Synthesis and Characterization of a PE-g-LCP Copolymer

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SYNOPSIS

The possibility of reinforcing polyethylene (PE) by blending it with a liquid crystalline polymer (LCP) rests on the successful improvement of phase compatibility and interfacial adhesion of these two structurally unlike polymers. The approach that is being considered in our laboratories consists of the synthesis of PE–LCP block or graft copolymers and of their use as compatibilizing agents for PE/LCP blends. In this work, the melt polycondensation of sebacic acid (S), 4,4'-dihydroxybiphenyl (B), and 4-hydroxybenzoic acid (H) has been carried out at temperatures up to 280°C in the presence of an oxidized low molar mass PE sample containing free carboxylic groups (PEox), with the main scope of demonstrating that a PE-g-LCP copolymer may be synthesized by this route. The polycondensation product has been fractionated by successive extractions with boiling toluene and xylene. The soluble fractions and the residues have been characterized by IR and NMR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TG, DTG), and scanning electron microscopy (SEM). The extractions and the analyses have been repeated on a PEox/LCP blend prepared by melt mixing PEox and preformed LCP (SBH 112, by Eniricerche). The results show that, whereas for the blend a fairly clean separation of PEox and SBH can be obtained by solvent extraction, this is not so for the polycondensation product. All analytical procedures concordantly show that a PEox-g-SBH copolymer has, in fact, been obtained. In effect, both PEox and SBH chain segments are present, with different relative ratios, in all fractions of the polycondensate. Moreover, a fairly quantitative esterification of the PEox carboxyl groups has been shown by IR analysis to take place in the adopted conditions. Preliminary morphological investigations carried out by SEM have shown that the addition of the synthesized graft copolymer into HDPE/SBH blends leads to an improvement of the interfacial adhesion. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Among polymer blends, those of flexible thermoplastics with relatively small amounts of liquid crystalline polymers (LCPs) are attracting ever increasing attention in industrial and academic laboratories because the LCP minor phase can, in principle, impart some of its remarkable qualities to the host resin.[1–3] However, the well-known advantages of the addition of 5–10% (w/w) of LCP into a flexible

matrix polymer, for instance, reduction of melt viscosity and mechanical reinforcement, depend strongly on morphology, which is, in turn, determined by a number of features connected with the nature of the blend components, such as miscibility, phase compatibility, interfacial adhesion, relative viscosity, etc. Very good mechanical properties have been reported for composites prepared by blending several thermoplastics with LCPs, when partial miscibility exists[4] and, on occasion, where they are not miscible or compatible.[5] Unfortunately, the majority of the available commercial thermoplastics are incompatible with common, wholly aromatic LCPs. Thus, mismatch of processing windows, poor dis-

persion, inadequate interfacial adhesion, and small elongation of the dispersed LCP droplets make, in many cases, the reinforcing effect of LCPs appreciably lower than expected from the law of mixtures.[6-8]

The addition of compatibilizing agents into intrinsically immiscible polymer blends can mean a substantial help for solving the problems of poor dispersion and low adhesion. Among the substances displaying compatibilizing activity, block or graft copolymers made up of chain segments having chemical structure and/or solubility parameters similar to those of the polymers being blended are most promising.

For the particular case of polyolefin/LCP blends, considerable modulus enhancements can be anticipated, on the basis of the Tsai-Halpin model, as a result of the addition of modest amounts of an LCP into, for example, polyethylene (PE)[9] or polypropylene (PP). However, the affinity of the latter polyolefins with thermotropic aromatic copolyesters or copolyesteramides is generally too low to grant adequate compatibility. And, in fact, the reinforcement of PP with different LCPs has normally led to blends with no improvement in the tensile strength, although some modulus enhancements were sometimes observed.[10-12] For these PP/LCP blends, the use of compatibilizers consisting of maleic–anhydride-grafted PP or of an ethylene-based reactive terpolymer was recently shown to play a positive effect on phase dispersion and adhesion and, thereby, on the mechanical properties of injection molded articles.[13-15] As for the blends of PE and LCPs, the few studies carried out so far on these systems[9,16-21] confirm that the poor compatibility of the two polymers, coupled with the strong differences between their melting/processing temperatures, prevents the attainment of good morphologies and enhanced mechanical properties. Slightly better results were found by some of us[19,21] by blending linear low density polyethylene (LLDPE) with a semiflexible liquid crystalline polymer: SBH 112 by Eniricerche, Milan, synthesized from sebacic acid (S), 4,4'-dihydroxybiphenyl (B), and 4-hydroxybenzoic acid (H) in the mole ratio 1 : 1 : 2. For these blends, the phase dispersion was good and the size distribution of the LCP droplets was fairly narrow. Moreover, the LCP phase was shown to play a nucleating effect for the crystallization of the LLDPE matrix. The mechanical characterization showed no reduction of the tensile strength and a 50% modulus increase over the LCP concentration range 0–20%, whereas the elongation to break decreased markedly only for SBH contents higher than 10%.[21] This re-

sult was attributed to a slightly better compatibility of LLDPE with this semiaromatic LCP. It is remarkable that, for blends of LLDPE with a low-melting wholly aromatic LCP, Harrison and coworkers failed to observe significant effects on elastic modulus and morphological characteristics by the use of compatibilizers such as ethylene-methacrylic acid copolymer and maleic–anhydride-grafted PE.[9,17,18]

The research project that is being carried out in our laboratories is aimed at the synthesis of block or graft PE–LCP copolymers and their use as compatibilizers for PE/LCP blends. Although some of the compatibilizers used to improve the performance of polyolefin/LCP blends were thought to become chemically bonded to one of the components,[22] no previous attempt was made, to our knowledge, at the synthesis of polyolefin–LCP block or graft copolymers. In a recent work,[23] the synthesis of a block copolymer, poly(butylene terephthalate-co-olefin), carried out by the condensation of terephthaloyl chloride, 1,4-butanediol and hydrogenated α,ω-dihydroxy polybutadiene with $M_n \sim 2000$, has been described. Surprisingly, the synthesis of this copolymer was not successful when performed by melt transesterification. Exploratory investigations carried out in our laboratories have shown that the transesterification involving high molar mass functionalized polyolefins and LCP monomers may be frustrated by slow diffusion processes.[24] For this reason, in this work, we choosed a fairly low molar mass PE sample ($M_w \approx 10,000$), with ca. 5 carboxylic groups per macromolecule, as the functionalized PE, the main scope of the study being that of proving that the synthesis of a PE-g-LCP copolymer may actually be accomplished by the melt transesterification procedure. Even if the compatibilizing ability of the resulting copolymer is expected to be poor, due to the low molar mass of the PE backbone, we felt that this study might be useful in view of future investigations to be carried out with higher molar mass functionalized polyolefins.

EXPERIMENTAL

Materials

The functionalized PE sample was supplied by Aldrich (cat. No. 19,192-2). This oxidized PE has an acid number of 28 mg KOH/g and a molar mass of ca. 10,000, which correspond to approximately 5 carboxylic groups per mol. This material is referred to hereinafter as PEox.

Sebacic acid (S), 4,4'-dihydroxybiphenyl (B) and 4-hydroxybenzoic acid (H), were supplied by Merck, Schuchardt, and Aldrich, and were used without further purification. For the polymer synthesis, the hydroxylated monomers B and H were used in the acetylated form. The acetylation was made with acetic anhydride and the products were purified by crystallization, as described elsewhere.[25]

The LCP was a laboratory sample (LCP1B/024) of SBH 112, kindly supplied by Eniricerche SpA, Milan. This copolyester was synthesized as described before.[25] Its inherent viscosity, 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.

A sample of an injection molding grade (A-1100) of high density PE (HDPE) was kindly supplied by Solvay & C.ie. The MFI of this sample was 10 g/min (230°C, 2.16 kg).

Spectroscopically pure toluene and xylene were used for the extraction experiments.

Synthesis of the PE-g-SBH Copolymer

The copolymer synthesis was performed in a pyrex reactor equipped with a stainless steel stirrer and connected to a vacuum line. The amounts of PEox and SBH monomers were calculated for the synthesis of ca. 30 g PE-g-SBH copolymer (50/50 w/w). The reagents were introduced into the reactor as a powder blend, together with a small amount of sodium acetate. The reactor was closed, purged with pure nitrogen, and immersed in a salt bath preheated to ca. 220°C. The SBH monomers melted at this temperature and gave rise to a clear low viscosity liquid, when used alone. In the presence of PEox, the mixture was a translucent liquid of higher viscosity, thus showing that molten PEox was homogeneously dispersed in the monomer mixture. The first stage of reaction was carried out under nitrogen atmosphere by stirring the mixture and gradually increasing the temperature of the bath to 280°C over a 3.5 h period. The temperature was not allowed to exceed the above value, contrary to the usual procedure for the synthesis of neat SBH,[25] in order to avoid the degradation of PEox. Byproduct acetic acid was distilled off, starting from ca. 250°C, and was condensed in a trap cooled with liquid nitrogen. The reaction mixture became increasingly opaque and viscous as long as acetic acid was distilled off. The polycondensation was completed under reduced pressure (ca. 0.01 mm Hg) for an additional 1 h period. This treatment led to the final evolution of acetic acid and other low molar mass substances that

sublimed on the reactor cover. At the end of the polycondensation, pure nitrogen was admitted to the reactor and the latter was opened under nitrogen blanket. The polymer was extracted with a stainless steel spoon while hot, and was then cooled and milled. The powder was finally washed with boiling acetone in order to extract any low molar mass compounds.

A 50/50 PEox/SBH blend was prepared in a Brabender apparatus equipped with a 30 mL mixing head, at 240°C and 100 rpm for 6 min.

80/20 HDPE/SBH blends were also prepared with the same technique, either with or without addition of 2.5, 5, or 8% (w/w) of the synthesized copolymer, in order to assess the compatibilizing effect of the latter.

Polymer Fractionation

Solvent extractions were made in Kumagawa apparatuses by introducing 3 g specimens of the powdered polymers in a thimble and extracting them with ca. 250 mL of refluxing solvent for 24–36 h. At the end of this period, the residual powder was washed with hot pure solvent and dried. The combined solutions were allowed to cool and the crystallized solid was separated by centrifugation. The residual solution was then concentrated by gentle heating and poured into excess methanol. The precipitate was filtered off, washed, and dried. The residue of the extraction with boiling toluene was again extracted with xylene by the same procedure.

Characterization

Infrared spectra of the copolymer, of the blend, and of their fractions were recorded on a Bio-Rad Win IR spectrometer. The specimens were in the form of KBr pellets because it was difficult, with some of the fractions, to prepare films with even thickness by hot molding or solution casting.

High-resolution solid-state ^{13}C NMR measurements were performed at 20°C on a Varian VXR 300 spectrometer operating at the ^{1}H resonance frequency of 300 MHz and the ^{13}C resonance frequency of 75 MHz. Hartmann–Hahn spin lock crosspolarization (CP) along with dipolar decoupling (DD) and magic angle sample spinning were used to obtain ^{13}C spectra from the solid state. The sample spinning at magic angle was carried out at 4000–5000 Hz in a Doty Scientific Co. (Columbia, SC) solids NMR probe. Powder specimens of ca. 200 mg were pressed into Macor rotors with Kel-F end caps. For all materials studied, 500–1000 scans were accumulated

with 3–10 s delay between pulse sequence repetitions. Chemical shifts relative to tetramethylsilane (TMS) were determined from the aromatic carbons line (132.1 ppm) of hexamethylbenzene (HMB) standard.

Spin lattice relaxation times for protons, T_1^H, were obtained at 20°C from a $180°$-τ-$90°$ pulse sequence followed by simultaneous 0.5 ms ^{13}C and ^{1}H spin lock and then acquisition of the ^{13}C magnetization with ^{1}H 50 kHz decoupling.

DSC measurements were carried out on a Perkin–Elmer DSC-7 apparatus, in argon atmosphere, using heating/cooling rates of 10°/min. Powder samples of ca. 10 mg were used. The base lines of the PE melting peaks were drawn from 70°C to the end of the transition; those of the PE crystallization peaks were back drawn from the beginning of the process to 50°C.

The TG and DTG curves of the samples were obtained on a TGS-2 Perkin–Elmer apparatus with a heating rate of 5°/min, under nitrogen.

The SEM observations were carried out on JEOL 550 and T300 electron microscopes. The compact specimens prepared by polycondensation and melt blending were fractured under liquid nitrogen, whereas the fractions prepared by solvent extraction were analyzed in the powder form.

RESULTS AND DISCUSSION

Copolymer Synthesis and Fractionation

The acidolysis reactions involved in the copolymer synthesis are schematically shown in Figure 1. As pointed out in the Experimental section, the amounts of the reagents were calculated in view of the production of a 50/50 (w/w) PEox-SBH copolymer. In principle, the formation of polyester cross bridges linking different PEox chains might be expected. However, no indication of appreciable crosslinking was observed under the reaction conditions used in this work. The yield of the crude copolymer was ca. 90% of theory and showed no difference with respect to that obtained for the synthesis of neat SBH.

The polycondensation product and the physical blend, hereinafter referred to as COP and MIX, respectively, were fractionated with PE solvents with increasing solubility parameters and boiling points, in order to gain information on the presence of a true copolymer in the different fractions. In fact, because SBH is known to be insoluble in aromatic hydrocarbons,[25] the presence of SBH segments in
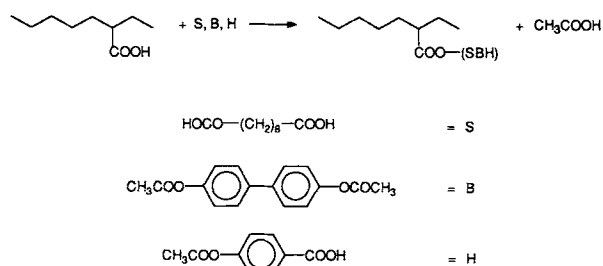

Figure 1 Reaction scheme.

the soluble fractions of COP would be a strong confirmation that SBH branches were actually grafted onto PEox. Moreover, because boiling toluene and xylene are powerful solvents for PEox, the presence of PE segments in the insoluble fractions would be additional confirmation of the presence of chemical bonds linking the two components.

The masses of the different fractions obtained from COP and MIX by solvent extraction are presented in Table I. It may be seen that no appreciable difference could be found between the two materials from the point of view of the masses of the different fractions. The characterization of the latter and the determination of their composition was done by a variety of techniques in order to get information on the structure of the polymers at molecular and supermolecular level.

IR Study

A FTIR investigation of MIX, COP, and their fractions allowed us to demonstrate that the carboxylic groups of PEox did, in fact, take part in the polycondensation reaction. The IR spectrum of MIX contains all bands characteristic for either component with no change in their position. This was expected because MIX is a mechanical blend of PEox and SBH. However, a small difference was noticed between the IR spectrum of MIX and the sum spectrum of PEox and SBH, in the carbonyl absorption region. In fact, the former spectrum displays a shoulder at ca. 1750 cm^{-1}, which is absent in the sum spectrum of the components. This might be taken as an indication that some kind of interaction between PEox and SBH occurs as a result of high temperature mixing in the Brabender.

The IR spectrum of COP differs from that of MIX, especially in the carbonyl group region (1500–1850 cm^{-1}), as it is shown in Figure 2, where the spectra of neat PEox and SBH are also shown for comparison together with that of the RXC fraction to be discussed later. The band of the stretching

Table I   Solvent Fractionation Data for the PEox/SBH Blend and the PEox-*g*-SBH Copolymer

Sample	Sample Code	Mass (g)	Mass (%)
PEox/SBH 50/50 blend	MIX	3.118	100
Acetone soluble	—	0.081	2.6
Toluene soluble	—	1.321	42.3
Idem, crystallized	CRM	1.110	35.6
Idem, precipitated	NCM	0.211	6.7
Xylene soluble	SXM	0.036	1.1
Xylene insoluble	RXM	1.680	53.9
PEox-*g*-SBH 50/50 copolymer	COP	3.123	100
Acetone soluble	—	0.040	1.3
Toluene soluble	—	1.231	39.4
Idem, crystallized	CRC	1.076	34.4
Idem, precipitated	NCC	0.155	5.0
Xylene soluble	SXC	0.179	5.7
Xylene insoluble	RXC	1.673	53.6

vibrations of the carbonyl groups of MIX is broad and displays many peaks and shoulders. The secondary peak at 1713 cm^{-1} coincides with the main absorption peak of pure PEox; whereas that at about 1734 cm^{-1} corresponds to the strongest absorbance of pure SBH. In the spectrum of COP, on the contrary, the peak at ca. 1713 cm^{-1} is practically absent.

Moreover, for COP, in addition to the maximum of absorbance at 1734 cm^{-1}, another maximum is observed at 1761 cm^{-1}, whereas this was only a shoulder of the main 1734 cm^{-1} absorbance for neat SBH. Because these two bands are characteristic for the carbonyls of the ester groups of aliphatic (1761 cm^{-1}) and aromatic (1734 cm^{-1}) acids, respectively, it can
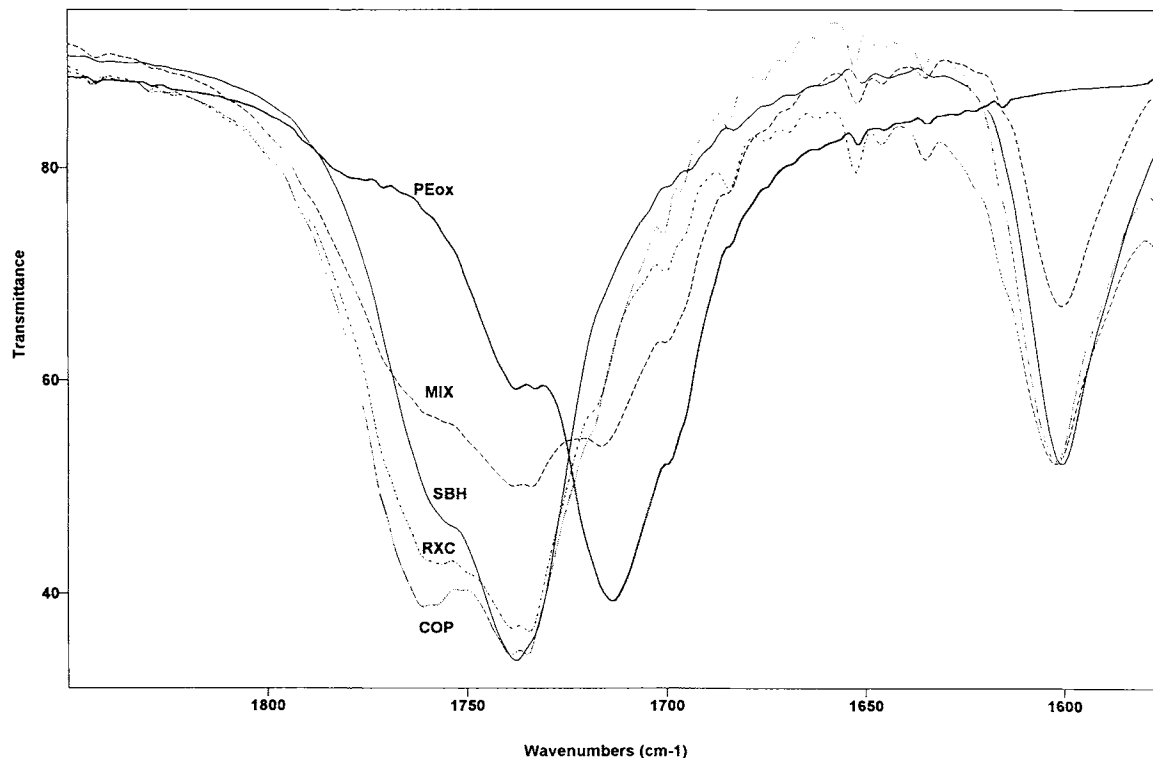
Figure 2   FTIR spectra of PEox, SBH, MIX, COP, and RXC in the 1850–1575 cm^{-1} region (Res. = 2 cm^{-1}; N. of scans: 32).

be concluded that there is a relatively higher concentration of aliphatic ester groups in COP than in SBH and MIX. A detailed discussion of the FTIR spectra of these materials will be given in a forthcoming article. However, the above observations demonstrate clearly that the carboxylic groups of PEox do enter into acidolysis reactions during the polycondensation carried out with the procedure used in this work.

The FTIR spectra of the different fractions of MIX and COP confirm the above conclusion. The spectra of the toluene soluble fractions of MIX (CRM and NCM) and COP (CRC and NCC) are shown in Figure 3. The spectra of CRM and NCM are practically indistinguishable from that of pure PEox. On the contrary, the spectra of CRC and NCC display bands characteristic of the SBH component, such as the band of aromatic rings at 1602 cm^{-1}. Moreover, a comparison of the carbonyl group absorption bands of CRC and NCC with that of COP shows that they are qualitatively similar and that, on a quantitative ground, the relative content of aromatic ester groups in CRC and NCC is lower than in COP. These data demonstrate that the toluene extraction of MIX leads to the solution of practically

pure PEox, whereas that of COP causes the solution of a PE-rich PE-g-SBH copolymer.

The IR spectrum of the xylene insoluble fraction of COP (RXC) (cf. Fig. 2) demonstrates that the relative concentration of aromatic ester groups is higher in this fraction than in COP, but it is still appreciably lower than in pure SBH. This shows that, even in this fraction, there are additional aliphatic ester bonds formed by the reaction of PEox with the SBH monomers.

All the IR informations agree with the assumption that, during the polycondensation reaction, copolymers with different relative content of PE and SBH branches are formed, either because of the different number of carboxylic groups of PEox entering the transesterification, or because of the different length of the grafted SBH branches. These copolymers dissolve to a different extent into the solvents used for fractionation, depending on their relative content of PE and SBH segments.

¹³C NMR Study

In Figure 4, the ¹³C NMR spectra of SBH, PEox, and RXC are presented. It may be seen from these
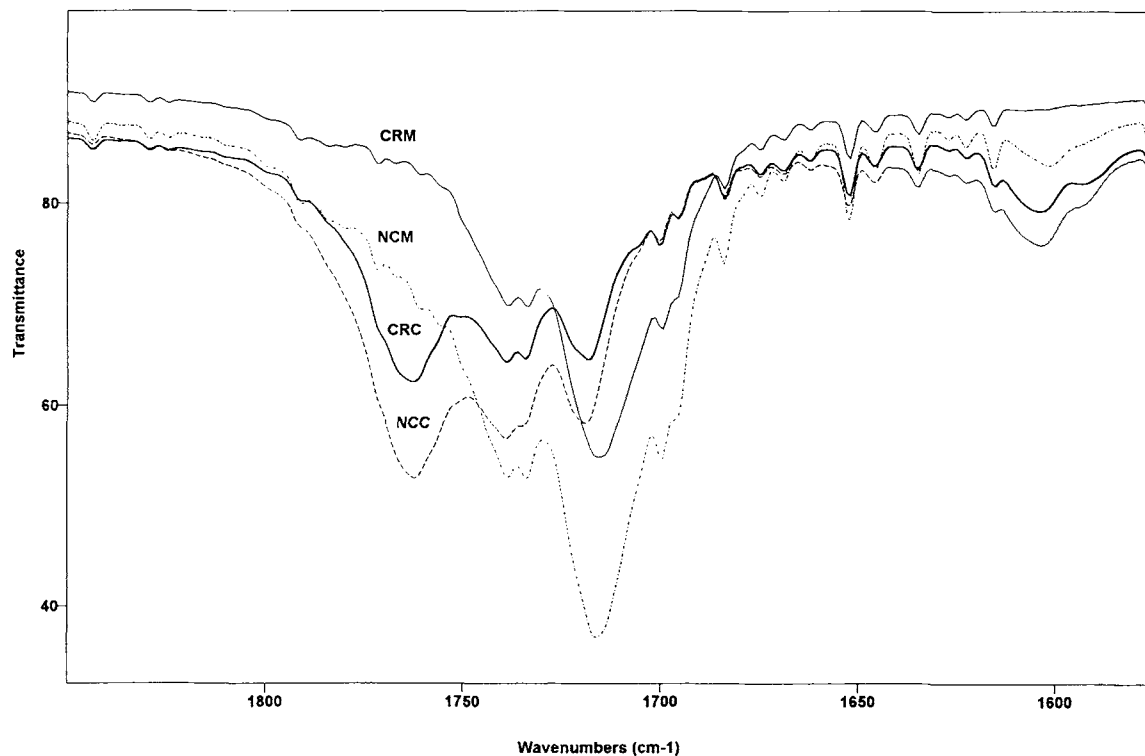
Figure 3 FTIR spectra of CRM, CRC, NCM, and NCC in the 1850–1575 cm^{-1} region (Res. = 2 cm^{-1}; N. of scans: 32).
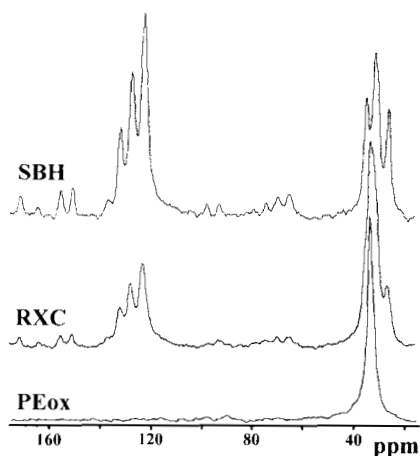
Figure 4 ¹³C NMR spectra of SBH, PEox, and RXC.

spectra that the aliphatic carbons of SBH give rise to resonances at 34.5, 31.0, and 25.8 ppm, whereas the methylene carbons resonance of PEox appears at 32.5 ppm. In the spectrum of RXC, the band of the PE-component at 32.5 ppm is clearly seen. This means that the insoluble fraction of COP contains significant amounts of PE chains. The presence of PE chains in a polymer sample having undergone two long-term extractions with toluene and xylene can only be interpreted through the presence of chemical bonds linking them to SBH segments.

The averaged values of the spin-lattice relaxation times for protons are shown in Figure 5. According to the linear additivity model, the relaxivity of a

blend should be intermediate between those of the components. This is, in fact, so for MIX, whose relaxation time (1.4 s) is lower than that of PEox and higher than that of SBH. The situation with COP is completely different: its relaxation (0.5 s) is faster than for either of the components. Nonadditivity can arise from any motional and/or conformational changes imposed by copolymerization; in both events such behavior may be attributed to the contact of the two components on a dimensional scale of several hundreds of Ångstroms.

DSC Measurements

The DSC traces of PEox, recorded with a scanning rate of 10°/min, show an asymmetric first-order transition peak with an enthalpy change of ca. 200 J/g. The temperatures of fusion and crystallization are of ca. 135 and 115°C, respectively. The thermal behavior of neat SBH is characterized by low-enthalpy ($\sim$ 6 J/g) crystal$\leftrightarrow$nematic transitions at ca. 230°C (heating), and 217°C (cooling)]. The endotherms/exotherms associated with this transition were hardly identifiable in the DSC traces of some of the fractions of COP and MIX, due to their relatively small ΔH value. For this reason, the DSC analysis was generally limited to a study of the transitions connected with the PE phase. The calorimetric data are collected in Table II.

The DSC results show that, after extraction with toluene and xylene, MIX gives rise to a residue
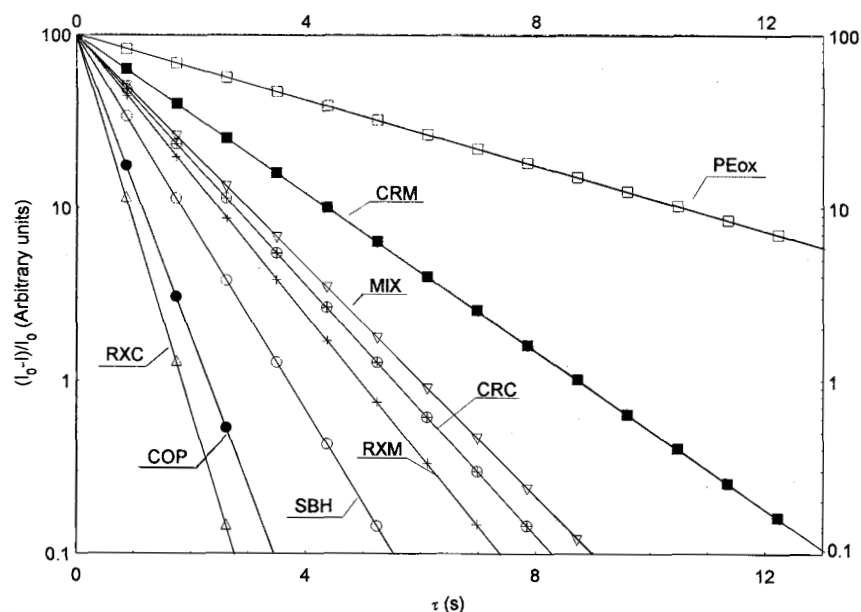
Figure 5 Proton spin-lattice relaxation times T_1^H for the studied samples (PEox, 4.6 s; CRM, 1.9 s; MIX, 1.4 s; CRC, 1.2 s; RXM, 1.1 s; SBH, 0.8 s; COP, 0.5 s; RXC, 0.4 s).

Table II   Temperatures and Enthalpies of Transition of the PE Phase of the Studied Materials

Sample	First Heating		First Cooling		Second Heating	
	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PEox	136.8	232.5	113.5	203.7	132.6	195.9
MIX	132.0	91.0	115.1	87.3	131.0	90.3
CRM	133.1	208.7	114.1	217.6	133.6	202.4
NCM	130.4	183.3	114.1	186.6	131.1	186.1
RXM	—	—	—	—	—	—
COP	127.9	81.7	107.4	82.4	126.5	81.0
CRC	129.3	190.4	108.2	167.9	128.6	172.4
NCC	127.6	148.3	107.0	137.0	126.6	127.7
RXC	124.7	35.8	105.0	29.4	120.1	26.7

(RXM) that does not contain DSC-detectable PE segments. This means that all PEox added into MIX is physically blended with SBH, and can easily be separated again by toluene extraction (it can be noticed from Table I that practically all PEox present in MIX is extracted by toluene: the amount subsequently dissolved into xylene as SXM, is, in fact, very small). It is noteworthy that the DSC characteristics of CRM practically coincide with those of pure PEox and are typical for polyethylene crystallized from solution.

The thermal properties of the COP fractions confirm that a PE phase is present in all of them, including RXC. The fusion temperature Tm of this phase is distinctly lower for the COP fractions than for the corresponding fractions of MIX (the comparison cannot be made with RXM, of course, because its PE content is practically zero). It is also interesting that Tm is progressively reduced along the series from CRC to RXC (cf. Table II), and that an even stronger reduction is concurrently found for the relevant enthalpies ΔHm and ΔHc. The latter can obviously be used to get an estimate of the COP fractions composition. This will be discussed later (cf. Table IV). All these findings are circumstantial evidence confirming the conclusion of the IR investigation. In fact, it is reasonable to assume that, for a PE-g-SBH copolymer, the temperature and the enthalpy of the transition associated with the PE phase are higher the fewer (and/or the shorter) are the SBH branches in the copolymer, and, therefore, the higher is the solubility in toluene and xylene. Conversely, Tm and ΔHm will be lower, the shorter the PE chains, and the higher is the relative content of SBH segments, and, therefore, the lower is the solubility.

It is also noteworthy that the temperatures of the crystal↔nematic transition of the SBH phase, when they could be measured confidently, corresponded to that of neat SBH only for RXM, whereas COP and its fractions showed lower values, thus providing further evidence in favour of copolymerization.

SEM Observations

The morphology of MIX, COP, and their fractions was investigated by SEM (Fig. 6). The micrograph of the fracture surface of MIX [Fig. 6(a)] clearly shows the biphasic morphology typical for a blend of immiscible polymers. The phase dispersion is neither fine nor uniform. The micrograph shown in Figure 6(a) displays SBH droplets of ca. 150 μm diameter in a PEox matrix. The morphology of COP is also uneven: Figure 6(b) and (c) show two zones of the fracture surface of this material. In Figure 6(b), a clear two-phase structure is observed: a distinctly fibrous phase appears dispersed as particles of various dimensions (0.2–20 μm) into an apparently homogeneous matrix. The larger fibrous particles are elongated and fractured [right hand side, Fig. 6(b)], thus showing that the interfacial adhesion is higher in COP than in MIX. The micrograph in Figure 6(c) shows that in this region of the specimen the biphasic character is much less clear: the fibrous appearance of the matrix is not as distinct as it is expected for typical LCPs, and, whereas some of the dispersed droplets appear free on the fracture surface, others are tightly bonded into the matrix. Despite the unevenness of the morphology of both MIX and COP, it can be safely concluded that MIX is made up of two cleanly separated phases poorly dis-
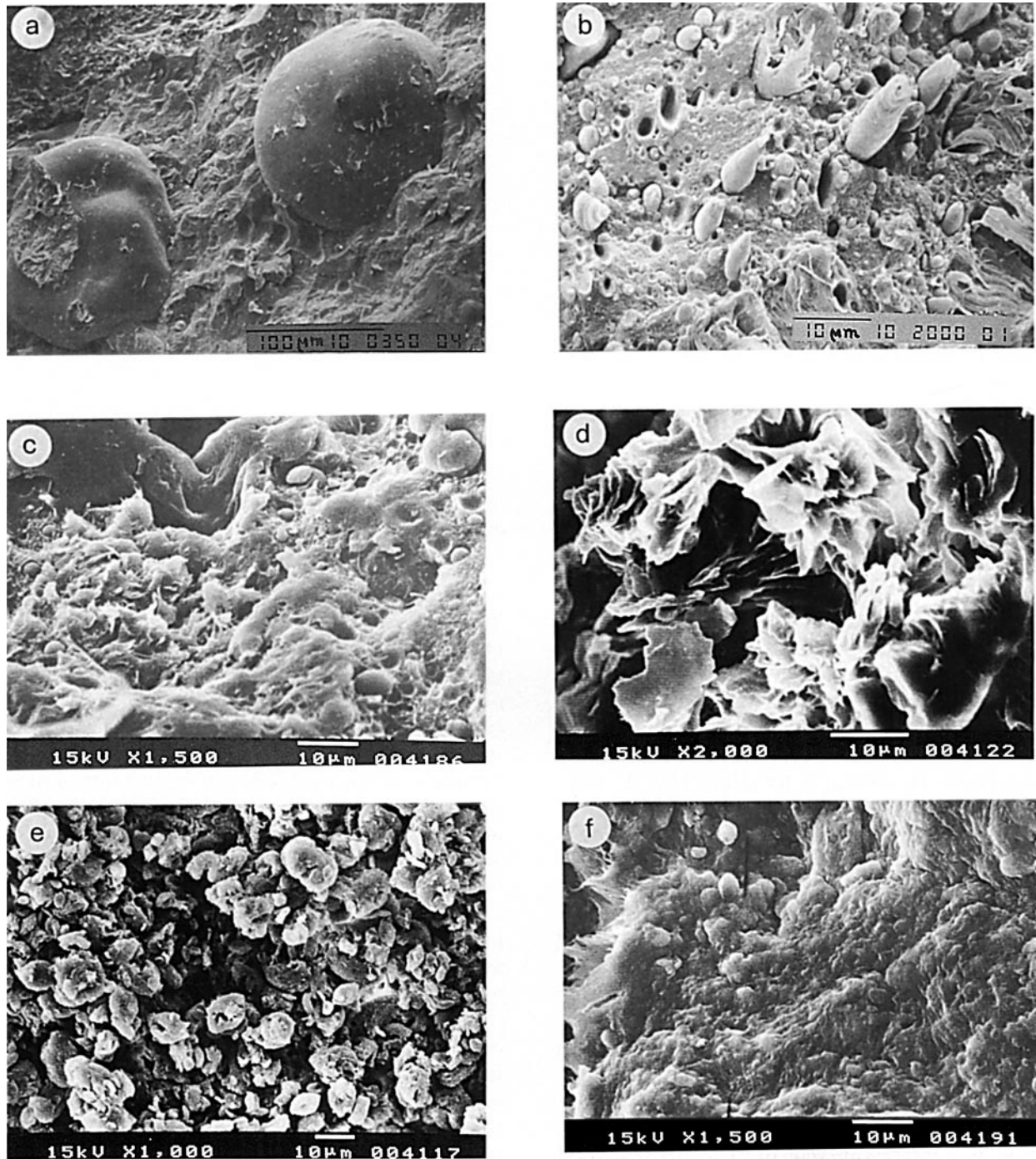
Figure 6   SEM micrographs of: (a) MIX; (b) and (c) COP; (d) CRM; (e) CRC; (f) RXC.

persed into one another, whereas for COP the phase dispersion, though not uniform, is much finer and the interphase interactions much more pronounced.

The micrographs of powder specimens of CRM and CRC are shown in Figure 6(d) and (e). The morphology of CRM is homogeneous and shows cluster-like hedrites and multilayer lamellar crystals

of PEox. That of CRC shows smaller multilayer hedrites and irregular lamellar crystals. This difference can be interpreted assuming that the latter fraction is made up of a copolymer with short SBH branches disturbing the PEox crystallization.

Whereas the morphology of RXM (not shown) is homogeneous and has the fibrous structure typical

for neat LCPs, that of RXC [Fig. 6(f)] is biphasic. The matrix has a slightly fibrous structure and the dispersed phase is in the form of small droplets (up to ca. 3 μm) intimately built up into the matrix. The morphology of RXC is typical for a graft copolymer rich of SBH branches. In conclusion, all SEM observations agree with the issues of IR, NMR, and DSC investigations.

TG Measurements

The TG curves of MIX, COP, and RXC are compared with those of PEox and SBH in Figure 7. Extensive degradation of PEox takes place in one step at temperatures above 400°C, and is over (almost 100% weight loss) at ca. 480°C. However, a very slow degradation starts already at around 270°C and leads to a weight loss amounting to approximately 6% at 400°C. Neat SBH, on the contrary, is perfectly stable up to 330°C. At higher temperatures, however, fast degradation of this polyester occurs, leading to a weight loss of ca. 40% at 400°C. At higher temperatures the SBH decomposition continues with a lower rate up to ca. 455°C. The weight loss is of ca. 80% at this stage and does not increase appreciably upon further heating.

The degradation process of MIX displays all the features of the two components, as it is expected for a mechanical blend. The final weight loss of ca. 90% is reached at ca. 480°C, as for pure PEox. As compared with MIX, the first-stage decomposition of COP takes place at appreciably lower temperatures. Between the two degradation steps of COP, a fairly wide plateau is observed in the temperature range 360–420°C, where the weight loss increases slowly from ~ 25 to ~ 35%. The final weight loss (~ 87%) is reached at ca. 480°C.

The temperature dependence of the weight loss of RXC resembles that of COP very closely. However, on account of the higher content of SBH, the first degradation step is more pronounced (40% weight loss at ca. 390°C) and the second step is slower and reaches a final weight loss of ca. 80% at 480°C. It is interesting that the TG curve of RXM (not shown) is practically coincident with that of neat SBH.

The first degradation step observed for MIX as well as for COP and RXC can be associated with the SBH (or, respectively, SBH-rich) phase. It has already been shown that this step takes place at lower temperatures, and is faster, when the SBH chains are chemically bonded to the PE molecules. On the other hand, the final degradation step associated with the destruction of the PE sequences
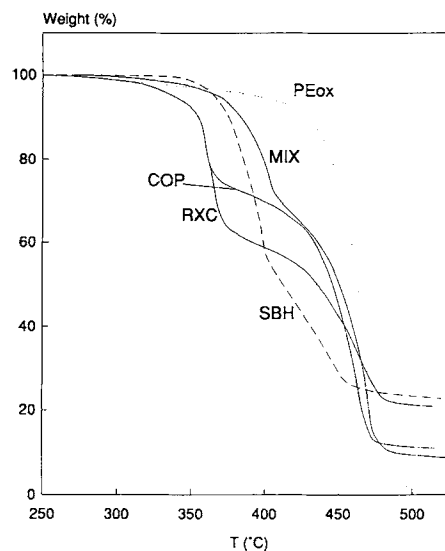
Figure 7 Thermogravimetric curves of PEox, SBH, MIX, COP, and RXC. (Nitrogen atmosphere; rate: 5°/min).

occurs at slightly higher temperatures for COP and its fractions. It is also interesting that the TG curves of COP and its fractions indicate that a slight degradation process takes place in the 320÷330°C temperature range. This is absent either in the pure components and in the blend and its fractions. Although the TG results cannot provide definite information on the mechanism of degradation of these materials, they represent further evidence in favor of a chemical interaction taking place between PEox and the SBH monomers during the fabrication of COP.

In Table III the temperatures and the approximate weight losses corresponding to the DTG peaks are shown for all investigated materials. Because neat PEox does not undergo significant degradation in the lower temperature region, the first DTG peak can be associated with the SBH content of the different samples. Thus, the DTG data can be used, together with those obtained by DSC, to calculate the approximate composition of the different fractions of COP. The results of this calculation are compared in Table IV with the estimates of DSC. The agreement is satisfactory for all materials, considering the rough approximation of both types of calculations. In fact, the DSC data are also affected by appreciable uncertainty because the enthalpy changes depend on both the content and the degree of crystallinity of the PE phase, but no account was made in the calculation of any change of the latter parameter for the different samples. With respect to CRC, whose DTG curve does not show a first-

Table III Differential Thermogravimetric (DTG) Data

Sample	Low-Temperature DTG Peak		High-Temperature DTG Peak	
	T (°C)	Wt Loss (%)	T (°C)	Wt Loss (%)
PEox	—	—	467	98
SBH	390	42	435	35
MIX	397	27	470	62
CRM	—	—	461	99
NCM	—	—	460	96
RXM	410	54	439	24
COP[a]	359	26	461	61
CRC	—	—	461	99
NCC[b]	430	19	461	79
RXC[a]	365	39	464	41

[a] The DTG curves of these materials display a low temperature (320 ÷ 330°C) shoulder, in addition to the two main peaks.
[b] The DTG peaks of this fraction are partially overlapped. The values of the relevant wt losses are affected by considerable uncertainty.

step degradation peak, it must be pointed out that the strong asymmetry of the DTG peak of this fraction probably accounts for the degradation of the SBH-rich phase, whose presence was revealed, on the other hand, either by DSC and IR analysis. The other data in Table IV are in fair agreement with the IR indications.

Preliminary Evaluation of the Compatibilizing Effect of COP

As already stated before, the main scope of this article was that of establishing that graft copolymers consisting of polyolefin main chains and LCP branches may be prepared by the melt polycondensation of LCP monomers carried out in the presence of preformed polyolefins containing reactive functional groups. An investigation of the capability of the particular copolymer prepared in this study to behave as a compatibilizer for HDPE/SBH blends is presently underway. Although it is not expected that the addition of COP to these blends will mean an appreciable improvement of their mechanical properties, due to the relatively low molar mass (ca. 10,000) of the oxidized PE used for the synthesis, a preliminary morphological investigation of HDPE/COP/SBH ternary blends has been carried out by SEM, in order to prove that COP can at least influ-

ence the interfacial interactions between the polyolefin and polyester phases.

In Figure 8, the SEM micrographs of the fracture surfaces of 80/20 HDPE/SBH blends without (a) and with 5% added COP (b) are compared. It is apparent that the presence of COP leads to a significant increase of interfacial adhesion. In fact, whereas the SBH droplets of the uncompatibilized blend are practically free within the PE matrix and their smooth surface appears unaffected by the fracture, those of the ternary blend are seen to be tightly matrix bound. Moreover, the latter LCP particles, as well as the matrix holes produced by the droplets pull-out, appear partly frayed and unraveled as a result of the fracture [cf. Fig. 8(b)]. This morphology indicates that, during blending, COP does actually migrate to the HDPE/SBH interface and plays a compatibilizing role.

CONCLUSIONS

It has been shown that a PE-g-LCP copolymer can be synthesized by the melt transesterification of the LCP monomers and a functionalized PE containing free carboxylic groups. The involvement of the latter groups in the reaction has been shown by IR analysis to be practically quantitative in experiments carried out with a relatively low molar mass functionalized PE. The compatibilizing effect of the copolymer prepared in this study has been preliminarily demonstrated by a morphological investigation of blends prepared from an injection molding HDPE grade and SBH. It is expected, however, that a substantial improvement of the mechanical properties of these blends will only be obtained by the use of PE-g-SBH copolymers synthesized from functionalized PEs of higher molar mass. On the other hand, an increase of the polyolefin molar mass beyond a certain limit will probably lead to difficulties in the copolymer synthesis, due to increasing diffusional

Table IV SBH Content of MIX and of COP Fractions, as Calculated from DSC and DTG Data

Sample	SBH (wt %) from DSC	SBH (wt %) from First DTG Peak
MIX	45–55	53
COP	50–57	49
CRC	5–10	0
NCC	20–30	28
RXC	70–75	75
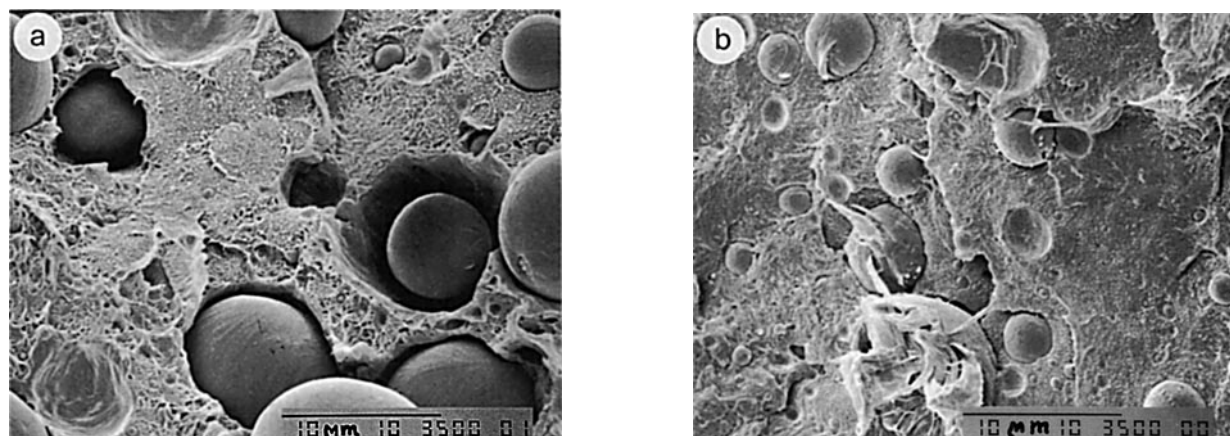
Figure 8 SEM micrographs of 80/20 HDPE/SBH blends: (a) neat; (b) compatibilized with 5% COP.

problems. Further studies are needed to clear up this point.

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