

# Investigations of graft copolymer compatibilizers for blends of polyethylene and liquid crystalline polyester: 1. FT i.r. study

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Graft copolymers of functionalized polyethylene having free carboxylic groups /PEox/ and liquid crystalline polyester SBH derived from sebacic acid, 4,4'-dihydroxybiphenyl and 4-hydroxybenzoic acid, prepared in various conditions, as well as fractionation products of the graft copolymers, were investigated by infra-red spectroscopy. The grafting has been followed by changes in the amount of carboxylic and aliphatic-aromatic ester groups. © 1997 Elsevier Science Ltd.

(Keywords: functionalized polyethylene; liquid crystalline polyester; graft copolymers)

## INTRODUCTION

In the field of new materials with improved properties, polymer blends are one of the groups developing rapidly. Existing polymers can be combined to provide materials which offer unique properties unattainable in either of the components. The properties of the blend depend also on the morphology, mainly on the degree of dispersion and diameter of the dispersed particles.

Blends of flexible thermoplastics with liquid crystalline polymers (LCP) have recently attracted considerable attention<sup>1</sup>. Unfortunately, the majority of thermoplastics are incompatible with common aromatic liquid crystalline polymers, resulting in a poor dispersion and low reinforcing effect. In order to improve miscibility of the polymers, compatibilizers are used. The latter are usually block or graft copolymers capable of acting as interfacial agents in polymer blends<sup>2–4</sup>. Usually the blocks of the compatibilizer are identical with the blend components. Such macromolecules are expected to be present at the interface of dissimilar polymers because part of the compatibilizer is miscible with one component and part with the other<sup>5</sup>. The compatibilizer is designed to reduce the interfacial energy, improve the interfacial adhesion and permit a finer dispersion during mixing of the blend components.

In our previous papers<sup>6,7</sup> the synthesis of PE-g-LCP copolymers as potential compatibilizers for PE/LCP blends has been described. The copolymers were prepared either by the reaction of a PE sample containing free carboxyl groups (PEox) with LCP monomers<sup>6</sup> or by the reactive blending of PEox with pre-formed LCP<sup>7</sup>. The LCP, referred hereafter to as SBH, was synthesized from sebacic acid (S), 4,4'-dihydroxybiphenyl (B) and 4-hydroxybenzoic acid (H) in the molar ratio of 1:1:2. In

order to define the structure of the copolymers, the latter were fractionated with boiling toluene and xylene, and the fractions characterized by differential scanning calorimetry (d.s.c.) and scanning electron microscopy (SEM). Some preliminary studies were also performed by means of i.r. and n.m.r. spectroscopy. In this paper the i.r. investigations are presented.

## EXPERIMENTAL

### Materials

In the work the following three groups of the products were characterized:

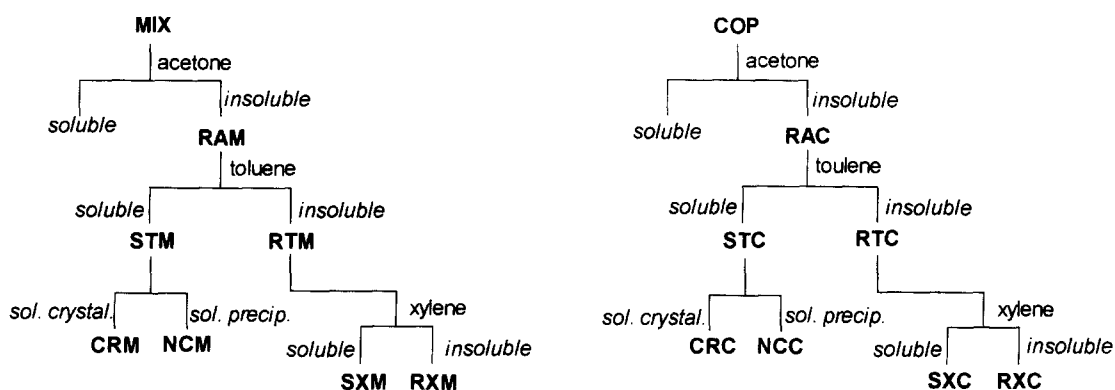
- (i) a mixture (MIX) of PEox with liquid crystalline polyester SBH and the products of extractions,
- (ii) the products of catalytic transesterification reactions of PEox and SBH carried out for 15, 60 and 120 min (COP15, COP60, COP120) and the compounds obtained after extraction,
- (iii) the copolymer (COP) of PEox with monomers from which polyester SBH was made and the products of extractions.

In all cases the weight ratio of PEox to SBH was 1:1. The extraction scheme and the sample designations are presented in *Scheme 1*.

### Measurements

I.r. spectra were recorded on a BIO-RAD FTS 40A spectrometer. The specimens were in the form of KBr pellets. For quantitative determination of the ratio of the amounts of PEox and SBH in the reaction products and fractionated samples, the second derivative spectra were used. The second derivatives were calculated with the aid of a WIN IR arithmetic program, using the Savitsky–Golay method (degree of polynomial 9 and number of convolution points 20) and using the baseline-to-peak technique.

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Scheme 1

## RESULTS AND DISCUSSION

In order to investigate the SBH/PEox system the FTi.r. method was used. This method was expected to be useful in determining the relative amounts of PEox and SBH components in the products of mixing (MIX) and esterification reactions (COP) as well as in the extraction products (RX, NC).

Due to the insolubility of the investigated compounds in solvents used in i.r. spectroscopy, the KBr pellets technique had to be used. Consequently it was impossible to determine the absolute values of the contents of the substrates, and only the intensity ratios of the bands characteristic for PEox and SBH could be calculated. These ratios were used to compare the contents of PEox and SBH in the products.

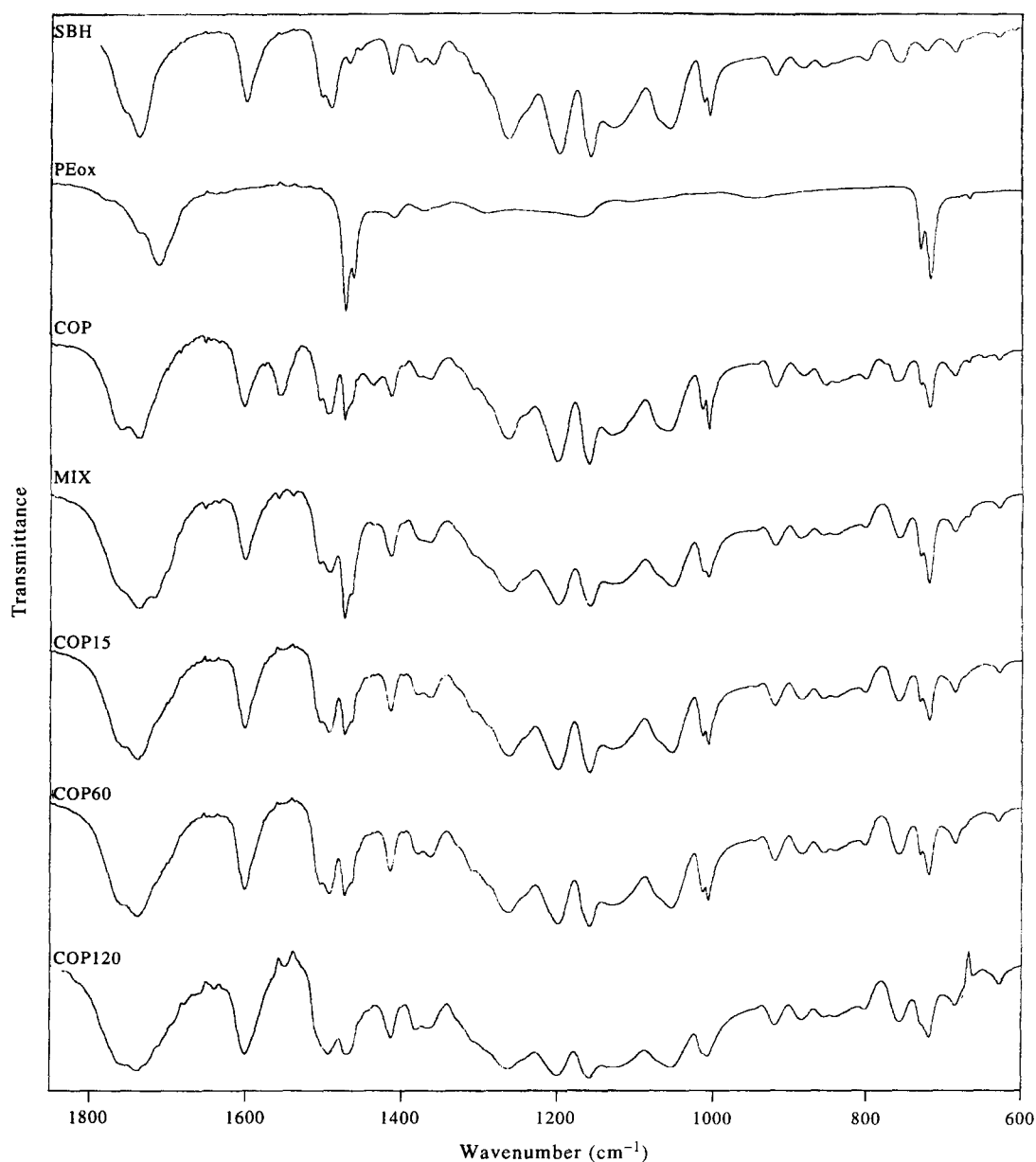


Figure 1 FTi.r. spectra of mixing, transesterification reactions and copolymerization reaction products

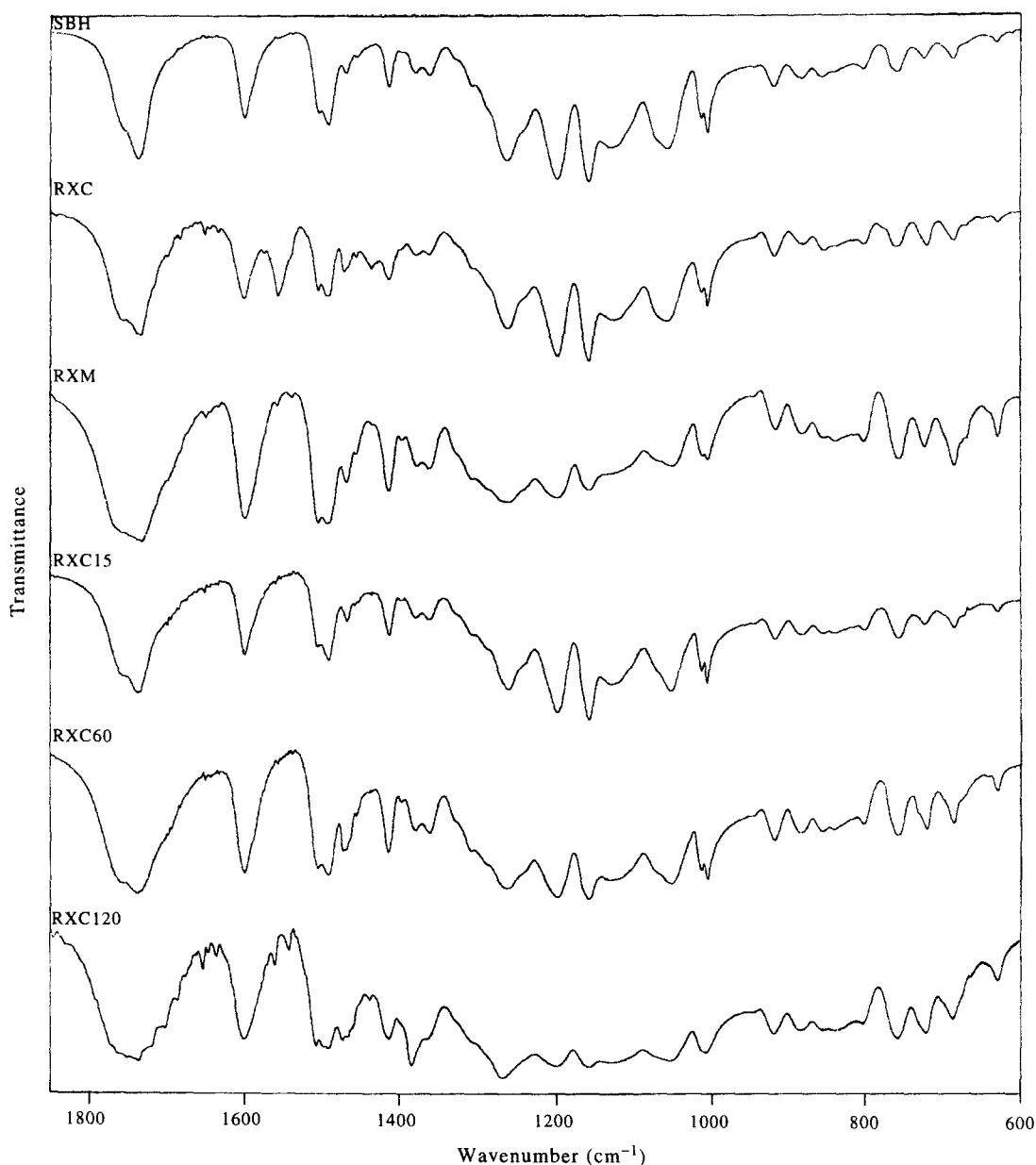


Figure 2 FTIR spectra of the fractions insoluble in xylene

Comparing the i.r. spectra of PEox and SBH with the spectra of mixture (MIX), products after esterification (COP, COP15, 60, 120) and after extraction (RX, NC) it may be noted that all the bands characteristic for PEox and SBH appeared in the spectra of the compounds investigated but with different intensities (Figures 1–3). However, the most interesting changes were observed for the bands arising from ester and acid groups in the region of  $1800\text{--}1700\text{ cm}^{-1}$ . Comparison of these bands yields certain information on the course of the esterification reaction under various conditions.

In order to determine the quantitative relations among the three kinds of the overlapped bands corresponding to C=O stretching vibrations, i.e. aliphatic–aromatic ester, aromatic–aromatic ester and acid, arithmetic calculations were used. The initial parameters for curve fitting program were obtained from the second derivatives. The centres of the overlapped peaks and their width at half-height in each derivative spectrum in the region of  $1850\text{--}1660\text{ cm}^{-1}$  were determined. On the basis of the data obtained from these calculations, the curve fitting program was initiated. We have chosen the ‘interactive’

procedure to correct the introduced parameters and particular peaks were computed. The results are shown in Table 1.

Analysing the spectrum of PEox and the data from curve fitting calculations (Table 1, no. 2) we found bands with comparable intensity at  $1714$  and  $1738\text{ cm}^{-1}$  characteristic, respectively, for associated and free acid C=O groups. Also the bands corresponding to the CH<sub>2</sub> group vibrations at  $2900\text{--}2800\text{ cm}^{-1}$ ,  $1472$ ,  $1460$ ,  $730$  and  $718\text{ cm}^{-1}$  were observed.

For SBH the band corresponding to C=O aromatic–aromatic ester groups at  $1731\text{ cm}^{-1}$  overlapped with the band at  $1758\text{ cm}^{-1}$  from aliphatic–aromatic ester groups was observed. The curve fitting procedure reveals very weak bands at  $1714$  and  $1740\text{ cm}^{-1}$  attributed to free and associated acid groups vibrations, respectively. It proves that a small amount of acid is present in SBH. The bands characteristic for aromatic ring vibrations were noted at  $1600$ ,  $1500$  and  $1006\text{ cm}^{-1}$ .

In the region of  $1300\text{--}1100\text{ cm}^{-1}$  some bands corresponding to the vibrations of C–O– in ester groups were seen. The bands arising from aliphatic –CH<sub>2</sub>– groups

**Table 1** 'Curve fitting' calculations of the areas of C=O groups of aliphatic–aromatic ester ( $A_{al-ar}$ ), aromatic–aromatic ester ( $A_{ar-ar}$ ), acid free ( $A_{afree}$ ) and acid associated ( $A_{aass}$ ) peaks

No.	Sample <sup>a</sup>	C=O aliphatic–aromatic ester band		C=O aromatic–aromatic ester band		C=O acid free band		C=O acid associated band	
		$\nu(\text{cm}^{-1})$	$A_{al-ar}/A_T^b$	$\nu(\text{cm}^{-1})$	$A_{ar-ar}/A_T^b$	$\nu(\text{cm}^{-1})$	$A_{afree}/A_T^b$	$\nu(\text{cm}^{-1})$	$A_{aass}/A_T^b$
1	SBH	1758.1	0.510	1731.3	0.262	1740.3	0.197	1713.6	0.030
2	PEox					1738.1	0.423	1714.3	0.577
3	COP	1762.1	0.493	1733.0	0.160	1741.4	0.179	1719.0	0.167
4	MIX	1762.0	0.422	1730.0	0.273	1739.3	0.072	1715.2	0.234
5	COP15	1759.8	0.571	1729.7	0.162	1741.8	0.049	1711.3	0.229
6	COP60	1759.5	0.581	1729.8	0.160	1741.4	0.046	1712.0	0.213
7	COP120	1761.1	0.587	1729.6	0.165	1737.7	0.109	1708.2	0.138
8	RXC	1761.8	0.440	1733.6	0.270	1742.1	0.194	1717.1	0.095
9	RXM	1765.5	0.496	1730.1	0.283	1745.8	0.068	1716.2	0.151
10	RXC15	1758.9	0.563	1733.8	0.223	1741.6	0.054	1714.2	0.160
11	RXC60	1762.2	0.600	1729.7	0.222	1742.1	0.099	1713.0	0.079
12	RXC120	1767.5	0.630	1734.4	0.201	1746.3	0.086	1708.0	0.083
13	NCC	1763.7	0.528	1733.3	0.014	1739.7	0.138	1719.0	0.319
14	NCM					1738.1	0.448	1715.5	0.551
15	NCC15	1759.3	0.403	1735.1	0.179	1741.4	0.080	1716.3	0.337
16	NCC60	1762.2	0.384	1735.6	0.127	1741.1	0.110	1717.4	0.379
17	NCC120	1764.1	0.360	1733.4	0.074	1738.7	0.119	1717.6	0.447

<sup>a</sup> Sample designations as in Scheme 1<sup>b</sup>  $A_T = A_{al-ar} + A_{ar-ar} + A_{afree} + A_{aass}$ 

were also present, but with lower intensity than that observed in PEox.

When comparing the FTi.r. spectra of SBH, PEox, COP and MIX (Figure 1) it can be concluded that MIX is the 'mechanical mixture' of SBH and PEox. However, the spectrum of MIX was not identical with that obtained by adding the SBH and PEox spectra (Figure 4). The differences mainly concerned the band corresponding to the stretching vibrations of C=O groups. In the spectrum obtained by adding the spectra of SBH and PEox there was a lack of the shoulder at about 1762 cm<sup>-1</sup>, which was visible in the MIX spectrum. It indicates some interactions between PEox and SBH (e.g. hydrogen bonds) or it may be a result of changes in PEox or SBH structure during preparation of MIX.

The spectrum of COP differed from that of MIX. The differences between COP and MIX can be noted,

**Table 2** Intensity ratios of aliphatic–aromatic ester bands to acid bands in the products of the reactions and after extraction

Sample <sup>a</sup>	$A_{al-ar}/(A_{afree} + A_{aass})^b$
MIX	1.38
COP	1.42
COP15	2.02
COP60	2.05
COP120	2.32
RXM	2.27
RXC	1.52
RXC15	2.63
RXC60	3.39
RXC120	3.72
NCM	—
NCC	1.15
NCC15	0.97
NCC60	0.79
NCC120	0.64
SBH	2.25

<sup>a</sup> Sample designations as in Scheme 1<sup>b</sup> Designations as in Table 1

particularly for the band characteristic for carbonyl group at 1765–1710 cm<sup>-1</sup> (Figure 1). For MIX this band, exhibiting many shoulders, is wide and of slightly lower intensity. In the case of COP the two overlapped bands at 1762 and 1733 cm<sup>-1</sup> characteristic for aliphatic–aromatic and aromatic–aromatic ester groups, and at 1741 and 1719 cm<sup>-1</sup> assigned to free and associated acid groups were observed. Comparing the data from curve fitting calculations for COP and MIX (Table 1, nos 1, 3 and 4) it may be noted that in MIX the relative amount of C=O aliphatic–aromatic band is smaller than in COP. It may indicate that carboxylic groups from PEox react during polycondensation. In the spectrum of COP the band at 1555 cm<sup>-1</sup> may be observed. This band was not seen in the case of the other compounds and may be ascribed to the COO<sup>-</sup> anion.

The spectra of the transesterification reaction products of PEox and SBH (COP15, COP60, COP120) exhibited the presence of the bands arising from the both components (Figure 1). In these samples (Table 1, nos 5, 6 and 7) the amount of acid groups decreased with the time of reaction, whereas the amount of aliphatic–aromatic ester groups increased. Thus with longer reaction time more acid groups are involved in the reaction to form aliphatic–aromatic ester groups. Some differences can also be seen in the spectra of the extraction products.

Spectra of the insoluble fractions obtained after the extraction procedure (in particular RXM and RXC15) were similar to that of SBH (Figure 2) in which only some changes for bands corresponding to ester and acid groups can be noticed. In the RXC60 and RXC120 spectra the bands characteristic for PEox were also visible.

Arithmetic calculations show higher contents of aliphatic–aromatic ester groups and considerably lower contents of acid groups in RXC60 and RXC120 than in COP60 and COP120 (Table 1, nos 11, 12 and 6, 7),

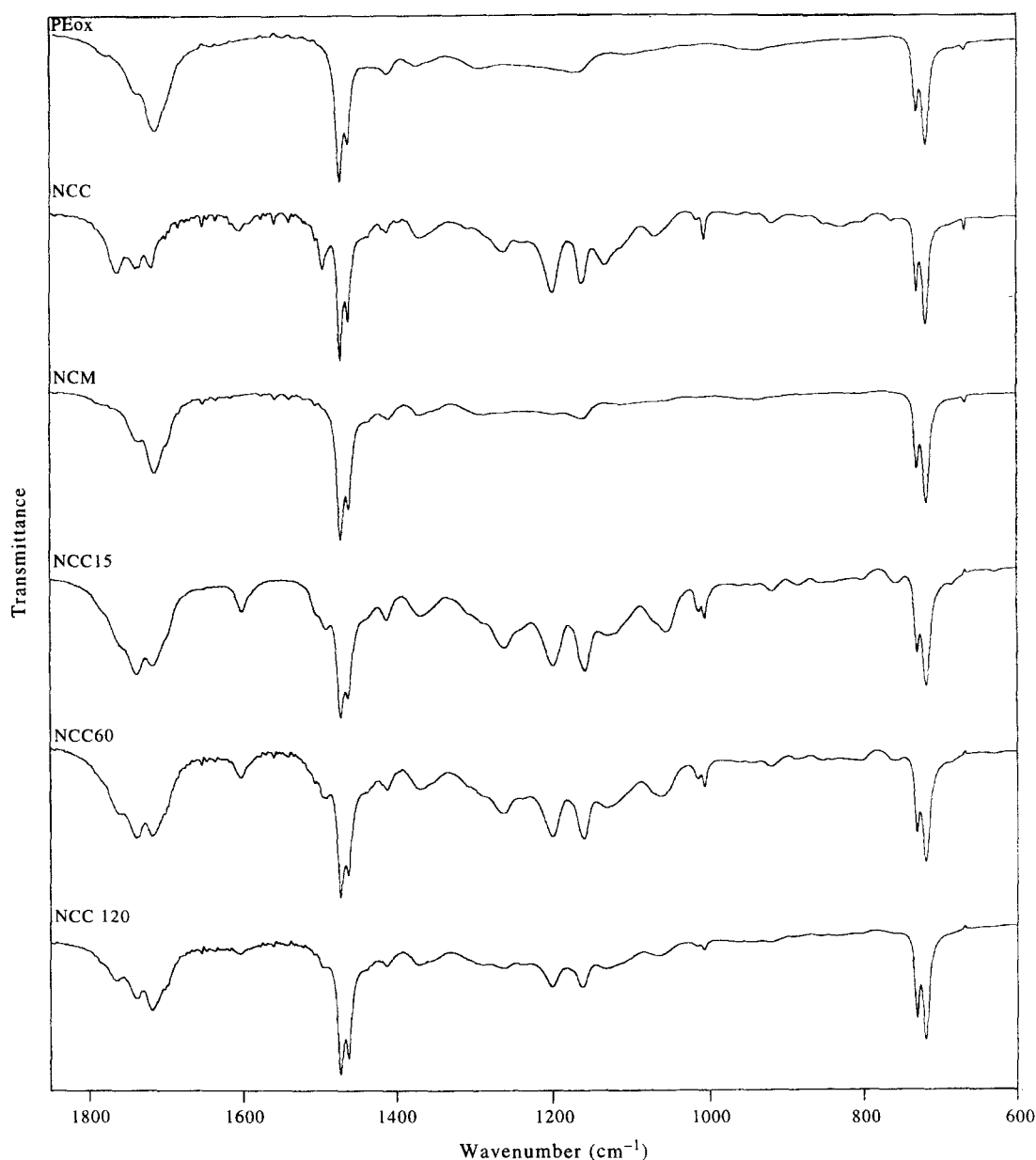


Figure 3 FTIR spectra of the fractions soluble in toluene

respectively. In the insoluble fractions the relative amount of aliphatic–aromatic ester bands increased with reaction time while the amount of acid bands decreased.

The soluble fractions spectra are similar to that of PEox (Figure 3) but the spectrum of NCM is almost identical to that of PEox. In NCM the intensity ratio of the bands at 1738 and 1715  $\text{cm}^{-1}$  is nearly the same as in PEox (Table 1, nos 14 and 2). The spectra of NCC15, NCC60 and NCC120 are very similar to that of PEox, but some bands characteristic for SBH can also be observed.

Computer calculations indicate that the amounts of acid groups in NCC15, NCC60, NCC120 are higher than in COP15, COP60 and COP120 (Table 1, nos 15, 16, 17 and 5, 6, 7), respectively, and they increase with the time of reaction. On the other hand the amounts of aliphatic–aromatic ester groups in these samples decrease with the reaction time. It may thus be concluded that the soluble fractions contain pure PEox (NCM) or PEox partly reacted with SBH (NCC15, NCC60, NCC120), while insoluble fractions consist of SBH reacted to a different

degree with PEox. Different amounts of the two components in the reaction products affect their solubility.

In conclusion, when the reaction time of PEox with SBH is longer, the amounts of aliphatic–aromatic ester groups relative to free carboxylic groups of PEox in the reaction products increase. It means that more carboxylic groups of PEox reacted with SBH (Table 2).

In the case of the fractions insoluble in xylene (RXC15, RXC60, RXC120) the intensity ratio of the aliphatic–aromatic ester bands to the carboxylic bands of PEox also increases with the time of reaction, but generally this ratio is much higher than in the case of the unfractionated products of the reactions. This ratio for RXM is very close to that for SBH, although the amounts of particular bands differ from each other.

For the soluble fractions the ratios of the aliphatic–aromatic ester bands to the carboxylic bands of PEox are lower than for the reaction products and decrease with the reaction time. It indicates that during longer reaction time more carboxylic groups of PEox have reacted with SBH lowering a solubility of the product. Consequently,

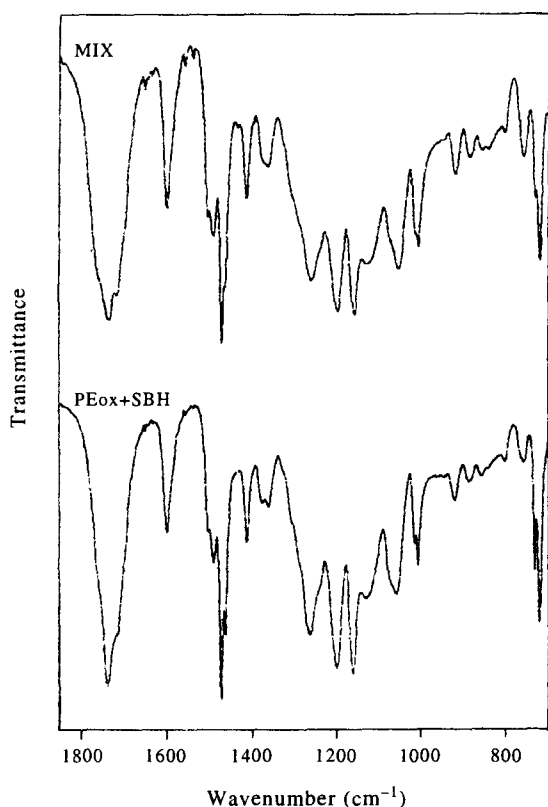


Figure 4 FTIR spectrum of MIX and the spectrum obtained by adding the PEOx and SBH spectra and dividing by 2

this product was found to be present in the insoluble fraction.

As seen from Table 1 the curve fitting program also allows us to observe the changes in the ratio between the free and associated acid groups during the reaction processes.

The above calculations concern the band arising from ester or acid groups and they show only the changes of this band during esterification and after extraction.

An attempt was made to utilize another absorption band for quantitative analysis of the contents of SBH and PEOx in the compounds investigated. The bands corresponding to aromatic ring vibrations appear only in SBH and can be considered as representative bands for this component. In PEOx, aside from the band attributed to acid groups, only the bands characteristic for aliphatic  $-CH_2-$  groups appear. The bands due to aliphatic groups appear also in the SBH spectrum but they are slightly shifted as compared to PEOx (Figure 1).

The common quantitative analysis is not useful in our case because the differences in position of bands investigated are not sufficiently large and the bands tend to overlap. Thus for the quantitative determination of the amounts of SBH and PEOx in our compounds the derivative spectra were used. It was found that the second derivatives of the bands characteristic for SBH aromatic ring vibrations at 1602 and 1006  $cm^{-1}$  exhibit maxima, while for PEOx the second derivative at these wavenumbers equals zero. For the bands characteristic for PEOx at 1472 and 718  $cm^{-1}$ , the second derivatives reach maxima, while for SBH they equal zero. However, the band at 1602  $cm^{-1}$  appears to be inadequate for quantitative analysis, because in some compounds investigated the second derivative bands at this position are too wide, with no clear maximum, whereas the band at 718  $cm^{-1}$  depends on the sample crystallinity. Thus to compare the contents of SBH and PEOx in the products, the bands at 1006 and 1473  $cm^{-1}$  have been chosen (Figures 5 and 6).

For the insoluble fractions RXM and RXC15, the second derivative at 1472  $cm^{-1}$  equals zero. It confirms that RXM and RXC15 contain pure SBH exclusively.

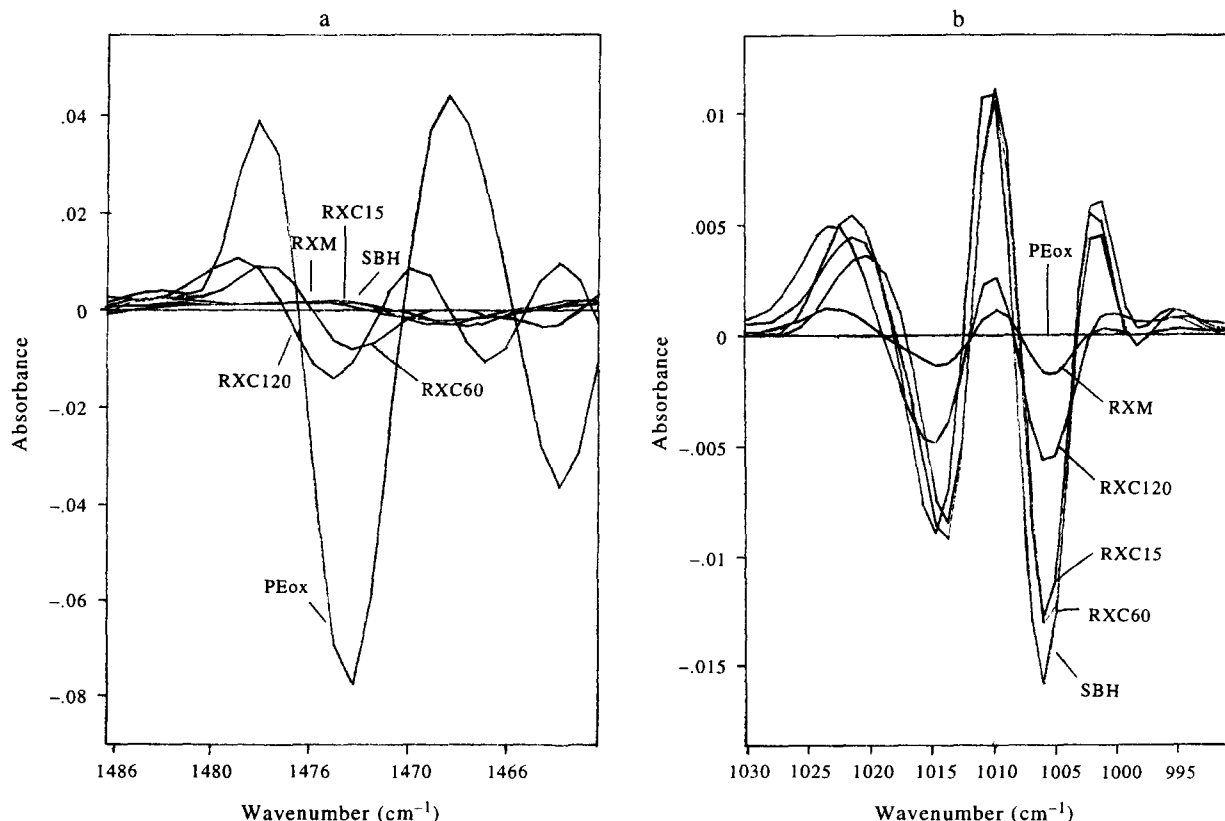


Figure 5 The second derivative spectra of the fractions insoluble in xylene

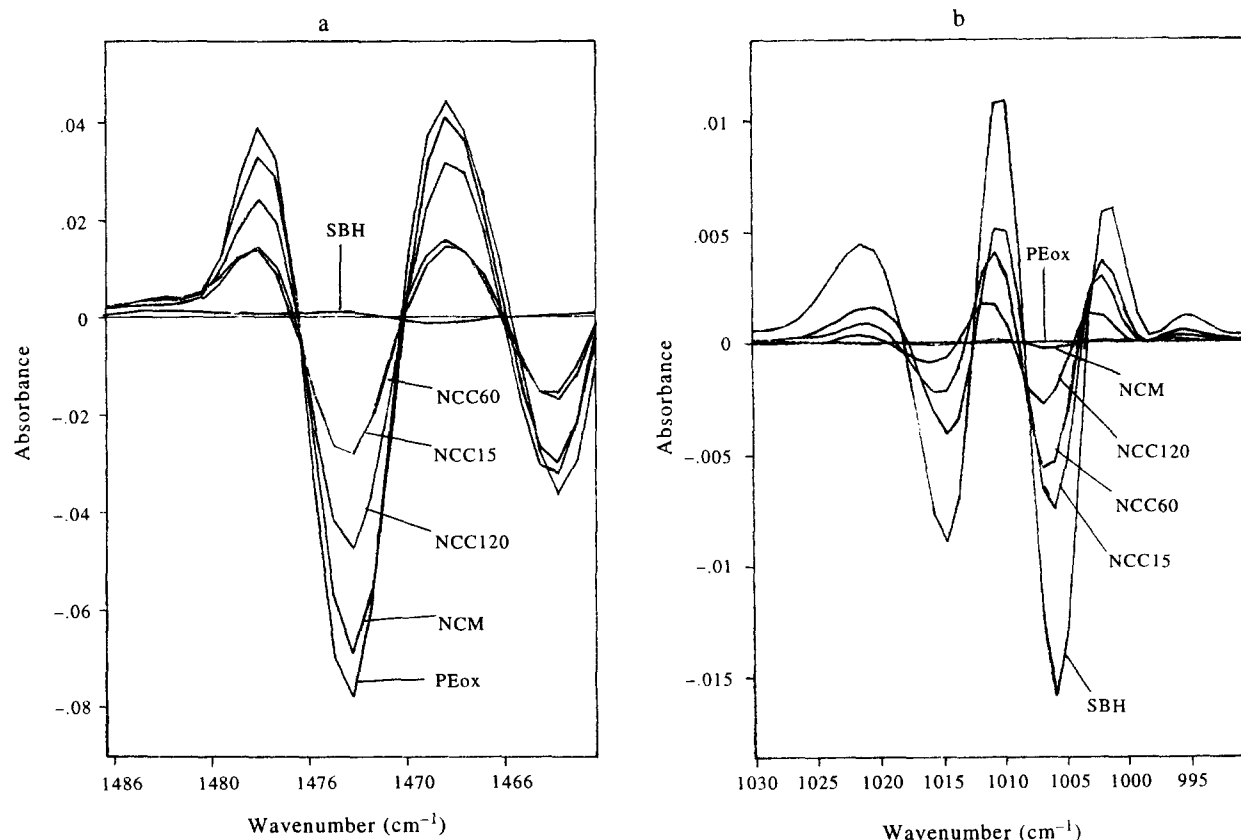


Figure 6 The second derivative spectra of the fractions soluble in toluene

Some amount of PEox can be found in the case of RXC60 and RXC120 (Figure 5). To determine the amounts of PEox in RXC60 and RXC120 the following ratios of the values of the second derivatives at 1472 and at  $1006\text{ cm}^{-1}$  have been calculated:

RXC60	0.57
RXC120	2.50

From these calculations it follows that in RXC120 there is about 4.4 times more PEox than in the case of RXC60. As mentioned above the spectra of the soluble fractions are similar to that of PEox and only small amounts of SBH have been found.

To determine the contents of SBH in soluble fractions, the ratios of the values of the second derivative at  $1006\text{--}1472\text{ cm}^{-1}$  (Figure 6) have been obtained:

NCC15	0.27
NCC60	0.20
NCC120	0.06

It indicates that in NCC120 there is about 3.4 times less SBH than in NCC60 and 4.5 times less than in NCC15. In the spectrum of NCM there is no band characteristic for aromatic ring and the second derivative of NCM at  $1006\text{ cm}^{-1}$  equals zero. It supports our previous conclusions that it is pure PEox.

In summary, it was demonstrated that during mixing of PEox with SBH with no catalyst added a mechanical mixture was obtained and after extraction the pure components can be separated. In the presence of the catalyst the esterification reaction occurred. The longer time of reaction causes more PEox to react with SBH.

After extraction the insoluble fractions were mainly SBH containing a certain amount of PEox, even though not all the acid groups in PEox chain reacted with SBH. The soluble fractions contained mainly PEox but with some acid groups reacted with SBH.

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