Morphology and Properties of Blends of Polyethylene with a Semiflexible Liquid Crystalline Polymer

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SYNOPSIS

Blends of three polyethylene (PE) samples (two HDPE grades and LLDPE) with an experimental sample of a semiflexible liquid crystalline polymer (SBH 1:1:2 by Eniricerche) have been prepared in a Brabender compounder. The processing-aid effect of the LCP has been demonstrated by the decreased energy required for extruding the blends, as compared to that needed for neat PE. The thermal properties, as studied by differential scanning calorimetry (DSC), have shown that the two components of the blends are immiscible. However, the dispersed SBH phase has been found to act as a nucleating agent for the crystallization of LLDPE, whereas no such effect was observed for HDPE. This has been taken as an indication that the phase interactions of SBH with LLDPE are more pronounced than with HDPE. The morphological study of the blends, done by scanning electron microscopy (SEM), has confirmed this conclusion. In fact, the SBH particles show a much better dispersion and a narrower size distribution in the LLDPE/SBH blends. The mechanical properties of the blends have been studied on compression-molded specimens. The results indicate that the reinforcing effect of SBH is practically none for both HDPE grades. In fact, the elongation at break decreases to very low values, and the tensile strength is also reduced, when the LCP concentration increases beyond 5–10%, whereas the tensile modulus does not vary appreciably, over the whole (0–20%) LCP range investigated. On the contrary, the tensile modulus of the LLDPE/SBH blends increases up to ca. 50%, and the elongation at break decreases more smoothly, on increasing the SBH content up to 20%. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

A great deal of attention has been paid during the last few years to blends of commercial thermoplastics with liquid crystalline polymers (LCPs).[1] The main benefits expected from the use of LCPs as blend components are: (1) the pronounced reduction of the melt viscosity, with consequent improvement of processability, and, (2) the reinforcing effect granted by the immiscible LCP particles, which can attain an oriented fibrillar morphology when the blend is processed under elongational flow conditions. *In situ* composites[2] have been prepared by the addition of LCPs into a great variety of flexible resins, such as polyamides, polyesters, polycarbonates, polysulfones, etc., and their morphology–processing–property relationships have been studied. On the contrary, comparatively few studies have been made on blends of LCPs with commercial polyolefins, such as polyethylene (PE) and polypropylene (PP). In particular, a C.A. search of the scientific literature has shown that PE has received very little consideration as a matrix for LCP blends.[3–6] This may be surprising, because one might expect a threefold modulus enhancement by the addition of only 5% LCP into PE,[4] or, perhaps, a significant improve-

ment of the processability of, e.g., ultra high molecular weight PE (UHMWPE), by blending it with an LCP.[7] However, there may be various reasons for this limited attention to PE/LCP blends. First of all, because most available thermotropic LCPs belong to the families of wholly aromatic copolyesters and copolyesteramides, they are expected to show very poor compatibility and interphase adhesion toward PE. Moreover, the processing temperatures of common aromatic LCPs lie in the 300°C range and are, therefore, much higher than those used for PE processing.

New semiflexible LCPs, prepared by melt polycondensation of equimolar amounts of an aliphatic diacid, e.g., sebacic acid (S), and 4,4'-dihydroxybiphenyl (B), with different quantities of 4-hydroxybenzoic acid (H), have been disclosed recently by Eniricerche.[8] These LCPs have melting points in the 150–300°C range, depending on the length of the polymethylene sequence in the diacid unit and on the composition. Thus, the polymer containing 25% S, 25% B, and 50% H (referred to as SBH 1:1:2) has a melting point of ca. 225°C, and a nematic mesophase, which is stable up to temperatures above that of initial decomposition.[9,10] The blends of these semiflexible LCPs with different commercial thermoplastics have been studied[11–14] and have been found to display some advantages, with respect to those involving wholly aromatic LCPs, either from the processing point of view, or for an improved phase compatibility, or both. Preliminary data on the rheological properties of PE/SBH blends have already been reported.[15]

In this article, the morphology and the thermal, rheological, and mechanical properties of blends of SBH 1:1:2 with different types of PE samples are described.

EXPERIMENTAL

Two commercial grades of high density PE (HDPE), produced by Enichem Polimeri, Milan: AF 5015 (MFI = 1.6 dg/min, $M_w \approx 2 \cdot 10^5$), and UG 6013 (MFI = 3.5 dg/min, $M_w \approx 1 \cdot 10^5$), were used as the blends matrices, as well as a sample of linear low density PE (LLDPE), also produced by Enichem Polimeri, Milan: Riblene LX 2211 (ethylene/butene-1 copolymer) (MFI = 1.0 dg/min). These samples will be referred to, hereinafter, as AF, UG, and LL, respectively.

The LCP was a laboratory sample (LCP1B/024 by Eniricerche) of SBH 1:1:2 copolyester, synthesized as described elsewhere[8–10] from 25% sebacic acid (S), 25% 4,4'-dihydroxybiphenyl (B), and 50%

4-hydroxybenzoic acid (H). The inherent viscosity of the LCP, measured in a 50/50 v/v 4-chlorophenol/1,2-dichloroethane solution (T = 25°C, c = 0.1 g/dL), was 0.88 dL/g. The LCP will be indicated as SBH in the following.

The polymers were dried in a vacuum oven at 100°C for at least 24 h before use. The blends were prepared by extrusion in a twin screw Brabender Compounder model 42/7 attached to a Brabender Plasticorder model 651. The thermal profile used throughout was 175, 220, and 240°C, and the rotational speed was 40 rpm. The extrusion torque and the flow rate were recorded during processing. The neat polymers were subjected to the same treatment. Blends with 0, 5, 10, and 20% SBH (w/w) were prepared.

The viscosity curves were determined at T = 240°C, using a capillary viscometer (Rheoscope 1000 by CEAST, Italy). The capillary had 1 mm diameter and length to diameter ratio (L/D) equal to 40. The data were corrected according to Rabinowitch, whereas the Bagley correction was neglected due to the high L/D ratio.

The calorimetric measurements were made using a Perkin–Elmer DSC4 apparatus, with a scanning rate of 10 deg/min. The specimens (ca. 10 mg) were heated up to 250°C and held at this temperature for 5 min before recording the cooling and the rerun heating traces. As described in the following section, for a study of the thermal behavior of the PE matrix, the initial temperature used for conditioning the specimens before measurement was 190 instead of 250°C. The crystallization and melting enthalpies were normalized to the PE content of the blends.

The extruded blends, in the form of threads of ca. 3 mm diameter, were broken in liquid nitrogen and the fractured surfaces, coated with gold, were viewed in a Jeol T300 scanning electron microscope (SEM) for the morphological study.

The stress–strain curves were obtained on an Instron model 1122 apparatus, using slabs prepared by compression molding in a Carver laboratory press at 240°C. The measurements were done at an elongational rate of 5.0 mm/min. The results were averaged on the basis of at least seven measurements. The elongation at break (EB) of the blends with 10% SBH showed poor reproducibility. In particular, the EB of five specimens of the 90/10 AF/SBH blend was found in the range of ca. 800%, whereas it was of ca. 100% for 2 of them.

RESULTS AND DISCUSSION

The addition of SBH into PE plays a processing-aid effect that could be easily demonstrated during
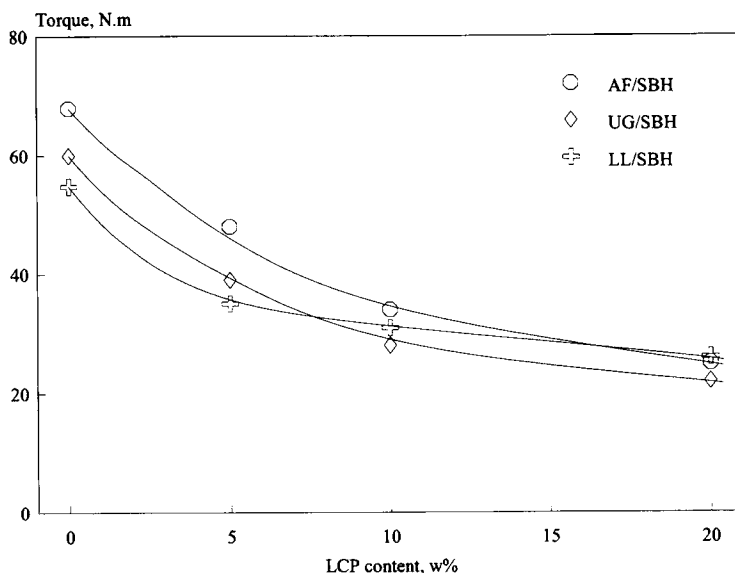
Figure 1 Extrusion torque vs. SBH content, for AF/SBH, UG/SBH, and LL/SBH blends.

the extrusion of the blends. In fact, whereas the flow rate was practically unaffected by the LCP addition, the energy required for extrusion, as measured by the applied torque, fell down appreciably upon increasing the LCP content. This is shown in Figure 1. A torque reduction of ca. 40% is obtained upon addition of only 5% LCP into either of the PE samples.

The viscosity curves measured for the three blend systems are shown in Figures 2–4. It is readily appreciated that the addition of SBH enhances the

shear thinning behavior of PE, and, particularly, of the HDPE specimens (AF and UG). The reduction of viscosity brought about by the LCP addition is demonstrated for all three systems by the viscosity-shear rate curves, and, even more clearly, in Figure 5 where the dimensionless viscosities measured at two shear rates (25 and 300 s^{-1}) are plotted against LCP concentration. In this figure, the curves of the different blends are displaced along the y axis to avoid overcrowding. As expected, the processing-aid effect is more evident at higher shear rates. This is
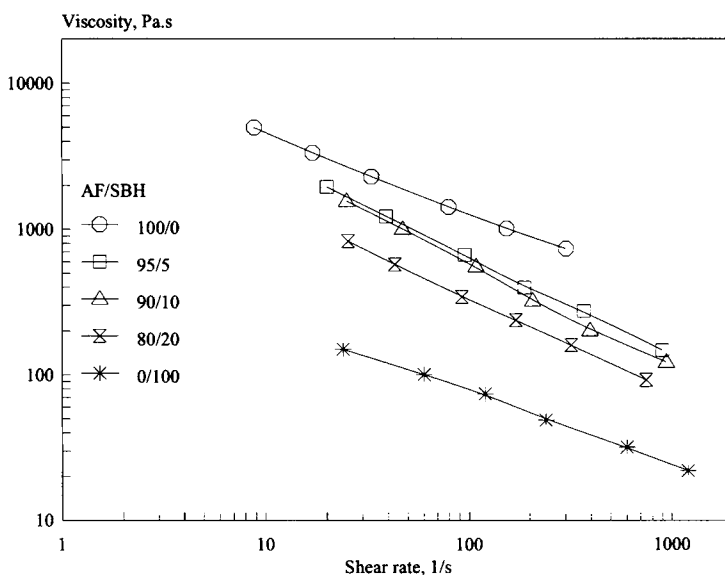
Figure 2 Viscosity curves measured at T = 240°C for AF/SBH blends.
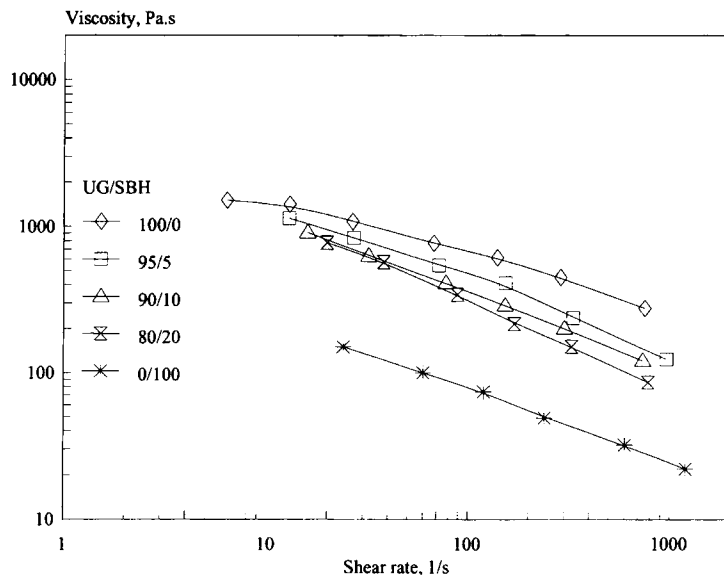
Viscosity, Pa.s

Figure 3   Viscosity curves measured at T = 240°C for UG/SBH blends.

especially so for the UG/SBH blends, because, among the three PE samples investigated, UG displays a rheological behavior characterized by smaller shear thinning. The reduction of viscosity is particularly evident at low LCP concentrations (0–5%): the addition of 5% SBH into any of the PE samples leads to a viscosity decrease of 40–60%, the higher values being found for the matrices with higher molecular weight, and for the higher shear rates.

Both calorimetric and microscopic analyses show that all investigated PE/SBH blends are biphasic in nature. Thus, as expected, SBH is not miscible

with PE, as demonstrated by the finding that its crystal←→nematic transition temperature is practically unaffected by blending it with this matrix.

The thermal behavior of the matrix was studied in more detail by recording the calorimetric traces obtained on cooling the specimens from 190°C, after keeping them at this temperature for 5 min in order to destroy the PE crystalline nuclei, and on reheating them. During this treatment, the SBH particles remained in the crystalline state. The results of the measurements are collected in Table I, together with the data obtained previously[9,10,16] for neat SBH
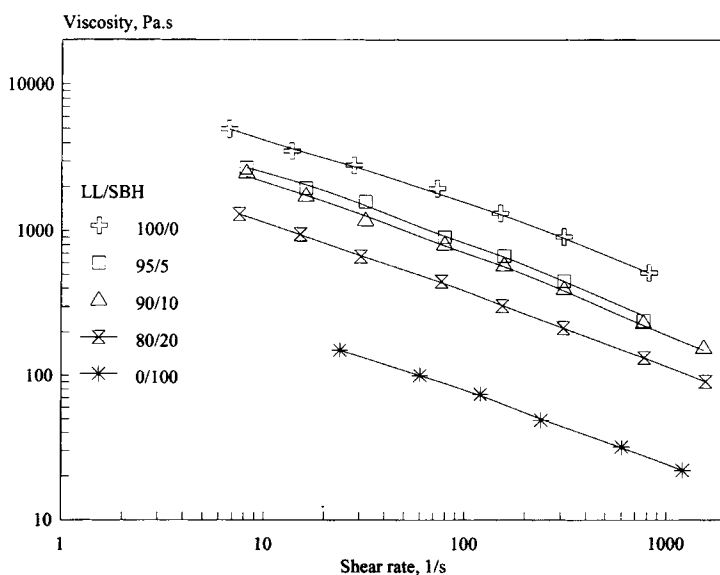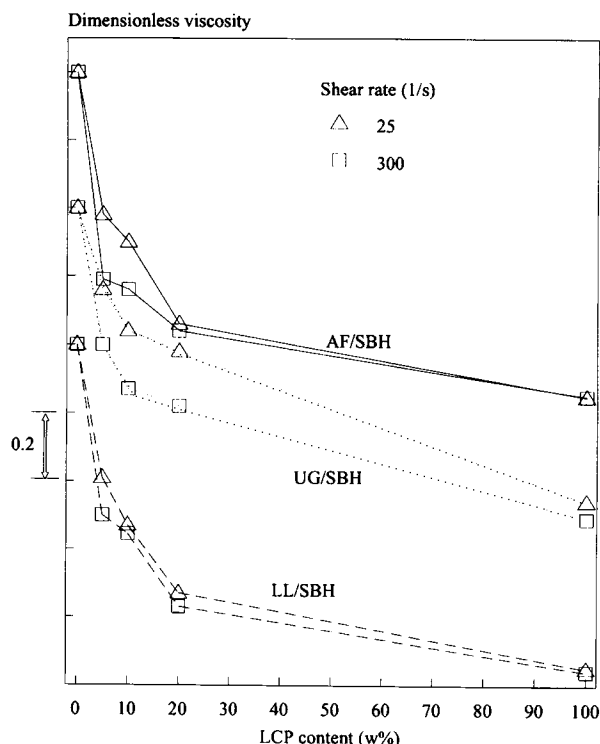
Viscosity, Pa.s

Figure 4   Viscosity curves measured at T = 240°C for LL/SBH blends.

Figure 5 Dimensionless viscosities (ratios of the blends viscosities to the viscosity of the matrix) of AF/SBH, UG/SBH, and LL/SBH blends, measured at two shear rates (25, and 300 s^{-1}), as a function of the SBH content.

1:1:2. It may be observed that the crystallization and fusion temperatures of AF and UG are barely affected by the presence of the LCP phase. On the contrary, a significant increase of the crystallization temperature Tc of LL is brought about by the SBH addition. This effect, which appears to be maximum for the 90/10 LL/SBH blend, has been considered as an indication that the LCP dispersed phase may act as a nucleating agent for the LL crystallization. A detailed study[17] of the nonisothermal and isothermal crystallization of LL has confirmed that the addition of SBH does actually lead to a strong increase of the relevant crystallization temperature T_c (in nonisothermal experiments) and crystallization kinetic constant (in isothermal experiments), as well as of the nucleation density. The finding that the effect tends to fade when the SBH concentration exceeds 10% has been interpreted[17] as being due to the observed decrease of the population density of the small (0.5–3 μm) LCP particles and the concomitant appearance of larger (5–20 μm) LCP domains (see below).

The mechanical properties of the PE/SBH blends were measured on slabs produced by compression molding of the extruded materials. As

it is shown in Figure 6, the tensile modulus (E) of both AF/SBH and UG/SBH blends is practically unaffected by the LCP addition, whereas that of LL/SBH blends increases slightly on increasing the SBH content (ca. 1.5 times, at 20% SBH).

The tensile strength (TS) of both HDPE polymers undergoes a measurable reduction when the SBH content exceeds ca. 5% (cf. Fig. 7). The extent of the reduction is comparable for the two polymers (ca. 44%, at 20% SBH, for AF, and ca. 36% for UG). The tensile strength of LL/SBH blends follows a qualitatively similar trend. However, the TS lowering is definitely smaller for this PE sample (ca. 18%, at 20% SBH).

The elongation at break (EB) is plotted in Figure 8 as a function of the LCP content. It is noteworthy that none of the PE specimens displays a strong EB reduction upon addition of small (5%) amounts of SBH. However, for all of them, EB falls to very low values when the SBH concentration is increased to 20%. As already mentioned in the experimental section, the reproducibility of the measurements made on 90/10 blends was poor. This may be understandable because the 5–15% LCP range is that where

Table I Calorimetric Data of PE/SBH Blends

| AF/SBH	T_c (AF) (°C)	ΔH_c (J/gAF)	T_m (AF) (°C)	ΔH_m (J/gAF)
100/0	116.4	182.2	133.4	192.7
95/5	116.8	183.9	132.6	193.1
90/10	116.3	169.8	133.3	179.8
80/20	115.8	173.1	134.7	183.1
UG/SBH	T_c (UG) (°C)	ΔH_c (J/gUG)	T_m (UG) (°C)	ΔH_m (J/gUG)
100/0	114.9	166.1	138.7	172.5
95/5	115.1	167.3	138.6	167.4
90/10	114.7	162.5	139.3	160.8
80/20	114.3	157.7	142.5	162.3
LL/SBH	T_c (LL) (°C)	ΔH_c (J/gLL)	T_m (LL) (°C)	ΔH_m (J/gLL)
100/0	100.7	107.8	118.3	116.2
95/5	107.0	105.0	121.4	115.0
90/10	112.2	127.9	126.1	141.7
80/20	107.0	104.1	121.6	112.5
SBH 1 : 1 : 2	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
	213.4	6.2	229.6	6.3

Scanning rate 10°/min.
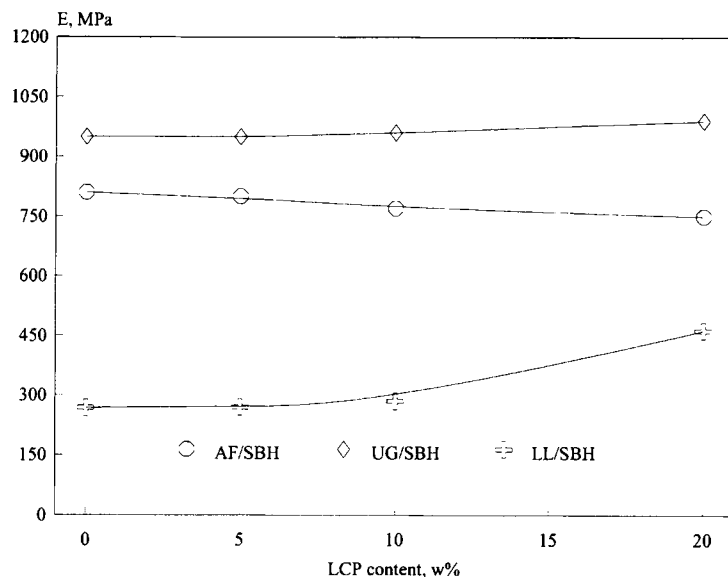
Figure 6   Tensile modulus of compression-molded slabs of AF/SBH, UG/SBH, and LL/SBH blends, vs. SBH content.

the strongest EB fall takes place. Among the three 90/10 blends, however, those based on LL and UG show the highest and, respectively, the lowest drawability.

The morphology of the blends was studied by scanning electron microscopy (SEM) on extrudates of ca. 3 mm diameter, fractured in liquid nitrogen. The micrographs of the AF/SBH blends are shown in Figure 9. They clearly show that the LCP represents the dispersed phase and that most LCP par-

ticles have spherical shape [Fig. 9(a), (c), (e)]. The dimensions of the spherical droplets increase markedly upon increasing the LCP content of the blends (0.5-2 μm, at 5% LCP; 0.5-5 μm, at 10% LCP; 1-25 μm at 20% LCP). On increasing the dimensions of the SBH particles, their shape changes and becomes progressively more irregular. As the micrographs in Figure 9(b), (d) and (f) demonstrate, larger LCP particles of irregular shape can be observed in addition to those described previ-
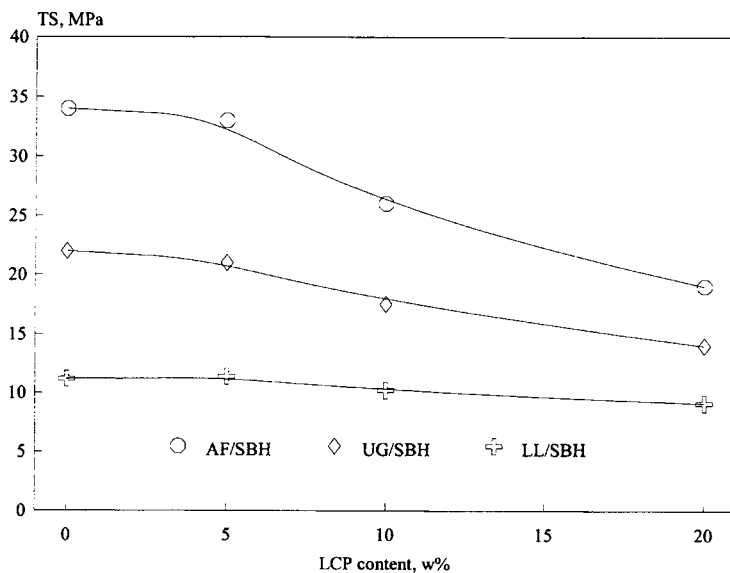
Figure 7   Tensile strength of compression-molded slabs of AF/SBH, UG/SBH, and LL/SBH blends, vs. SBH content.
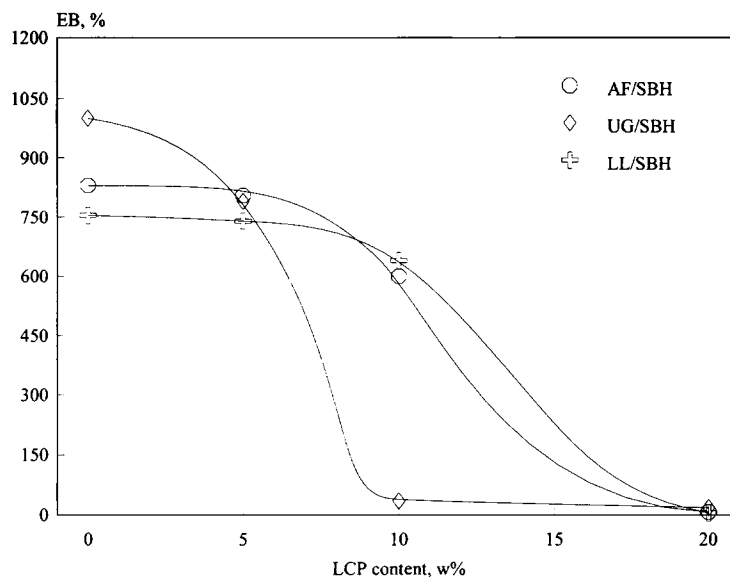
Figure 8 Elongation at break of compression-molded slabs of AF/SBH, UG/SBH, and LL/SBH blends, vs. SBH content.

ously. These larger particles are fairly rare in the 95/5 blend, and their size does not generally exceed ca. 15 μm [Fig. 9(b)]. On increasing the SBH concentration, both the population and the dimensions of these larger particles increase. An approximate estimation of the size distribution of the LCP particles in the 80/20 AF/SBH blend indicates that 50–70% of the LCP is present in the form of large (up to ca. 150 μm), irregular particles [Fig. 9(f)], whereas this proportion is of ca. 20% and 5% in the 90/10 and the 95/5 blends, respectively.

It may be concluded that, for the 95/5 blend, the SBH phase is dispersed in the AF matrix as fine, spherical droplets and that the size distribution of the latter is sufficiently narrow. In the 80/20 blend, on the contrary, the uniformity of LCP dispersion is very poor. An intermediate situation prevails for the 90/10 blend. Because the interphase adhesion is low for all PE/SBH blends, the observed dependence of morphology on SBH concentration can adequately explain the concomitant change of the deformability of these blends, as expressed by the EB vs. composition plots in Figure 8. In particular, the morphological characteristics of the 90/10 AF/SBH blends can satisfactorily account for the scarce reproducibility of the EB measurements.

The micrographs of the fracture surfaces of the UG/SBH blends are shown in Figure 10. It may be clearly seen that the morphology of these blends is qualitatively similar to that of the blends based on AF, as far as the effect of the LCP concentration on the droplets size and size distribution is concerned.

However, a comparison with the micrographs in Figure 9 shows that the average particle size is generally larger in the UG/SBH blends, especially in the low LCP concentration range. Moreover, for these blends, the concentration of the "larger" particles [cf. Fig. 10(b), (d) and (f)] is appreciably higher, thus showing that the distribution of the droplets dimensions is less uniform in the UG matrix. These features of the UG/SBH blends, with respect to the AF/SBH blends, may be ascribed to the lower molecular weight and lower viscosity of UG and can, in turn, explain the difference in the dependence of EB on LCP content for these two types of materials.

A general conclusion that can be drawn from the observation of the micrographs shown in Figures 9 and 10 is that the blends of HDPE with SBH, independent of the molecular weight of the matrix (at least in the range investigated), display scarce propensity to attain a morphology with well elongated LCP particles. In fact, although the processing conditions adopted in this work (extrusion through a die of 3 mm diameter, with no melt drawing) are certainly not the best ones in view of the fibrillation of the dispersed LCP phase, the same procedure was actually found to induce sufficient elongation of the LCP droplets in other LCP/polymer blends.[1] Since, as it is shown in Figures 2–4, the viscosity of SBH is appreciably lower than those of all PE samples investigated, the LCP particles are expected to undergo some elongation in the converging zone at the inlet of the extrusion die. However, they probably
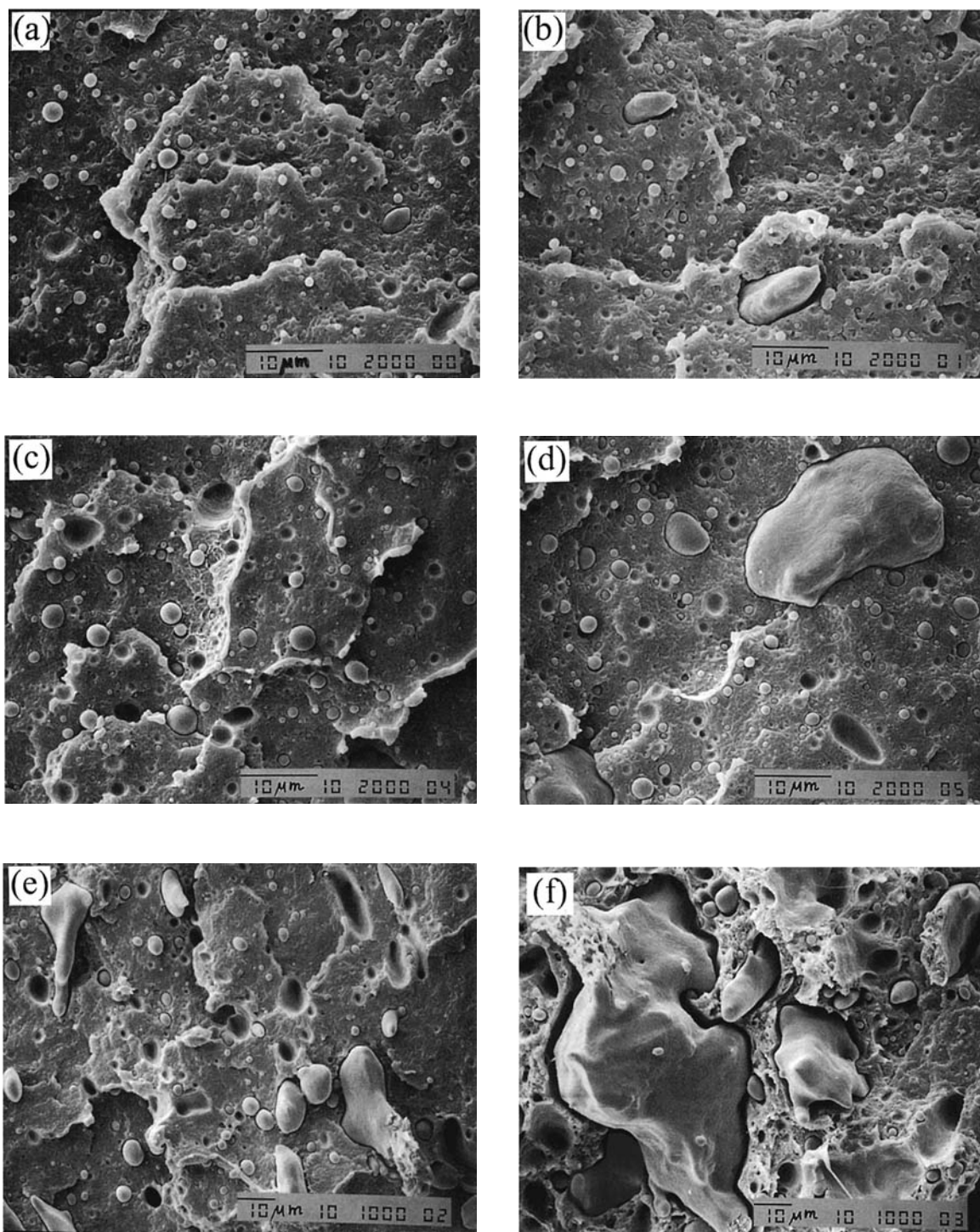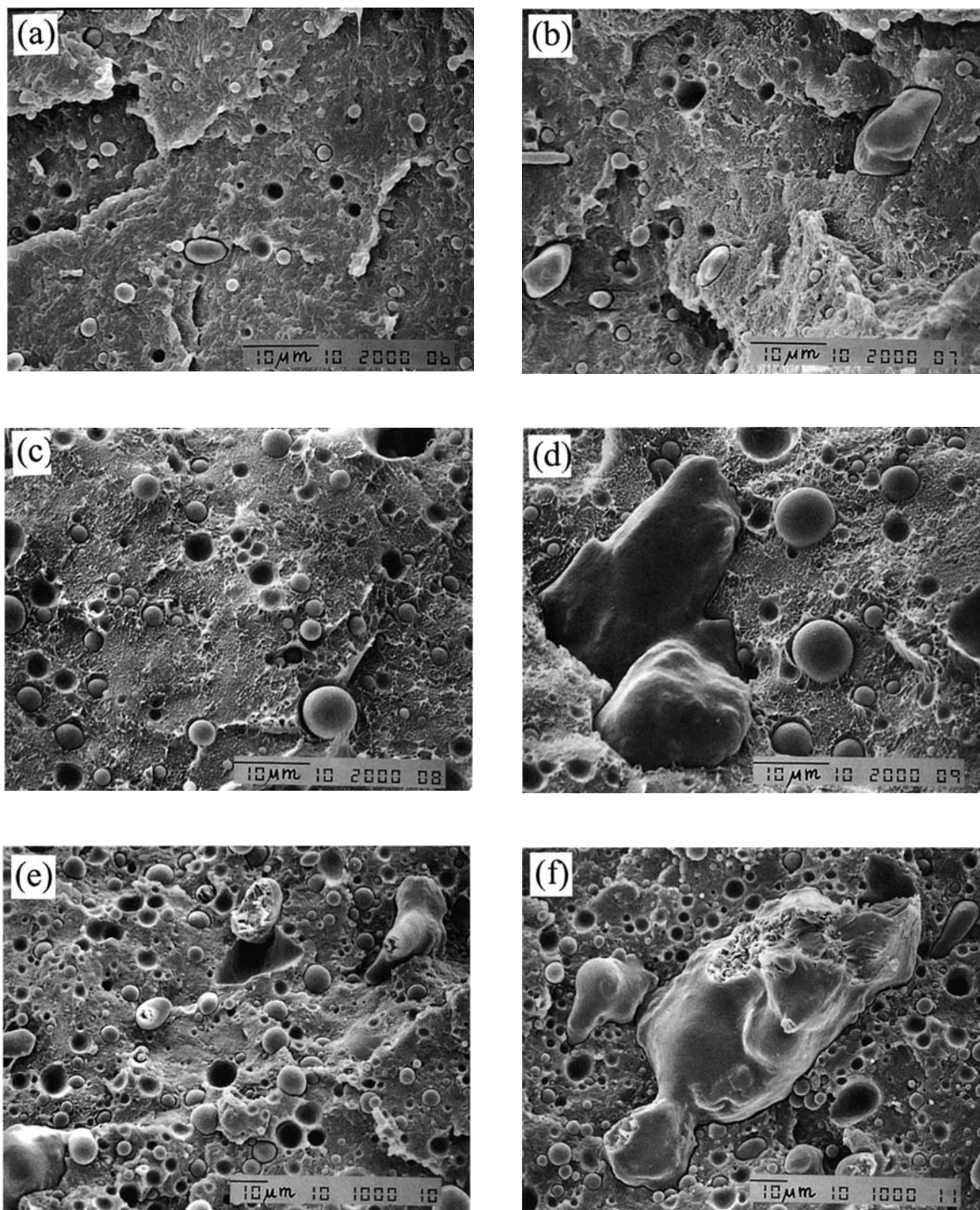
Figure 9 SEM micrographs of the fractured surfaces of AF/SBH extruded threads: (a) 95/5; (b) rare zones of 95/5; (c) 90/10; (d) some zones of 90/10; (e) 80/20; (f) several zones of 80/20.

relax and coalesce into large domains of irregular shape, or break into smaller spherical droplets within the die and/or at the die exit. The relatively low relaxation time of the semiflexible LCP used in this work, as compared to wholly aromatic LCPs, probably helps this shape rearrangement. This

Figure 10   SEM micrographs of the fractured surfaces of UG/SBH extruded threads:
(a) 95/5; (b) few zones of 95/5; (c) 90/10; (d) several zones of 90/10; (e) 80/20; (f) many
zones of 80/20.

mechanism seems to account either for the absence of fibrils and for the presence of both small spherical droplets and large LCP particles in the specimens used for SEM examination. The fact that the population of large domains was found to increase with the LCP concentration seems to agree with the view

that these domains are formed by the coalescence of smaller particles.

The morphology of the LL/SBH blends displays some interesting differences, with respect to those of the HDPE/SBH blends discussed above. First of all, no LCP domain with abnormally large dimensions was found in these blends (Fig. 11). This means that the tendency of the SBH particles to coalesce is lowered when the matrix is LL. With this polymer, therefore, a much better dispersion of LCP droplets is obtained, and their size distribution is considerably narrower. Another important difference is that, whereas the smaller LCP particles (0.5–3 μm) still have a spherical shape, the larger ones (ca. 10 μm), which are visible in the 80/20 blend [Fig. 11(c)], are elongated into ellipsoids or filaments, some of which appear fractured. The reason for the different morphology of LL/SBH blends, with respect to those of HDPE/SBH blends, is certainly to be attributed to differences between the

phase interactions of the two systems, because both the processing conditions and the viscosity ratios are similar.

On the basis of the experimental results obtained in this work, it may be concluded that the phase interactions in LL/SBH blends are more efficient than in either AF/SBH and UG/SBH blends, and that the surface tension of the SBH particles is lower if the latter are dispersed in an LL matrix. The information obtained by calorimetry, as well as that provided by the mechanical testing, appears in agreement with this conclusion.

A comparison of the behavior of the blends studied in this work with that of blends of PE with wholly aromatic LCPs is not easy. On the other hand, the latter blends require much higher processing temperatures (> ca. 280°C), and this difference may hamper a safe comparison. Moreover, the literature information on these blends is rather limited and, to some extent, contradictory. In fact, Hsu, Lichkus,
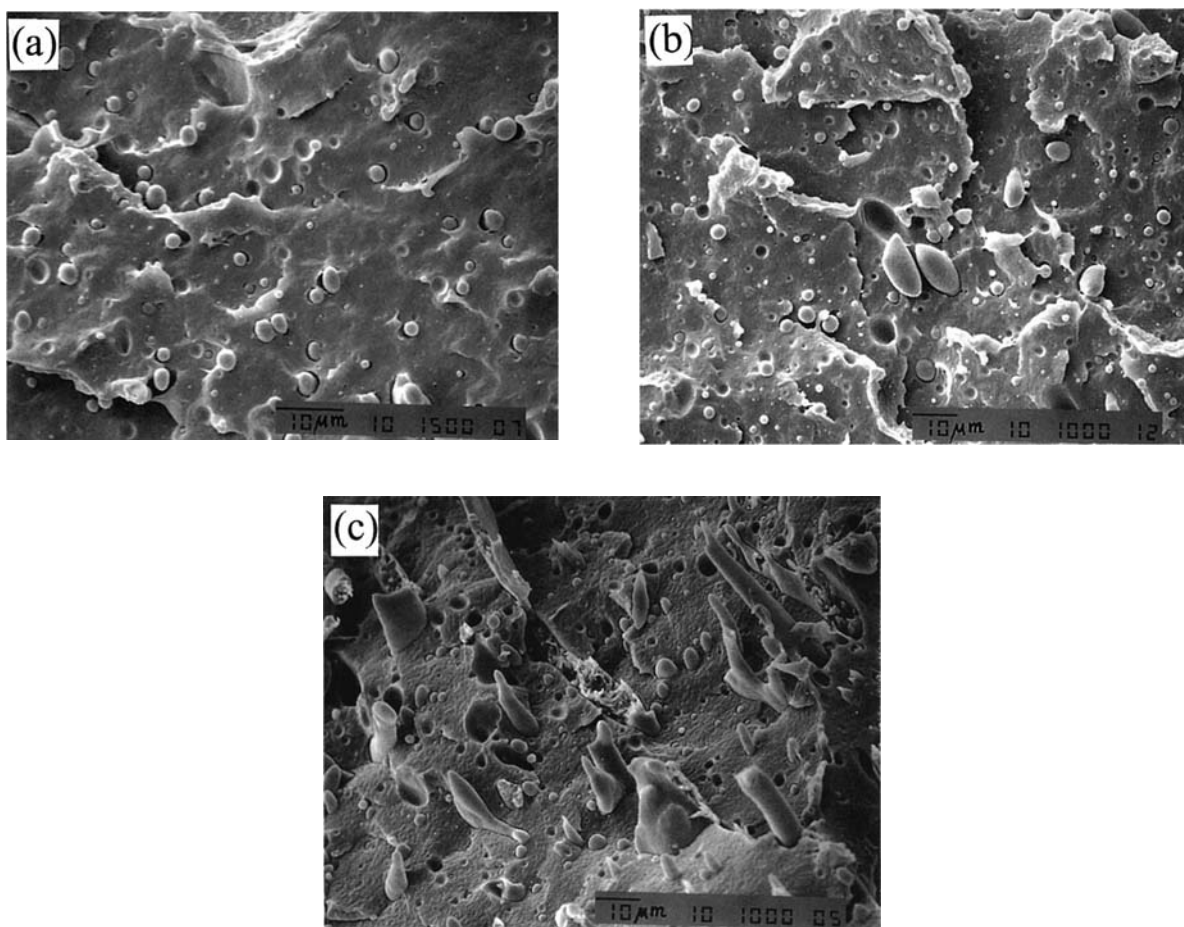
Figure 11 SEM micrographs of the fractured surfaces of LL/SBH extruded threads: (a) 95/5; (b) 90/10; (c) 80/20.

and Harrison,[5] who used a low melting (210–230°C) experimental wholly aromatic LCP of the Vectra series (Hoechst–Celanese), with undisclosed composition, found that the dispersion and the elongation of the LCP particles in blown PE films were very limited, and that, therefore, the modulus enhancement was much lower than expected. Moreover, the use of an ethylene–methacrylic acid copolymer as compatibilizer failed to improve the results.

On the other hand, Harada et al.[3] found that the blends of a HDPE sample with Vectra-A950 (a wholly aromatic copolyester supplied by Polyplastics Co.) show good fibrillation of the LCP in both extruded and injection molded specimens. However, even for these PE/LCP blends having the desired morphology, the measured mechanical properties were found to increase appreciably only for LCP contents of 30% or more.

CONCLUSION

The results of our preliminary investigation demonstrate that the use of a semiflexible LCP such as SBH 1:1:2 allows one to process the PE/LCP blends without changing the conditions commonly used to process neat PE. For all PE samples considered, a fairly strong processing-aid effect of the LCP was demonstrated. Although the interphase adhesion was always found to be poor, it was shown that some kind of phase interaction takes place between SBH and LLDPE. The crystallization temperature of the latter polymer was found to increase by ca. 10°C upon addition of SBH, thus indicating that this LCP may act as a nucleating agent for LLDPE. Moreover, the LL/SBH blends were shown to be characterized by good and fairly uniform dispersion of the LCP particles, and their mechanical properties were slightly improved by an increase of the SBH content. On the contrary, poor dispersion of the LCP and, as a consequence, inadequate reinforcing effect was observed with both HDPE specimens. Further investigation is being carried out on the crystallization behavior of LL/SBH blends, as well as on the morphology and the properties of blend specimens prepared under elongational flow conditions.

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