

## Determination of small interactions in polymer composites by means of FTIR and DSC

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Received: 8 November 1999/Revised version: 31 January 2000/Accepted: 1 March 2000

### Summary

This paper studies polymer composites formed by a polystyrene matrix (PS) and a block copolymer of poly(styrene-butadiene) (SBS). Two series of polymer composites with different compositions have been prepared: the first by extrusion followed by injection and the second by dissolution and evaporation of the solvent from the injected samples. The comparison of the FTIR spectra of the polymer composites with those simulated by addition of the spectra of the component polymers allows the detection of differences attributed to the existence of interactions between both polymers that cause partial miscibility between them. The results obtained are corroborated by differential scanning calorimetry.

### Introduction

The addition of an elastomeric reinforcement to a rigid polymer improves its tenacity. Materials made in this way are known as polymer composites. In them, the modification achieved depends on numerous factors such as the morphology of the reinforcement, its ratio and compatibility (partial miscibility) of the polymers used (1,2). Though the polymer composites used are generally immiscible they have to display favourable intermolecular interactions to obtain the necessary interfacial adhesion allowing the desirable improvement in properties. In many cases, the origin of the intermolecular forces causing compatibility is not wholly known, therefore the application of techniques leading to the detection of characteristic features of these phenomena is particularly interesting.

One of the techniques used in the detection of intermolecular forces in polymer composites is FTIR spectroscopy. The position, form and intensity of spectral bands provides useful information about the microstructure of polymers at a molecular level, although, in most cases, the effects of intermolecular forces on the spectrum are small, due to its low energetic level as compared to the intrachain covalent bonds. In any case, FTIR spectroscopy has been widely used to study miscible blends of polymers, specially when relatively strong interactions appear as hydrogen bonds (3). In the case of polymer composites with weaker intermolecular forces, the spectral subtraction has occasionally been used to show the small changes produced (4). Thermostable materials reinforced by glass fibre (5), materials based on polyethylene with wood (6) and composites based on polycarbonate and acrylonitrile-butadiene-styrene (7) have been studied. The materials to be considered in this paper are polymer composites formed by a polystyrene matrix (PS) and an elastomeric component formed by a block copolymer of poly(styrene-butadiene) (SBS).

The technique of differential scanning calorimetry (DSC) has also been used to study polymer composites. In general, a polymer composite is deemed to be miscible when one single glass transition temperature is observed. Both techniques have proved to be satisfactorily complementary in numerous works (8,9).

In this study, PS/SBS polymer composites have been prepared with different composition ratios by methods of extrusion and subsequent injection of these materials; their characteristics have been compared to those of polymer composites made by simulation from the spectra of the component polymers and, also, to polymer composites obtained through dissolution-evaporation of the injected samples in order to detect different levels of interaction. Samples were later subjected to calorimetric analysis to complete the results.

## Experimental

### *Materials*

PS was supplied by BASF ESPAÑOLA, S.A., commercially known as E-143. This degree has an average molecular mass of 274 000, glass transition temperature of 81°C and a melt flow index of 0.768 g/min.

The disperse phase is the SBS copolymer provided by REPSOL, known as CALPRENE 416. It is a block copolymer styrene-butadiene-styrene containing 30% styrene and is obtained by polymerization in solution.

### *Preparation of polymer composites*

To prepare the polymer composites, two procedures have been followed: the first consists of the extrusion-injection of pellets from both materials and the second consists of the dissolution of the materials resulting from the former process followed by evaporation of the solvent obtained from a film.

In the polymer composites obtained by injection, the operating parameters were: injection pressure = 30 MPa; backpressure (for a better blending) = 15 MPa; Temperature = 190 °C; injection time = 0.7 s; total time of process = 30 s. These conditions were established following the manufacturer's recommendations regarding the temperatures of the PS and SBS process and the parameters of the mould to avoid imperfections in the piece. The injection machine was a BOY 22.

Polymer composites obtained by dissolution were made from the materials attained by extrusion-injection being dissolved in toluene and evaporating the solvent at 70°C on NaCl crystals.

Percentages of the prepared polymer composites, expressed in SBS weight percent were: 0% (pure PS), 20%, 40%, 60%, 80% and 100% (pure SBS).

### *FTIR spectroscopy*

Spectra of the extruded material have been obtained from the homogeneous dispersions of finely divided material (7 mg) in KBr submitted to compression at 167 MPa to consolidate the formation of pellets.

Spectra of samples by dissolution were obtained from films on NaCl crystals. Films were prepared under identical conditions to eliminate as much as possible the effect of the concentration difference and the evaporation rate.

Spectra were obtained on a Nicolet 510 M spectrophotometer with CsI optics averaging 200 scans at a resolution of 2 cm<sup>-1</sup>. Spectra were stored on disk for subsequent treatment.

## DSC

Thermograms were obtained on a Mettler DSC 30 calorimeter. The sample mass was selected between 9 and 11 mg, being small enough to avoid problems with temperature gradients. The temperature range studied was between -120 and 100°C. The heating rate was 10 °C/min. Calibration of temperatures and energies was performed with a standard of In, Pb and Zn, using the very same analytical conditions as with samples.

## Results and discussion

### FTIR spectroscopy

A study of the films obtained has been carried out by comparing their spectra over time; spectra were recorded every 24 h to detect any possible alterations caused by changes in the polymer conformations in the polymer composites. No differences have been detected which suggests that these polymers do not change their conformation at room temperature.

Three types of spectra have been compared: spectra obtained in KBr pellets of the injected samples, spectra of films prepared by dissolution of the former samples and spectra obtained by point-to-point addition of spectra corresponding to the pure original polymers, in ratios simulating the compositions.

The simulated spectra of the compositions studied represent the theoretical spectrum of the polymer composite if no type of interaction exists between the polymers. The spectra obtained from films show some differences when compared to the simulated. Displacements can be observed in the absorption maxima of some bands. This means that some of the dipoles existing in the polymers undergo vibrational alterations due to the change in their environment caused by the presence of another component. Alterations occur by the participation in intermolecular interactions which make the partial miscibility possible.

Some of the bands where the mentioned displacements occur are found at: 910  $\text{cm}^{-1}$ , 965  $\text{cm}^{-1}$  and 3002  $\text{cm}^{-1}$ . Figures 1 and 2 show examples of these alterations which are observable in the compositions studied being higher in the polymer composites containing a greater proportion of SBS. This was expected, for in the polymer composites with the highest contents of SBS there are more dipoles altered in their vibrational behaviour by the change of their environment and therefore, the displacement can be larger.

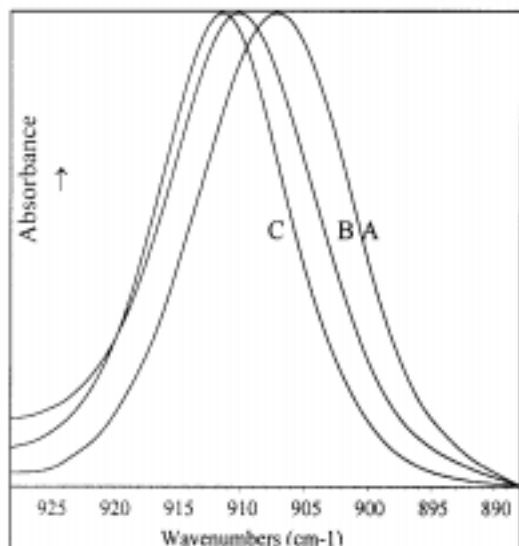


Figure 1: Infrared spectrum in the region of 900-920  $\text{cm}^{-1}$ .  
 A: Simulated polymer composite (40% SBS).  
 B: Polymer composite film (40% SBS).  
 C: Polymer composite film (80% SBS).

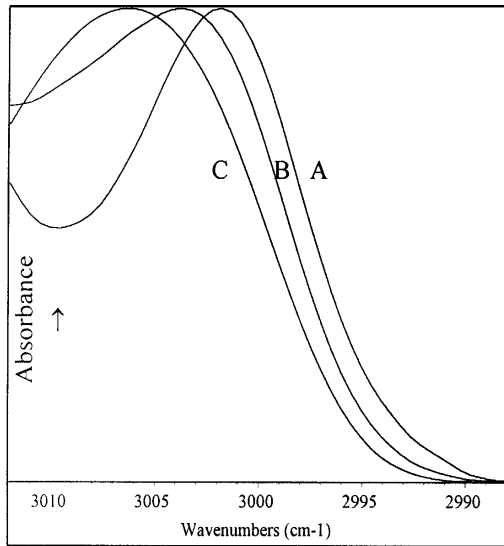


Figure 2: Infrared spectrum in the region of 2990-3010  $\text{cm}^{-1}$ .  
 A: Polymer composite film (20% SBS).  
 B: Polymer composite film (40% SBS).  
 C: Polymer composite film (80% SBS).

The bands at 910 and 965  $\text{cm}^{-1}$  are attributed to out of plane deformation vibrations of the phenyl ring in polystyrene and the vinyl-1,2 and trans-1,4 units in polybutadiene. The band at 3002  $\text{cm}^{-1}$  is assigned to C-H stretching modes of the phenyl ring in PS and the RHC=CHR groups in polybutadiene (10,11).

The displacement of these bands with respect to the positions which they should, in theory, occupy shows them to be sensitive to the presence of interactions between both components and they have been used in this study to establish some comparisons between the various types of spectra. Other papers (12) also mention the sensitivity of the out-of-plane vibration in PS to compatibility.

A comparison of the spectra of the injected samples obtained by KBr pellets with the spectra simulated from the spectra of the pure components also allows the observation of displacements in the indicated bands; this implies the existence of a detectable degree of interaction between polymers in the injection operation. As it also occurs with film samples, the higher the SBS concentration in the polymer composites the higher the displacement. An example is shown in figure 3.

The comparison of spectra of the same polymer composites obtained by film, injection and simulation indicates the existence of a different molecular interaction level between polymers in accordance with the preparation method. The greatest differences with respect to the theoretical spectrum, visible as a greater displacement of the maximum of the absorption band, correspond to the spectra obtained from the film, while differences found from the pellets of the injected polymer composite show a smaller displacement. These results indicate that on dissolving together both polymers, it is easier to establish interactions than when injecting them together; this is possibly due to the greater mobility and molecular contact. However, the extrusion-injection method enables obtaining a polymer composite in which an intermolecular contact visibly occurs in the mentioned bands. Some of these spectra are shown in figure 4.

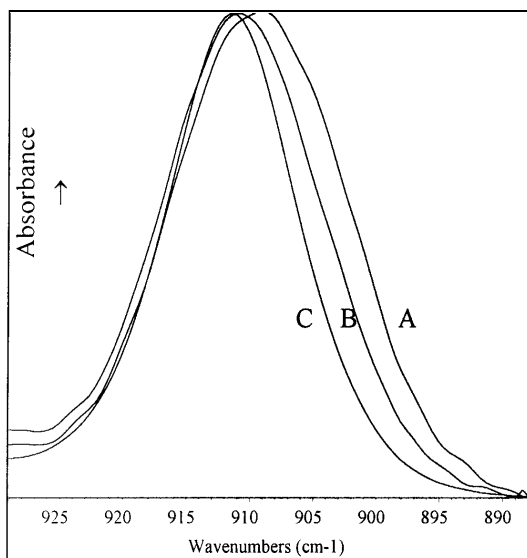


Fig. 3 Infrared spectrum in the region of 900-920  $\text{cm}^{-1}$ .  
 A. Injected polymer composite (40% SBS).  
 B. Injected polymer composite (80% SBS).  
 C. Polymer composite film (80% SBS).

The small displacements observed indicate, in every case, that the intermolecular forces causing them are weak (13) and do not permit to clearly establish which groups are involved. The sensitivity of the band associated with the out-of-plane deformation vibration of the phenyl ring suggest the participation of this group in the interaction, but butadiene could also be involved as their vinyl-1,2 and trans-1,4 units show bands at the same frequencies. Since the homopolymer polybutadiene is incompatible with PS (14), the vinyl-1,2 and trans-1,4 are hardly thought to be involved in associations causing miscibility.

#### DSC

The existence of only one transition temperature ( $T_g$ ) is usually considered as a criterion of compatibility in a polymer composite. In incompatible polymer composites, the  $T_g$  of both components are observed separately, but the existence of partial miscibility is usually manifested by their displacements (15,16).

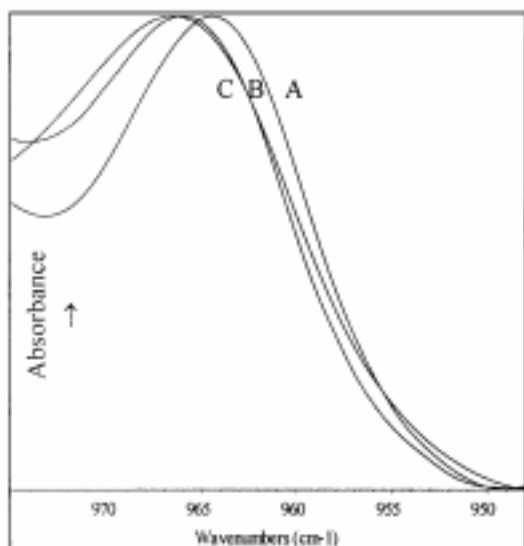


Figure 4: Infrared spectrum in the region of 950-970  $\text{cm}^{-1}$ .  
 A: Simulated polymer composite (20% SBS).  
 B: Injected polymer composite (20% SBS).  
 C: Polymer composite film (20% SBS).

A number of samples obtained by PS and SBS extrusion-injection were subjected to DSC analysis to determine the corresponding  $T_g$ . Results are illustrated in figures 5 and 6. Based on very reproducible thermograms, the glass transition temperatures were determined (table 1).

The  $T_{g1}$  corresponds to the butadiene domains present in polymer composites, thus, it is neither detected in the pure PS nor in the sample containing 20% of SBS as the low butadiene proportion does not permit its observation. In the other polymer composites and in the SBS as well, the glass transition temperature appears at  $-89^\circ\text{C}$  and does not change on increasing the SBS proportion.

The  $T_{g2}$  is assigned to PS and it increases with the SBS proportion. The polymer composite containing 80% of SBS and the sample of pure SBS do not show  $T_{g2}$ , because the PS quantity is too low to be detected.

The  $T_{g1}$  does not show any displacement on varying the SBS proportion. This is attributed to the fact that the present polybutadiene regions are not affected by the presence of PS. Actually, polybutadiene and PS are considered as incompatible polymers and, therefore, their polymer composites are made with the copolymer SBS which consists of a central nucleus of butadiene with PS branches, the latter allowing an appropriate partial miscibility to achieve interfacial adhesion in the polymer composites. Displacements observed in the  $T_{g2}$  indicate that PS establishes interactions with the copolymer SBS and that PS grafts allow partial miscibility with the matrix.

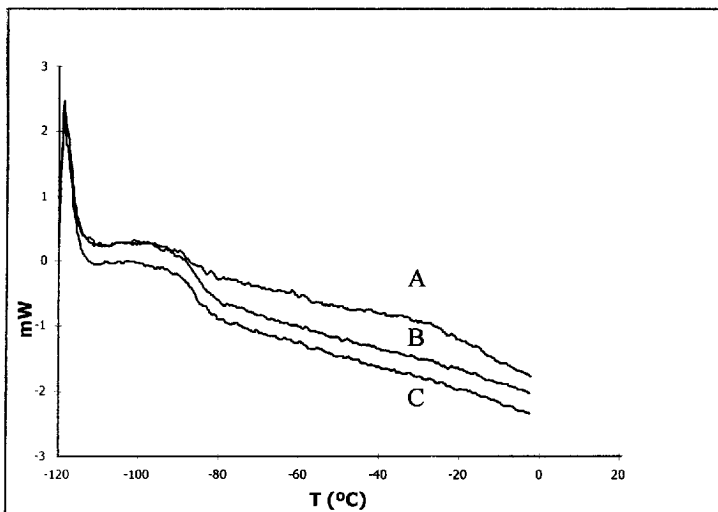


Figure 5: Thermograms of injected polymer composites in the range from  $-120$  to  $20^\circ\text{C}$ .

A: 40% SBS.  
B: 60% SBS.  
C: 80% SBS.

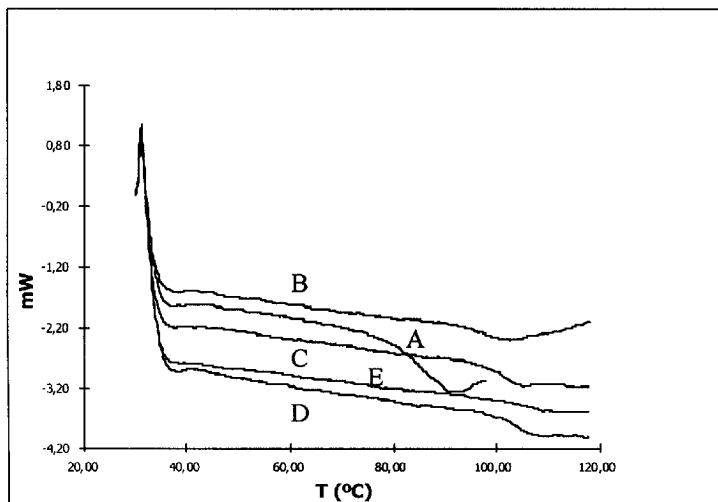


Figure 6: Thermograms of injected polymer composites in the range from  $20$  to  $120^\circ\text{C}$ .

A: 0% SBS.  
B: 20% SBS.  
C: 40% SBS.  
D: 60% SBS.  
E: 80% SBS.

SAMPLE	T <sub>g1</sub> (°C)	T <sub>g2</sub> (°C)
PS	Not observable	81
20 % SBS	Not observable	92
40 % SBS	-89	98
60 % SBS	-88	100
80 % SBS	-89	Not observable
100 % SBS	-89	Not observable

Table 1: Values of glass transition temperatures of polymer composites injected with different proportions of SBS.

## Conclusions

FTIR spectroscopy is an adequate technique to study small interactions in polymer composites. Even in the case of preparing polymer composites with very similar materials, spectral bands sensitive to compatibility have been found which prove to be useful to characterize the environment of the individual components of the polymer composite. These bands were found by comparison with the spectra of incompatible polymer composites of the same composition, simulated from spectra of the initial polymers without the need of using spectral subtraction. Changes detected in spectra consist of displacements in the absorption maxima of some bands, similar to those assigned to partial miscibility in other polymer composites. The assignment of compatibility sensitive bands to the ring out-of-plane deformation seems to indicate the participation of the benzene ring in the intermolecular forces associated to partial miscibility. Polymer composites industrially made by injection have been compared to polymer composites obtained from the same samples by dissolution and evaporation of the solvent. Results showed that the level of miscibility reached in the polymer composite obtained by injection is lower than the one achieved by dissolution-evaporation.

Differential scanning calorimetry complements the mentioned conclusions since the T<sub>g</sub> of butadiene remained constant in the thermograms obtained by the DSC technique, which means butadiene does not participate in the interactions causing miscibility. The T<sub>g</sub> corresponding to PS showed a displacement indicating that the chains of this polymer, grafted in the butadiene nucleus, were responsible for the partial miscibility of SBS with PS. It was, therefore, verified that there is no participation of butadiene in the interactions between both polymers, being the benzene ring the one intervening in the establishment of forces providing interfacial adhesion to the material.

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