Reactive Blending of a Functionalized Polyethylene with a Semiflexible Liquid Crystalline Copolyester

L. I. MINKOVA,[1,*] Ts. MITEVA,[1] D. SEK,[2] B. KACZMARCZYK,[2] P. L. MAGAGNINI,[3] M. PACI,[3] F. P. LA MANTIA,[4] and R. SCAFFARO[4]

[1]Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria, [2]Institute of Polymer Chemistry, Polish Academy of Sciences, 34, M. Curie str., 41800 Zabrze, Poland, [3]Department of Chemical Engineering, University of Pisa, via Diotisalvi 2, 56126 Pisa, Italy, and [4]Department of Chemical Engineering, University of Palermo, viale delle Scienze, 90128 Palermo, Italy

SYNOPSIS

Reactive blends (50/50 w/w) of a low molar mass polyethylene containing free carboxylic groups (PEox) and a semiflexible liquid crystalline polyester (SBH 1 : 1 : 2, by Eniricerche) have been prepared at 240°C in a Brabender mixer, in the presence of Ti(OBu)$_4$ catalyst, for different mixing times (15, 60, and 120 min). In order to prove the formation of a PE-g-SBH copolymer, the blends have been fractionated by successive extractions with boiling toluene and xylene. The soluble fractions and the residues have been analyzed by Fourier transform infrared (FTIR) spectroscopy, thermogravimetry (TG and DTG), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). All analytical procedures concordantly show that PE-g-SBH copolymers with different compositions, arising from differences of either the number of PEox carboxylic groups entering the transesterification or the length of grafted SBH branches, are formed as a result of blending. Depending on the relative content of PE and SBH segments, the copolymers dissolve in the solvents, together with any unreacted PEox, or remain in the residues, together with neat SBH. Qualitative IR analyses and quantitative TG measurements have shown that the amount of copolymers increases strongly with the mixing time. Preliminary SEM observations indicate that the unfractionated products of the reactive blending carried out with long (120 min) mixing times lead to improved interfacial adhesion and phase dispersion when added to PE/SBH blends. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The use of thermotropic liquid crystalline polymers (LCPs) as the minor phase of polymer blends is currently the object of active investigation because LCPs are known to considerably decrease the melt viscosity of the thermoplastics and, simultaneously, improve the mechanical properties of the final articles.[1-3] However, most commercial thermoplastics are incompatible with LCPs, and this very often causes poor interfacial adhesion between matrix and filler; therefore, the resulting reinforcing effect of the LCP addition is practically much lower than expected on the basis of the law of mixtures.[4-6]

In the particular case of LCP blends based on commercial polyolefins, such as polyethylene (PE)[7-10] and polypropylene (PP), compatibility and interphase adhesion are generally too low to grant acceptable mechanical properties. This is expected since most available LCPs belong to the families of wholly aromatic copolyesters or copolyesteramides whose structure and polar characteristics are not best suited to match those of polyolefins. Even a semiflexible liquid crystalline polymer with fairly long polymethylene sequences such as that developed by Eniricerche, SBH 1 : 1 : 2, containing 25% sebacic acid moieties in addition to hydroxybenzoic and dioxybiphenyl ones, has been shown to display very poor compatibility in blends with two HDPE grades.[11,12]

The addition of appropriate compatibilizers may help solving the problems of poor dispersion and

---

poor adhesion in blends of incompatible polymers. Among compatibilizing agents, block or graft copolymers made up of segments with chemical structure and solubility parameters that are identical or similar to those of the polymers being blended appear best suited to the scope. Therefore, we undertook a research aimed at the synthesis of PE-*g*-LCP copolymers to be used as compatibilizers for PE/LCP blends. In a previous paper,[13] the successful synthesis of a PE-*g*-LCP by the polycondensation of the LCP monomers carried out in the presence of a PE sample containing free carboxylic groups has been described. It has been shown that practically complete grafting of LCP chains onto the carboxylic functional groups of the polyolefin takes place, which leads to a product characterized by a wide distribution of the mass ratios of the two components. The compatibilizing ability of the product with respect to HDPE/LCP blends has also been preliminarily demonstrated. In this work, the synthesis of similar PE-*g*-LCP copolymers carried out by the reactive blending of the same functionalized PE with preformed LCP has been investigated.

It is known that the melt mixing of condensation polymers may give rise, under appropriate conditions, to transesterification reactions leading to the formation block or graft copolymers. The studies on compatibilization and transesterification reactions observed both below and above the melting point in binary polyester blends, including those comprising LCPs, have been reviewed recently.[14] Transesterification reactions leading to new copolyesters or to compatibilization of polymer blends have been described for blends of different thermotropic LC polyesters with, e.g., poly(hexamethylene terephthalate), poly(butylene terephthalate), polycarbonate, and polyarylate.[15-18] Concerning polyolefins, a suggestion has been made that maleic anhydride modified PP may give rise to graft copolymers when melt blended with LCPs.[19] The resulting blends are reported to display lower interfacial tension and enhanced adhesion between the PP and LCP phases; moreover, the compatibilization of these PP/LCP blends is reflected in a significant improvement of tensile modulus, tensile strength, and surface finish.[19-21] To our knowledge, no previous report has been made on the reactive blending of LCPs with functionalized PE.

EXPERIMENTAL

The functionalized PE, hereinafter indicated as PEox, was a commercial specimen (Aldrich, Cat.

No. 19,192-2) of oxidized polyethylene, with an acid number of 28 mg KOH/g and a molar mass of ca. 10,000, which corresponds to an average content of ca. 5 carboxylic groups per macromolecule.

The semiflexible LCP was a laboratory sample (LCP1B/024) kindly supplied by Eniricerche SpA, Milan. This is an essentially random copolyester, synthesized from sebacic acid (S), 4,4'-diacetoxybiphenyl (B), and 4-acetoxybenzoic acid (H) in the mole ratio 1 : 1 : 2, as described elsewhere,[22] and is referred to in the following as SBH. The inherent viscosity of SBH, 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 melting and crystallization temperatures of SBH, as measured by DSC, were 230 and 217°C, respectively; and the relevant enthalpy changes were of 4–6 J/g.[23]

An injection molding grade (A-1100) of HDPE was kindly supplied by Solvay & C.ie, Rosignano Solvay. 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.

Blending of PEox and SBH, in the 50/50 (w/w) ratio, was carried out in a Brabender apparatus equipped with a 30 mL mixing head at 240°C and 100 rpm, under nitrogen. Ti (O-Bu)₄ was used as the transesterification catalyst. The reactive blends prepared with mixing times of 15, 60, and 120 min are referred to hereinafter as COP15, COP60, and COP120, respectively. A physical blend of PEox and SBH of similar composition was also prepared, in the absence of catalyst, with a mixing time of 6 min and is referred to as MIX. HDPE/SBH and HDPE/COP120/SBH blends were also prepared with the same procedure used for MIX. All polymers were accurately dried (at least 12 h at 110°C, under vacuum) before blending. All blends were milled, washed with acetone, and dried.

Solvent extractions were performed in Kumagawa devices. A small amount (3–5 g) of the blends was placed in a thimble and extracted with about 250 mL of refluxing toluene for 30–36 h. At the end of this period, the solution was isolated, cooled, and poured into excess methanol. The precipitated polymer was then filtered, dried, and weighed. The insoluble fraction in the extraction thimble was dried, weighed, and extracted once more with boiling xylene, by the same procedure.

Infrared (IR) spectra of the polymers and their blends and blend fractions were recorded on a Bio-Rad Win IR spectrometer. KBr pellets were used because it was difficult to obtain films with even
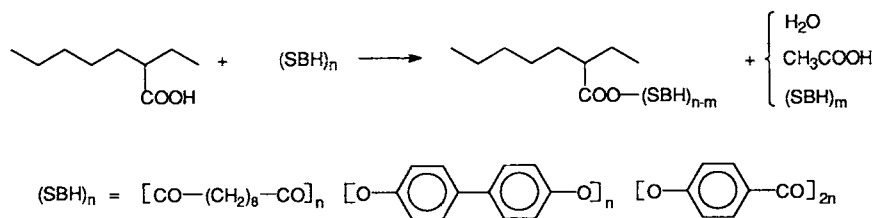
Figure 1 A scheme of the possible reactions of PEox with SBH.

thickness by hot molding, probably due to the high fluidity of the PEox component.

Differential scanning calorimetry (DSC) measurements were carried out under nitrogen atmosphere, with a heating/cooling rate of 10°C/min, on a Perkin Elmer DSC-4 apparatus. 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 thermogravimetric (TG) and DTG curves of the samples were obtained on a TGS-2 Perkin Elmer apparatus with a heating rate of 5°C/min, under nitrogen atmosphere.

Scanning electron microscopy (SEM) observations were made using a JEOL 550 scanning electron microscope. The samples were fractured in liquid nitrogen, and the fracture surfaces were coated with gold.

RESULTS AND DISCUSSION

The formation of a PE-g-SBH copolymer by the reactive blending of PEox and SBH is expected to occur either by the reaction of the free carboxyl groups of PEox with the hydroxyl (or acetoxyl) end groups of SBH, or through the acidolysis of the ester groups within the SBH chain, as shown schematically in Figure 1. As a consequence, either water or acetic acid, or an SBH molecule of reduced degree of polymerization, are the by-products. On the other end, both water and acetic acid can in turn give rise to hydrolysis or acidolysis of SBH chains. In principle, crosslinking of PEox due to the formation of SBH bridges might also be expected to occur.[24] However, neither spectroscopic characterizations nor melt viscosity evaluations made by measuring the applied torque during reactive blending[25] provided evidence of crosslinking in our experiments.

In order to gain insight into the nature of the new material obtained by reactive blending of PEox and SBH, the blends were fractionated with boiling toluene and xylene, which are good solvents for PEox. The results of these experiments are collected in Table I. It may be seen that, as expected, the masses of the soluble and insoluble fractions of MIX are almost equal. On the contrary, for the reactive

Table I Solvent Fractionation of the Blends

Sample	Weight Sample (g)	Fraction	Weight Fraction (g)	Weight Fraction (%)	Code
MIX	3.118	acetone	0.081	2.6	
		toluene	1.401	44.9	NCM
		xylene	0.036	1.2	SXM
		insoluble	1.600	51.3	RXM
COP15	4.114	acetone	0.082	2.0	
		toluene	2.077	50.4	NCC15
		xylene	0.080	2.0	SXC15
		insoluble	1.875	45.6	RXC15
COP60	5.007	acetone	0.091	1.8	
		toluene	2.009	40.1	NCC60
		xylene	0.154	3.0	SXC60
		insoluble	2.753	55.1	RXC60
COP120	5.400	acetone	0.1613	3.0	
		toluene	1.4230	26.4	NCC120
		xylene	0.4427	8.2	SXC120
		insoluble	3.3730	62.4	RXC120
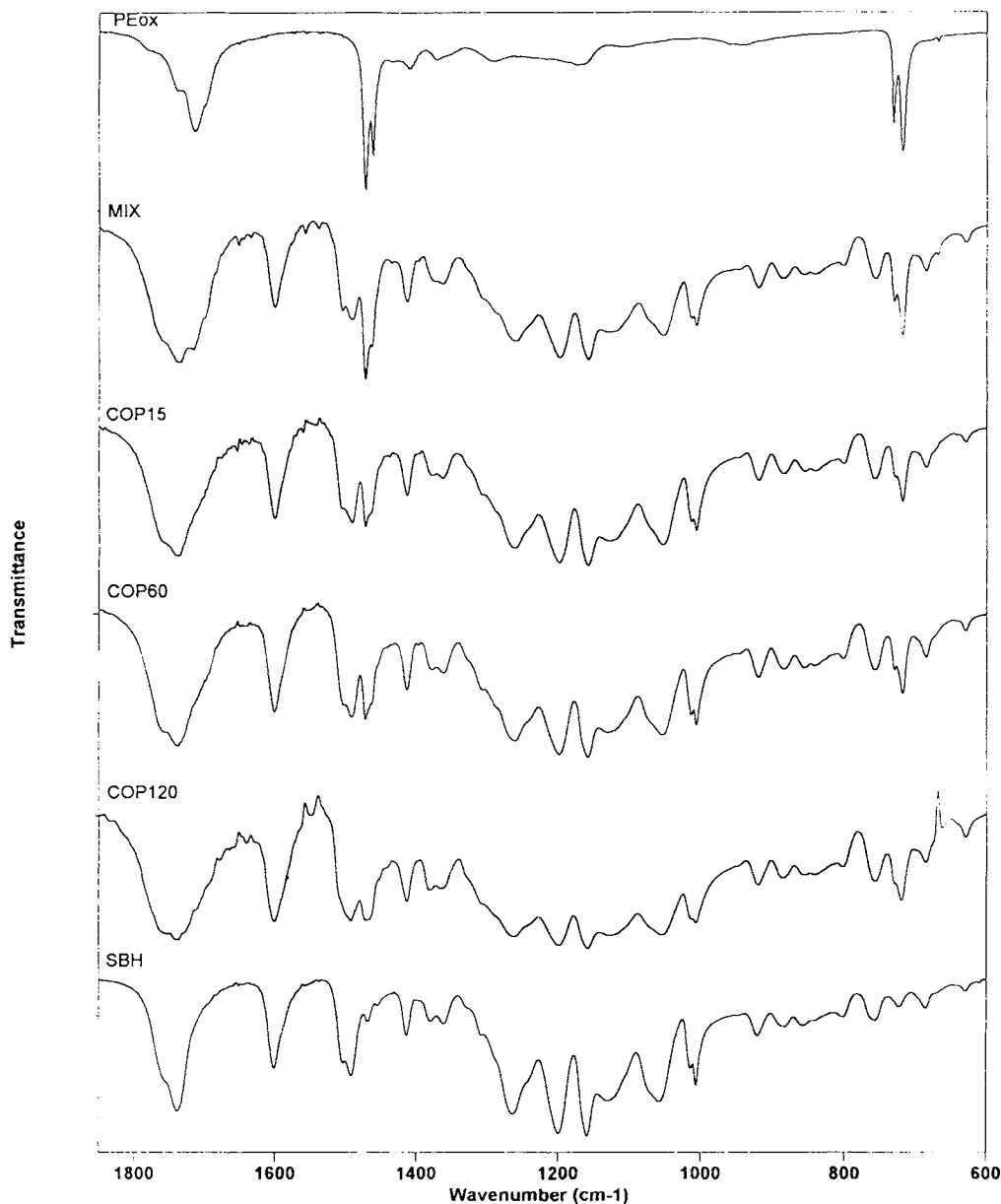
Figure 2   IR spectra of PEox, SBH, MIX, COP15, COP60, and COP120 (see Table I for sample codes).

blends, such equivalence is not found. Moreover, upon increasing the mixing time, the insoluble residue increases from ca. 45 to ca. 62%, the toluene-soluble fraction decreases markedly (from 50 to 26%), and the xylene-soluble fraction increases from 2 to 8%. All these effects may be interpreted in terms of a progressive grafting of SBH chains onto the PEox molecules. It might be argued that the observed increase of the insoluble residue could be accounted for by PEox crosslinking taking place during reactive blending. In order to check this point, powder specimens of the insoluble fractions were treated

with concentrated NaOH solution in ethanol for several hours, under reflux, so as to hydrolize completely the SBH chains. The resulting solids were washed with pure ethanol and dried. They proved to dissolve completely in boiling toluene and to display the melting temperatures and enthalpies expected for pure, uncrosslinked PEox. It can be concluded, therefore, that a PE component is found in the insoluble fractions of the reactive blends because of chemical bonding to SBH chains. Also, the relative increase of the amount of material which is soluble in xylene may be explained through the for-

Table II Curve Fitting Calculation of the Areas of C=O Groups of Aliphatic–Aromatic Ester, Aromatic–Aromatic Ester, and Acid Peaks

Sample	C=O Aliphatic–Aromatic Ester Band			C=O Aromatic–Aromatic Ester and Acid Free Band			C=O Acid Association Band		
	$\nu[cm^{-1}]$	$A_{al\text{-}ar}$	$A_{al\text{-}ar}/A_T$	$\nu[cm^{-1}]$	$A_{ar\text{-}ar}$	$A_{ar\text{-}ar}/A_T$	$\nu[cm^{-1}]$	A_{acid}	A_{acid}/A_T
SBH	1759.2	9.886	0.519	1736.1	8.633	0.453	1713.3	0.510	0.026
PEox				1738.2	6.072	0.539	1714.3	5.184	0.460
MIX	1765.3	10.762	0.349	1738.5	14.569	0.472	1713.8	5.457	0.177
COP15	1761.7	12.118	0.569	1735.9	5.272	0.247	1709.8	3.919	0.184
COP60	1762.2	15.396	0.587	1735.2	7.795	0.297	1711.6	3.038	0.116
COP120	1763.5	18.694	0.583	1733.7	11.820	0.368	1715.5	1.580	0.049

$A_T = A_{al\text{-}ar} + A_{ar\text{-}ar} + A_{acid}.$

mation of PE-g-SBH copolymers having a lower content of SBH segments.

The composition of the blends and of their fractions has been analyzed by IR, DSC, TG, and SEM investigations.

FOURIER TRANSFORM INFRARED (FTIR) INVESTIGATIONS

The FTIR spectrum of PEox displays the bands at 1714 and 1738 cm^{-1}, which are characteristic, respectively, for associated and free C=O groups of carboxyl functionalities, and the bands corresponding to the CH$_2$ group vibrations at 2900–2800, 1472, 1460, 730, and 718 cm^{-1} (Fig. 2). For neat SBH, the band corresponding to the C=O groups of the aromatic-aromatic ester at 1738 cm^{-1}, overlapping with that at 1760 cm^{-1} due to the aliphatic-aromatic ester groups, and the bands characteristic for aromatic ring vibrations at 1600, 1500, and 1006 cm^{-1} are observed (Fig. 2). In the 1300–1100 cm^{-1} region of the SBH spectrum, the bands corresponding to the vibrations of the ester C—O groups are also seen. The bands characteristic of the CH$_2$ vibrations are also present in this spectrum, but their intensity is clearly lower than for PEox.

The IR spectra of the mechanical blend MIX and of the reactive blends COP15, COP60, and COP120 display all the bands typical for both PEox and SBH (Fig. 2). However, meaningful changes could be observed for the ester and the carboxyl bands. Curve fitting calculations carried out to analyze the partially overlapping bands characteristic for aliphatic-aromatic ester, aromatic-aromatic ester, and carboxyl groups led to the results shown in Table II. It is apparent that the concentration of carboxyl groups decreases markedly with the time of reactive

blending. This is in agreement with the expected progressive formation of PE-g-SBH copolymer on the assumption that the carboxyl groups of PEox react preferentially with the end groups of SBH and that significant amounts of the by-products (water or acetic acid) escape from the reaction mixture before giving rise to hydrolysis or, respectively, acidolysis of SBH. On the other hand, the results in Table II demonstrate that the concentration of the aliphatic-aromatic ester groups increases concurrently, thus confirming the above interpretation.

The IR spectra of the insoluble residues of all blends are compared in Figure 3 with the spectrum of neat SBH. The close similarity between the latter and the spectra of RXM and RXC15 is apparent and confirms, on one side, that the solvent extraction does actually lead to efficient separation of the neat polymers from the mechanical blend (MIX) and, on the other, that reactive blending has little effect, if any, on the composition of the insoluble residue, when carried out for only 15 min. On the contrary, in the RXC60 and RXC120 spectra, the bands characteristic for PEox become visible, thus confirming that a portion of the latter polymer becomes chemically bonded into the SBH-rich (insoluble) material after longer mixing times.

The comparison of the IR spectra of the soluble fractions with that of neat PEox confirms the above conclusion. In fact, as it is visible in Figure 4, the spectrum of NCM is practically identical to that of PEox, whereas those of NCC15, NCC60, and NCC120 clearly show the additional presence of bands, characteristic for SBH segments, whose intensities increase with increasing the reactive blending time.

The above mentioned calculations (Table II), concerning the bands typical for the ester and carboxyl groups, illustrate the changes undergone by
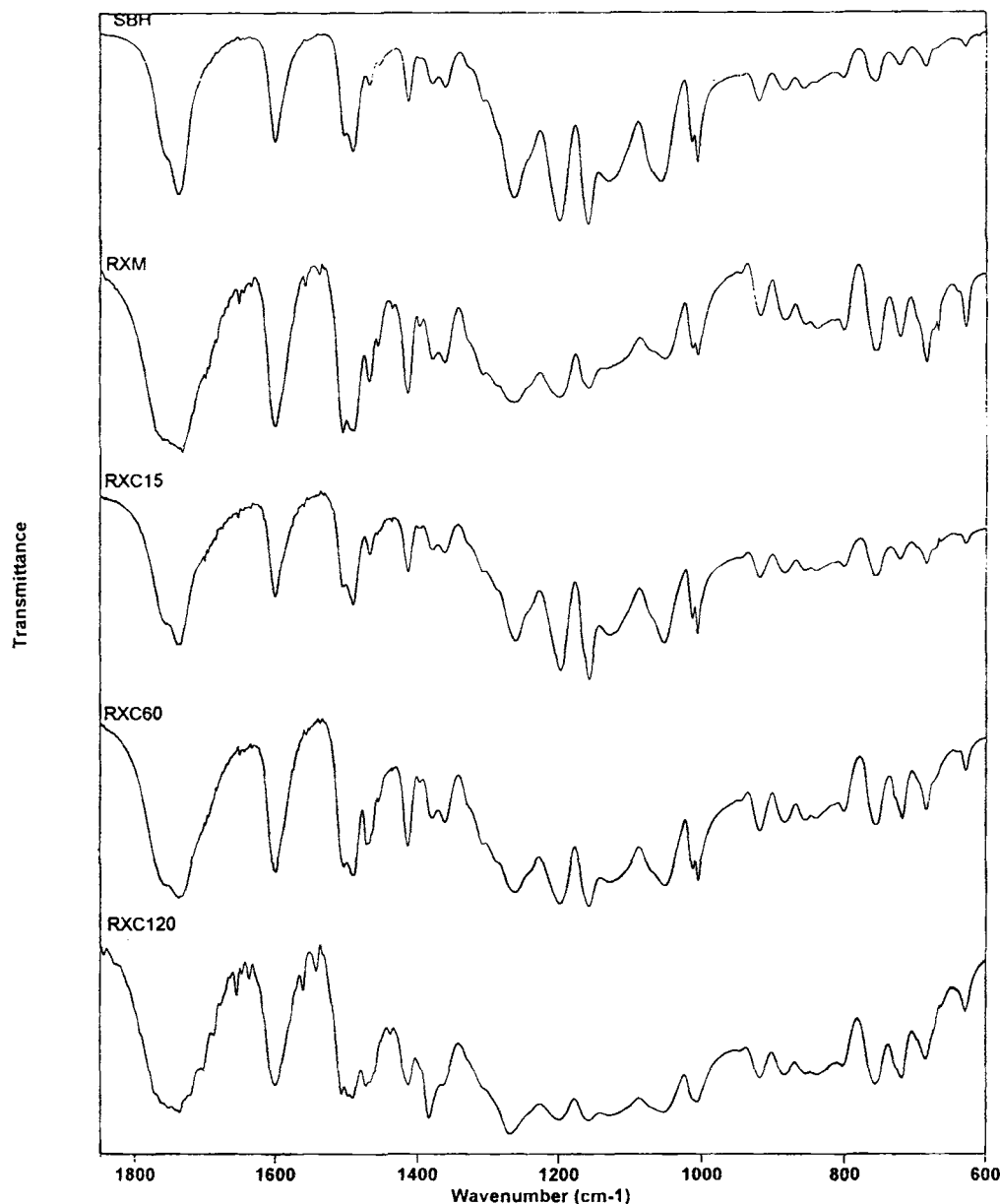
Figure 3   IR spectra of SBH and of the xylene-insoluble residues of the blends.

the relevant IR bands as a function of mixing time. However, they do not provide quantitative information on the contents of SBH and PEox chains in the investigated materials. For this reason, we have tried to use other absorption bands for a quantitative analysis of the soluble and insoluble fractions. In particular, we have found that, in our systems, the second derivative of the band characteristic for SBH aromatic ring vibrations at 1006 cm^{-1} exhibits a strong maximum, whereas for PEox, the second derivative at this wave number equals zero. Also, the second derivative of the bands characteristic for PEox at 718 and 1472 cm^{-1} displays maxima, whereas it is equal to zero for SBH. Therefore, these wave numbers can be used for a determination of the relative amounts of PEox and SBH in the different fractions. Thus, for RXM and RXC15, the second derivative at 1472 and at 718 cm^{-1} equals zero, and this confirms that these two fractions are practically composed by pure SBH. On the contrary, the calculations of the second derivative at the same wave numbers, carried out for the insoluble residues RXC60 and RXC120, show that PE segments are present in these fractions and that the PE content of RXC120 is about 3.5 times higher than that in RXC60. This is evidence that the quantity of the
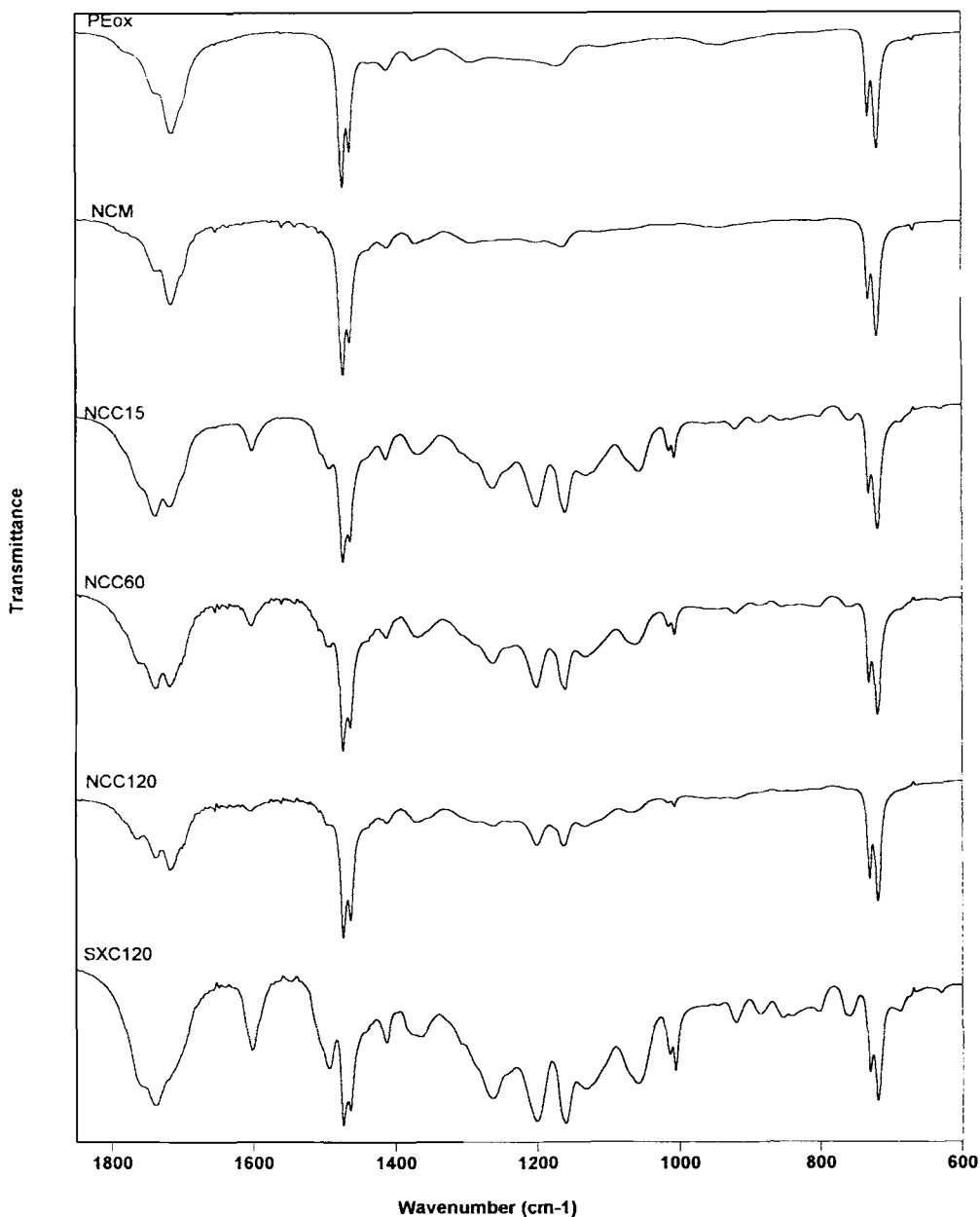
Figure 4 IR spectra of PEox and of the soluble fractions of the blends.

insoluble PE-g-SBH copolymer increases markedly with the mixing time.

As for the second derivative calculated at the wave length (1006 cm^{-1}) typical for the aromatic vibration of SBH, the calculations show that no SBH segments are contained in the NCM fraction, thus confirming that this consists of pure PEox. The toluene soluble fractions NCC15, NCC60, and NCC120, on the contrary, do contain SBH segments. It is interesting that the content of SBH segments in these fractions decreases on increas-

ing the mixing time. This may be tentatively explained assuming that, for longer mixing times, the amount of toluene soluble PE-g-SBH macromolecules with low SBH content is reduced by further grafting with more (or longer) SBH branches. This assumption is confirmed by the finding that the SBH content calculated for the xylene soluble fractions increases with mixing time and that, e.g., SXC120 contains ten times more SBH than the corresponding toluene soluble fraction NCC120.
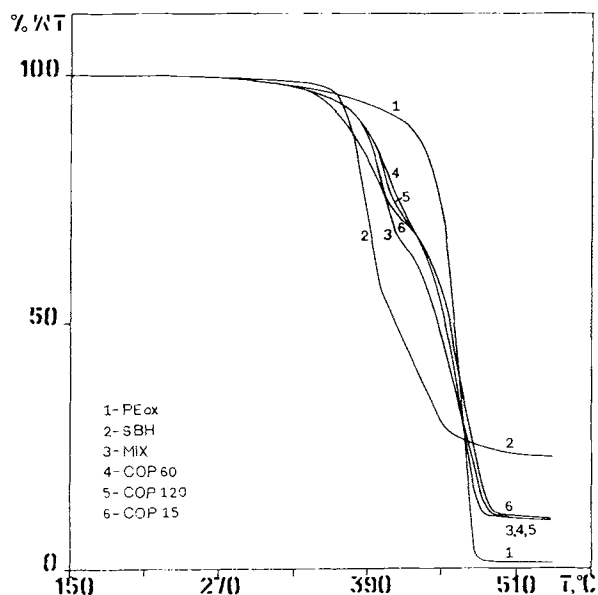
Figure 5 TG curves of MIX, COP15, COP60, and COP120 and of neat PEox and SBH.

THERMOGRAVIMETRIC MEASUREMENTS

The TG curves of MIX, COP15, COP60, and COP120 are shown in Figure 5, together with those of the pure components; those of the different fractions of COP120 are shown in Figure 6. Extensive degradation of PEox takes place in one step at fairly high temperature (>400°C) and leaves only a very small residue (ca. 0.5%) at 490°C. The degradation of SBH, on the contrary, occurs in two stages, characterized by different rates.[23] The destruction processes of MIX and of the reactive blends COP15, COP60, and COP120 also proceed in two stages as it could be expected (Fig. 5). The temperatures of the maximum destruction rate (T_{max}) of these two stages were determined from the peaks of the corresponding DTG curves and are collected in Table III.

From the weight losses corresponding to the two degradation stages, the approximate (estimated error: ca. 5%) SBH contents of the different materials can be calculated. The relevant figures are shown in Table III. In agreement with FT IR and DSC measurements, the SBH content is found to be zero for NCM, and this confirms that toluene fails to extract the SBH phase from the physical blend. According to the DTG calculations, the SBH content of NCC60 and NCC120 is also negligible and this is at variance with the qualitative indication of FT IR spectroscopy. The discrepancy is thought to be due to the rough approximation of the DTG calculation, which hampers the reliable detection of small SBH

contents. This explanation is supported by the fact that an SBH content of ca. 12% is actually found from DTG calculation for NCC15 which, among all toluene soluble fractions, was shown by IR to possess the highest content of SBH segments.

The DTG calculations also demonstrate that the SBH content of the insoluble residues decreases markedly upon increasing the mixing time, i.e., from 100% of RXM and RXC15 to 90% of RXC60 and to 73% of RXC120. Correspondingly, an increase of the content of SBH is observed for the toluene-insoluble, xylene-soluble fractions as it is shown by the IR analysis and is confirmed by the DTG calculation carried out for SXC120 (Table III).

It may be concluded that, upon increasing the mixing time, an increasing amount of PE-g-SBH copolymer is formed. For short (15 min) mixing times, most of the copolymer is soluble in toluene, and this is interpreted assuming that it contains a limited number of short SBH branches. As the mixing time increases the number and/or the length of the SBH branches increases, this leads to an increasing amount of copolymers which, depending on their SBH content, are found either in the xylene soluble fractions or in the insoluble residues.

DSC MEASUREMENTS

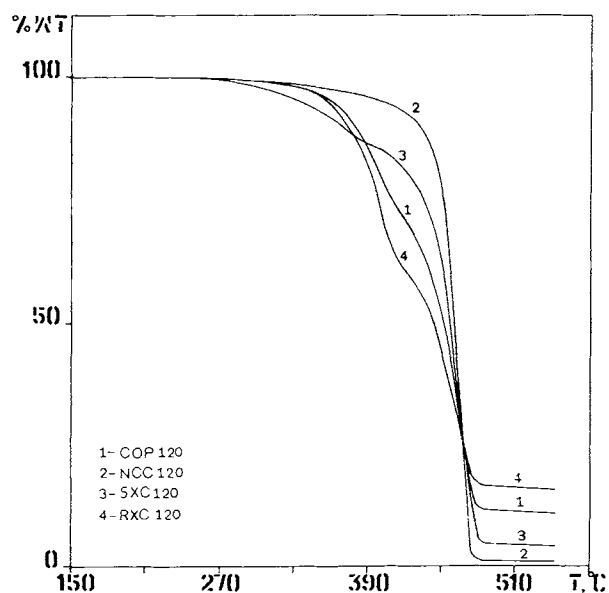As expected, the DSC traces of all PEox/SBH blends (MIX, COP15, COP60, and COP120) display

Figure 6 TG curves of COP120 and of its soluble and insoluble fractions.

**Table III   TG (DTG) Data of Reactive Blends and Their Fractions**

| Sample	T_{max} Ip (°C)	T_{max} IIp (°C)	Residue (%)	SBH Content (wt %)
PEox	—	467.0	0.5	—
SBH	390.0	435.0	21.2	100
MIX	397.1	470.0	9.6	55
NCM	—	460.0	3.7	—
RXM	410.0	438.0	21.9	100
COP15	392.9	471.4	10.1	52
NCC15	370.8	460.0	3.1	12
RXC15	396.8	437.5	20.8	100
COP60	408.6	467.1	9.7	53
NCC60	—	464.3	1.6	—
RXC60	407.1	455.7	16.2	90
COP120	398.6	464.3	11.0	51
NCC120	—	461.4	0.9	—
SXC120	364.3	467.1	4.3	27
RXC120	398.6	464.3	15.1	73

both peaks associated with the first-order transitions of the two components. However, the temperatures and enthalpy changes of the crystal-nematic transitions of the SBH component could not be reliably measured because the relevant peaks were usually broad and of very low intensity (ΔHm = ~ 6 J/g for neat SBH[23]). The calorimetric data of all investigated materials are collected in Table IV, and the DSC traces of the insoluble residues of solvent fractionation are shown in Figure 7.

Table IV   Temperatures and Enthalpies of Fusion/Crystallization of the PE Phase of the Blends and Their Fractions

Sample	Cooling T_c (°C)	Cooling ΔHc (J/g)	Second Heating T_m (°C)	Second Heating ΔHm (J/g)
PEox	115.2	192.3	132.6	190.5
MIX	115.1	87.3	131.0	90.3
NCM	114.1	186.6	131.1	186.1
RXM	—	—	—	—
COP15	111.4	91.1	127.0	86.9
NCC15	111.6	180.0	128.3	180.2
RXC15	96.8	0.7	108.6	1.2
COP60	111.8	86.0	126.1	81.3
NCC60	110.2	184.0	127.1	182.2
RXC60	102.9	27.6	115.4	21.7
COP120	111.2	73.8	128.1	73.5
NCC120	113.1	180.9	128.1	177.2
SXC120	108.4	107.3	119.6	104.5
RXC120	103.2	36.0	116.3	33.2

From Table IV, it can be noticed that the temperatures and enthalpies of the PE component of MIX correspond closely to those of neat PEox, as
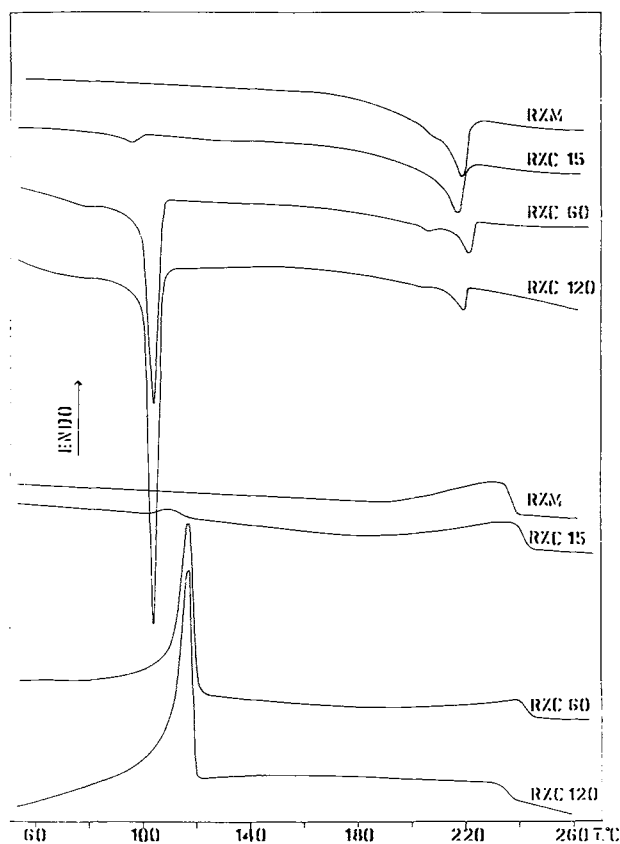
Figure 7 DSC traces of crystallization and second melting of the blends residues.
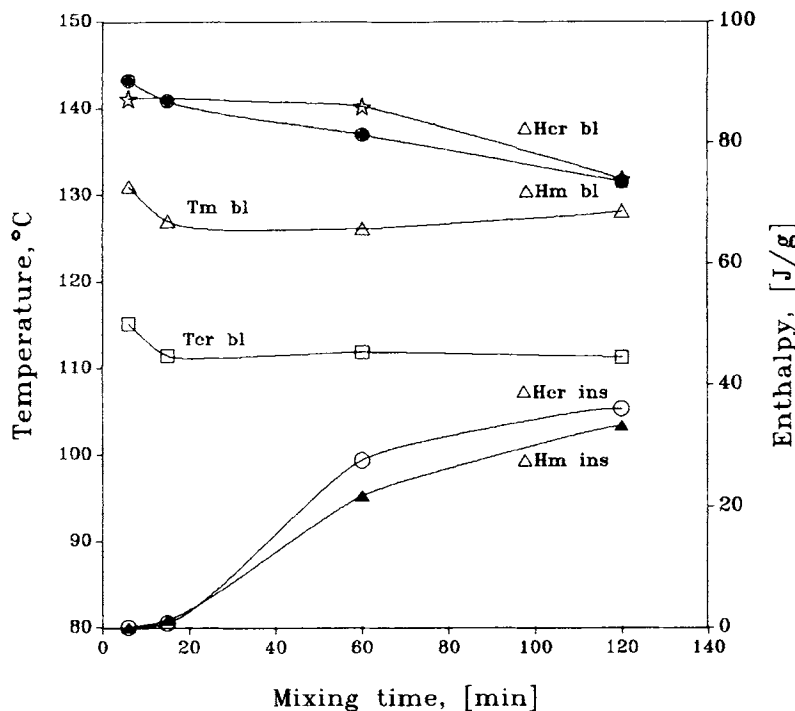
Figure 8 Temperatures and enthalpies of crystallization and second melting of the PE component in the blends and the residues as a function of mixing time.

it is expected for a mechanical blend. The transition temperatures of the PE component of COP15, COP60, and COP120, on the contrary, are ca. 4°C lower, and the relevant enthalpies decrease slightly on increasing the mixing time (Fig. 8). This is evidence supporting the presence of PE-g-SBH copolymers in these blends.[26]

The calorimetric data in Table IV also demonstrate that the soluble and insoluble fractions of MIX consist essentially of neat PEox and SBH, respectively, whereas those of the reactive blends contain significant amounts of the other component, too. In particular, the insoluble residues of the reactive blends clearly show the presence of a PE component that is chemically bonded to SBH (Fig. 7). The latter conclusion, which comes out from the characterizations described before, is also confirmed by the finding that the temperatures of melting/crystallization of the PE component of these insoluble fractions are appreciably lower than those of pure PEox. As it is clearly shown in Figure 8, the enthalpy of melting/crystallization of PE in the residues increases strongly with the mixing time, thus confirming that the quantity of PE-g-SBH copolymer concurrently increases. The contents of PE chains in the insoluble residues, calculated on the basis of the melting/crystallization enthalpies, are

in fair agreement with those found by TG as described before.

SEM OBSERVATIONS

The SEM micrographs of MIX and COP60 are shown in Figure 9, together with those of their insoluble residues. Both blends display a two-phase morphology. The micrograph of MIX [Fig. 9(a)] was taken on a zone of the fracture surface where a very limited number of relatively small (<10 μm) SBH particles are present. Actually, other zones of this blend showed much larger (>150 μm) droplets, and this shows that the phase dispersion of MIX is very poor.[13] In COP60 [Fig. 9(b)], a relatively uniform dispersion of smaller (1–5 μm) SBH particles can be observed. The interphase adhesion is also appreciably enhanced with respect to MIX.

The SEM micrographs of the insoluble fractions of MIX and COP60 [Figs. 9(c) and (d)] reflect their different compositions. The morphology of RXM [Fig. 9(c)] appears homogeneous and fibrous, as expected for neat SBH. That of RXC60 [Fig. 9(d)], on the contrary, shows a two-phase morphology. On the basis of the composition calculated for this residue from TG data (Table III), it can be assumed
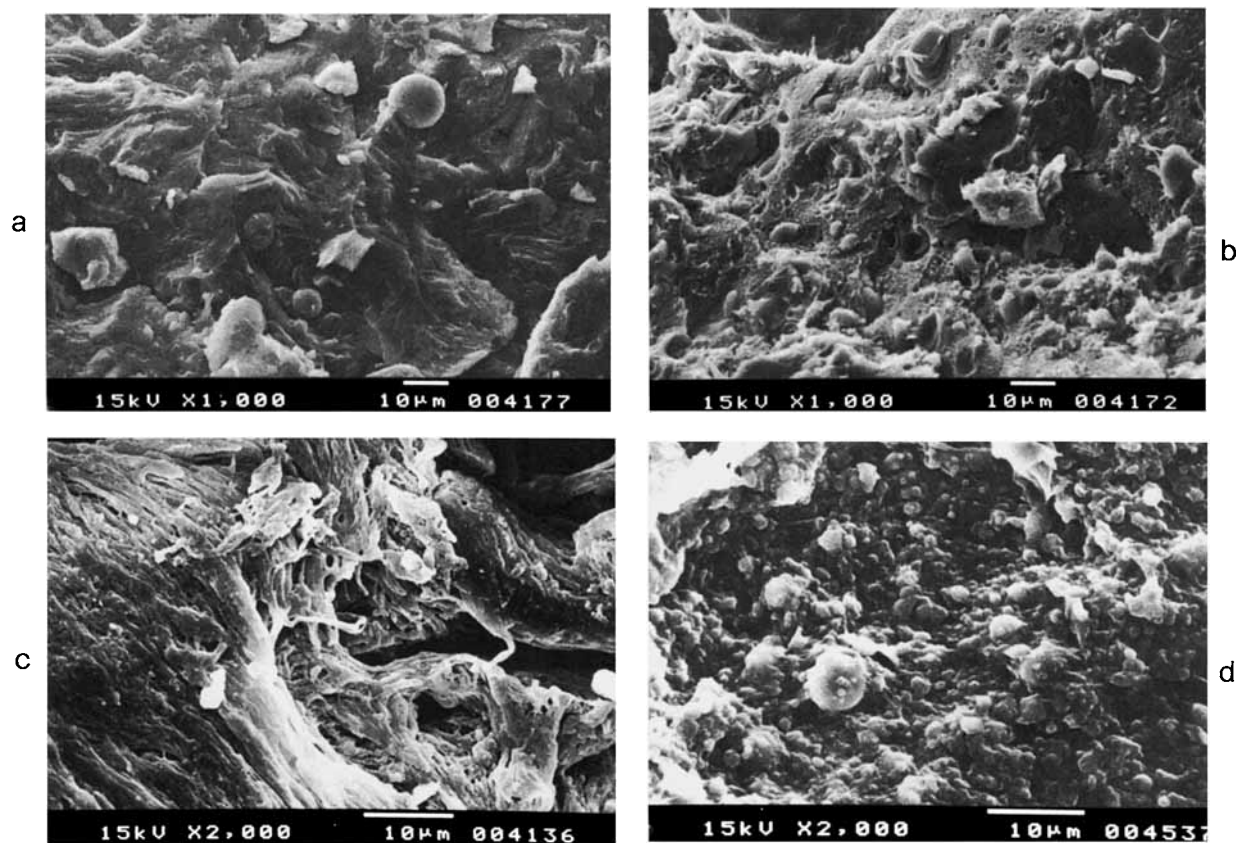
**Figure 9** SEM micrographs of MIX (a), COP60 (b), RXM (c), and RXC60 (d).

that the matrix is made of practically pure SBH and the minor phase consists of PE-g-SBH copolymer. The morphologies of RXC120 and RXC15 (not shown) are very similar to those of RXC60 and RXM, respectively, as expected on the basis of the compositions of these fractions, given in Table III.

The toluene soluble fractions have been shown by IR and TG measurements to consist mainly of PEox, with minor amounts of SBH segments, whose content is maximum (ca. 12%) for NCC15. It may be interesting to point out that even the SEM micrograph of the latter fraction fails to show the presence of a dispersed phase. This can be explained assuming that SBH is contained in this fraction as fairly short branches chemically bonded to the PE chains and is therefore unable to segregate as a separate phase.

CONCLUSION

In a previous work,[13] it was shown that PE-g-SBH copolymers may be synthesized by the melt poly-

condensation of the SBH monomers carried out in the presence of a PE sample containing functional carboxyl groups (PEox). The results of this work demonstrate that similar PE-g-LCP copolymers may also form during the reactive blending of PEox with preformed SBH. The extent to which these copolymers are produced increases with the mixing time and, on a composition ground, approaches that found by the polycondensation method when the mixing time is of ca. 120 min. Therefore, it can be expected that the reactive blends prepared in this work may also display a compatibilizing effect toward mechanical PE/SBH blends. To prove this, preliminary experiments were made through the preparation and the morphological characterization of 80/20 HDPE/SBH blends containing different amounts of COP120, as described in the experimental section. In Figure 10, the SEM micrograph of the 76/8/16 HDPE/COP120/SBH ternary blend is compared to that of the 80/20 HDPE/SBH binary blend. The improvement of both phase dispersion and interfacial adhesion brought about by the addition of COP120 is evident. Similar results were
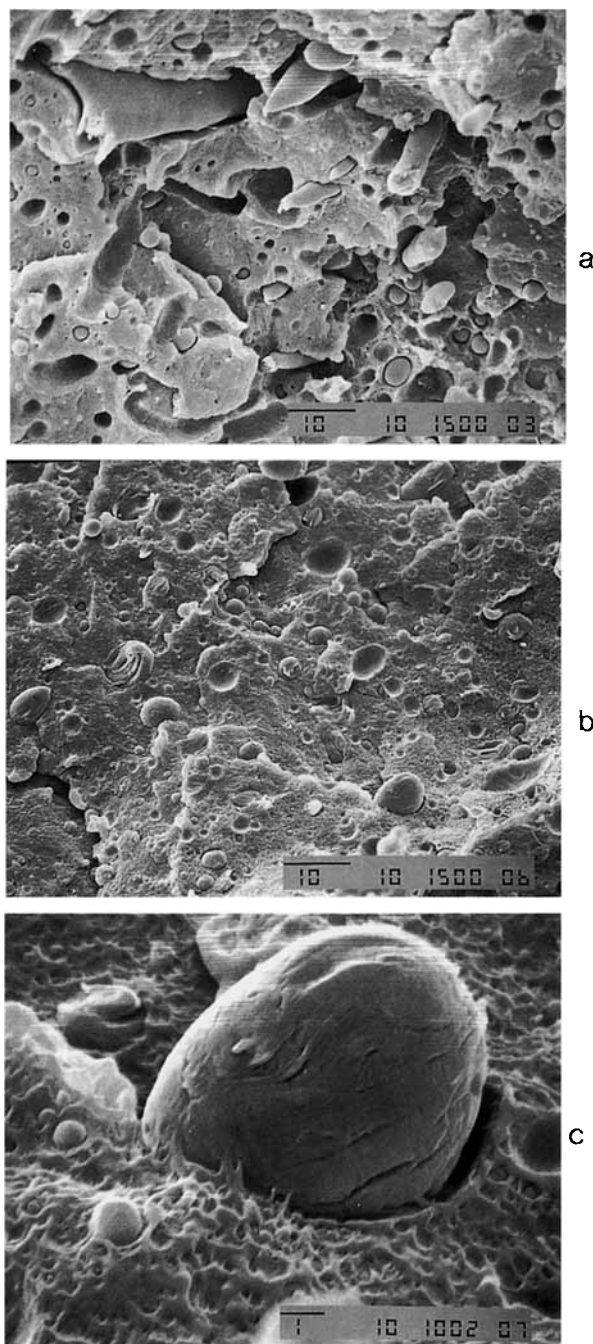
Figure 10 SEM micrographs of 80/20 HDPE/SBH (a) and 76/8/16 HDPE/COP120/SBH (b) and (c) blends.

also found in the previous work by the addition of the PE-*g*-SBH copolymer prepared by polycondensation. However, these preliminary SEM investigations are not sufficient for a reliable comparison of the compatibilizing effects of the two materials. On the other hand, on the basis of the present results, it may be concluded that the PE-*g*-SBH co-

polymers prepared by the two procedures have slightly different structures. In fact, whereas in the polycondensation described in the previous paper,[13] a fairly quantitative esterification of the PEox carboxyl groups was shown to take place, the reactive blending described here leads to a lesser extent of grafting, but the length of the SBH branches is probably higher. A rheological and mechanical characterization of HDPE/SBH blends containing the two types of alleged compatibilizers is underway.

REFERENCES

1. F. P. La Mantia, *Thermotropic Liquid Crystal Polymer Blends*, Technomic Publishing Co., Lancaster, 1993.
2. W. Brostow, *Polymer*, **31**, 979 (1990).
3. D. Dutta, H. Fruitwala, A. Kohli, and R. A. Weiss, *Polym. Eng. Sci.*, **30**, 1005 (1990).
4. G. Crevecouer and G. Goeninckx, *Polym. Eng. Sci.*, **30**, 532 (1990).
5. R. A. Weiss, N. S. Chung, and D. Datta, *Am. Chem. Soc. Prep.*, **30**, 544 (1989).
6. B. R. Bassett and A. F. Yee, *Polym. Comp.*, **11**, 10 (1990).
7. T. Harada, K. Tomari, A. Hamamoto, S. Tonogai, K. Sakaura, S. Nagai, and K. Yamaoka, *SPE Antec-92*, 1992, p. 576.
8. A. M. Lichkus and J. R. Harrison, *SPE Antec-92*, 1992, p. 2257.
9. T. C. Hsu, A. M. Lichkus, and J. R. Harrison, *Polym. Eng. Sci.*, **33**, 860 (1993).
10. E. G. Fernandes, I. Giolito, and E. Chiellini, *Thermochim. Acta*, **235**, 67 (1994).
11. U. Pedretti, A. Roggero, F. P. La Mantia, and P. L. Magagnini, *SPE Antec-93*, 1993, p. 1706.
12. F. P. La Mantia, C. Geraci, M. Vinci, U. Pedretti, A. Roggero, L. I. Minkova, and P. L. Magagnini, *J. Appl. Polym. Sci.*, **58**, 911 (1995).
13. P. L. Magagnini, M. Paci, L. I. Minkova, Ts. Miteva, D. Sek, J. Grobelny, B. Kaczmarczyk, *J. Appl. Polym. Sci.*, to appear.
14. R. S. Porter and L. H. Wang, *Polymer*, **33**, 2019 (1992).
15. G. V. Laivins, *Macromolecules*, **22**, 3974 (1989).
16. K. Friedrich, M. Hess, and R. Kosfeld, *Makromol. Chem., Macromol. Symp.*, **16**, 251 (1988).
17. L. H. Wang and R. S. Porter, *J. Polym. Sci.*, **B31**, 1067 (1993).

18. C. M. McCullagh, J. Blackwell, and A. M. Jamieson, *Macromolecules*, **27**, 2996 (1994).

19. A. Datta and D. G. Baird, *Polymer*, **36**, 505 (1995).

20. A. Datta, A. M. Sukhadia, J. P. Desouza, and D. G. Baird, *SPE Tech. Pap.*, **49**, 913 (1991).

21. A. Datta, H. H. Chen, and D. G. Baird, *Polymer*, **34**, 759 (1993).

22. P. L. Magagnini, U. Pedretti, G. Perego, B. Bresci, S. Carrozzino, and A. Roggero, U.S. Pat. 4,833,229 (1989).

23. U. Pedretti, A. Roggero, V. Città, E. Montani, F. P. La Mantia, and P. L. Magagnini, in *Processing and Properties of Liquid Crystalline Polymers and LCP Based Blends*, D. Acierno and F. P. La Mantia, Eds., ChemTec Publishing, Toronto, 1993, p. 43.

24. L. M. Robeson and A. B. Furtek, *J. Appl. Polym. Sci.*, **23**, 645 (1979).

25. A. M. Zaldua, M. E. Muñoz, J. J. Peña, and A. Santamaria, *Macromol. Rapid Commun.*, **16**, 417 (1995).

26. B. Wunderlich, *Macromolecular Physics*, Vols. 2 and 3, Mir, Moscow, 1979 and 1984, respectively.