blends are due to the lower degree of crystallinity of PP and to the higher surface free energy of PP crystals and SBH LC domains. The results obtained confirm the compatibilizing efficiency of COPP towards iPP/SBH blends.

In order to evaluate the influence of the nature and the concentration of the compatibilizers upon the microhardness of the blends, the experimentally obtained H values are plotted as a function of COPP concentration for iPP/SBH 90/10 and for iPP/SBH 80/20 blends in Fig. 5. The H values calculated using Eq. (4) and taking into account the degree of crystallinity for each sample are also included in Fig. 5. It can be observed that an increase in the compatibilizer concentration up to 5 wt% leads to an increase in the hardness values. The further increase in the compatibilizer concentration up to 10 wt% almost does not change or even decreases the blend hardness. The nature of the compatibilizer does not affect significantly the hardness behavior. This is in perfect agreement with the effect the compatibilizer has upon the dimension reduction of the dispersed SBH particles.

It is well known that there is a correlation between the microhardness (H) of crystalline polymers and the modulus of elasticity (E) [6]; however, it should be emphasized that while the plastic deformation of lamellae when measuring H depends primarily on the crystal thickness and perfection, in the case of the elastic modulus a determining factor is the amorphous layer, which is elastically deformed [6]. On the grounds of the mechanism of hardness indentation, namely that the loading cycle is elastic–plastic and the unloading cycle is elastic, Lawn and Howes [24] derived a plot which is an indicator of the position taken by different materials in the elastic–plastic spectrum. According to this plot material having a relation $H/E = 0.176$ for a Poisson's ratio $\nu = 0.4$ can be considered as an ideal elastic material, while for an ideal plastic material this relation is $H/E = 0$.

The H/E values for some of the materials were obtained using preliminarily measurements of the elastic modulus from a tensile test (Table 3). It should be noted that for the neat SBH the value $E = 420$ MPa demonstrates that the mechanical properties of this semiflexible LCP are fairly low in the unoriented state. It has been shown, however, that when the SBH is processed under conditions granting strong orientation, the mechanical characteristics are noticeably improved. The H/E value of SBH indicates that this material takes a position close to plastic material in the elastic–plastic spectrum [6]. A similar value (0.05) is obtained for chain-extended isotropic polyethylene [6]. As seen according to the H/E values obtained for the blends, the compatibilized blend is positioned in the elastic–plastic spectrum much closer to elastic material than the uncompatibilized blend [6]. This is in perfect agreement with the values of elongation at break, which for the uncompatibilized

Table 3 The experimental microhardness values (*H*), the value of the elastic modulus (*E*) [22] and the values of *H*/*E* for some of the materials

Sample	*H* (MPa)	*E* (MPa)	*H*/*E*
iPP	89	980	0.090 ± 0.003
SBH	27	420	0.064 ± 0.003
iPP/SBH 80/20	78	890	0.087 ± 0.003
iPP/COPP50/SBH 77.5/5/17.5	94	950	0.100 ± 0.003

blend is 9%, while for the compatibilized blend this value is 15%. These results confirm the compatibilizing efficiency of COPP, leading to enhanced adhesion between the blend components.

Conclusion

The investigation of the Vickers microhardness of uncompatibilized and compatibilized iPP/SBH blends shows that the addition of 2.5, 5 or 10 wt% of PP-*g*-SBH compatibilizer leads to an increase in the microhardness of the blends. The strong positive deviation of the experimental hardness values from the additive ones was interpreted by the increase in the degree of crystallinity of PP and by the decrease in the surface free energy of PP crystals and of SBH LC domains. It was demonstrated that the increase in the compatibilizer concentration up to 5 wt% leads to an increase in the hardness values, while a further increase in the compatibilizer concentration up to 10 wt% does not change or even decreases the blend hardness. The nature of the compatibilizer does not affect significantly the hardness values. The investigation of the correlation between microhardness values and values of the elastic modulus shows that the compatibilized blends take a position in the elastic–plastic spectrum much closer to the elastic material than the uncompatibilized blends do. The results confirm the compatibilizing efficiency of PP-*g*-SBH copolymers towards iPP/SBH blends.

Acknowledgement This work was carried out within the joint research project between the Bulgarian Academy of Sciences and C.N.R., Italy.

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