Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 44 (2003) 6627–6631

polymer

www.elsevier.com/locate/polymer

Miscibility and interactions in polystyrene and sodium sulfonated polystyrene with poly(vinyl methyl ether) PVME blends. Part II. FTIR

A.A. Bhutto[a,*], D. Vesely[b], B.J. Gabrys[c]

[a]Department of Physics, Government Degree and Postgraduate College, Larkana, Sindh, Pakistan
[b]Department of Materials Science, University of Oxford, Parks Road, Oxford OX1 3PH, UK
[c]Department of Computing, Faculty of Mathematics and Computing, The Open University in the South, Foxcombe Hall, Boars Hill, Oxford OX1 5HR, UK

Received 13 May 2003; received in revised form 11 July 2003; accepted 7 August 2003

Abstract

The miscibility and specific interactions of polystyrene (PS) and sodium sulfonated polystyrene (Na-SPS) with poly(vinyl methyl ether) (PVME) blends (ranging from 10 to 90% PS by weight) were examined experimentally by FTIR spectroscopy. The FTIR studies at different temperatures have shown that changes in spectra of polymer blends, as reported in the literature can be explained by temperature changes in pure homopolymers. This indicates that molecular interactions, which are responsible for miscibility, are not detectable by infrared absorptions and are therefore of unspecific strength and location. The FTIR of SPS/PVME blends show that sulfonate groups of PS affect polymer miscibility through changes in configuration of molecules, rather than through direct interaction with the PVME.

Keywords: Miscibility; FTIR; Poly(vinyl methyl ether)

---

1. Introduction

Specific interactions between chemical groups of two blend components can play an important role in polymer mixtures. Specific attractive interactions lead to exothermic mixing which favours miscibility and there is a range of such interactions of varying strengths, which has been identified in polymer blends [1] and such interactions are generally defined for small molecules. It should be noted that the extension of this concept to polymers is not always straightforward: it is more difficult to identify interactions in polymers, the spectroscopy is more complex, and molecular conformations are less certain. This situation is further complicated because researchers use different names and definitions to describe similar interactions.

It has been suggested [2–4] the well-known polymer mixture polystyrene (PS) and poly(vinyl methyl ether) (PVME) that the miscibility at low temperature of this particular polymer pair originates from the specific interaction between the lone-pair electrons of PVME and the phenyl ring of PS. However, recent quasielastic neutron scattering experiments [5] do not support these conclusions. The present study aims to clarify this issue: that these attractive interactions have been observed through the changes in IR absorption peaks of PS, SPS and PVME upon mixing and with increasing temperature and form part of a wider investigation [6].

2. Experimental

2.1. Materials

PS and SPS with different levels of sulfonation (1.18, 2.7 and 5.2 mol%) were obtained as powder from Exxon Chemicals of USA with $\bar{M}_w = 300,000\ \mathrm{g\ mol^{-1}}$ and $\bar{M}_w/\bar{M}_n = 1.06$. Poly(vinyl methyl ether) PVME, was purchased from Scientific Polymer Products, Inc. (Ontario, New York), as a 50% (w/w) solids solution in toluene. Its molecular weight $\bar{M}_w = 95,000$, was quoted by the company as determined by gel permeation chromatography (GPC). Both polymers were used without further purification.

---

* Corresponding author. Tel.: +92-741-458674.
E-mail address: phpgaab@hotmail.com (A.A. Bhutto).

0032-3861/$ - see front matter © 2003 Published by Elsevier Ltd.
doi:10.1016/j.polymer.2003.08.005

2.2. Sample preparation

All the solutions were prepared by the procedure described in the previous paper [7]. Thin films were obtained by casting the polymer solutions of pure PS and composition up to 30% PS on to a Teflon-coated surface (Petri dish) at room temperature, and subsequently kept in a vacuum oven at 60 °C for 1 week. For pure PVME (due to it being soft and sticky) potassium bromide discs at room temperature were used. These films were sufficiently thin to exhibit absorbance in the range where Beer's law is obeyed. The solvent was then rapidly evaporated by placing the sample in a vacuum oven at 40 °C for 3 days.

2.3. Measurements

Infrared spectra were obtained using a Nicolet-710 and 60SXB FTIR spectrophotometer of the Materials Engineering Department, Brunel University London. The number of scans per sample was 200 and resolution of the measurements was 4 cm^{-1}. The recorded wave number range was 400–4500 cm^{-1}. All the spectra were recorded at room temperature and for phase separation the films were subsequently annealed up to 160 °C (both homopolymers and the PS/PVME (50:50) blend) at 25° intervals.

3. Results and discussion

In order to elucidate the role played by intermolecular interactions in the miscibility of these blends, IR absorption of the individual polymer components, PS, SPS and PVME was measured and compared to that in the mixtures. In the infrared spectrum of PS, a number of bands showed small changes in position or shape when PS is blended with PVME. The assignment of these bands is tabulated in Table 1, which serves to identify the conformational changes as discussed below.

Table 1
IR absorption assignment for PS/PVME blends at room temperature

Assignments	Wave numbers (cm^{-1})		
	PS	PVME	Blend
C–H aromatic stretching vibration	3002–3103	–	3001–3102
C–H asymmetrical stretching vibration of CH_2	2924	2931	2926
C–H symmetrical stretching vibration of CH_2	2850	2886	2850, 2883
C–H asymmetrical stretching vibration of CH_3	–	2971	2971
C–H stretching vibration of CH_3	–	2820	2820
C–C stretching frequency of ring in plane	1601	–	1601
C–H stretching vibration of ring in plane	1583	–	1583
C–H stretching vibration of ring in plane	1493	–	1493
C–H deformation of CH_2	1452	–	1452
C–H deformation of CH_3	–	1462	–
C–O stretching vibration	–	1132	1132
C–C stretching vibration	–	1107	1107
CH_3 rocking mode	–	1085	1085
C–H bending vibration of ring in plane	1069	–	–
C–H bending vibration of ring in plane	1028	–	1028
C–H out-of-plane bending vibration of ring	756	788	758
C–H out-of-plane bending vibration of ring	698	–	700

Figs. 1 and 2 show the FTIR spectra of PS and PVME, respectively, in the high-frequency region from 2700 to 3200 cm^{-1}. The high-frequency spectra of PS consist of seven absorption bands. The bands with peak locations at 3002, 3026, 3060, 3082 and 3103 cm^{-1} are due to the C–H stretching of benzene ring CH groups on the PS side-chain. The bands with peak positions of 2924 and 2850 cm^{-1} are due to the C–H stretching vibration of the CH_2 and CH

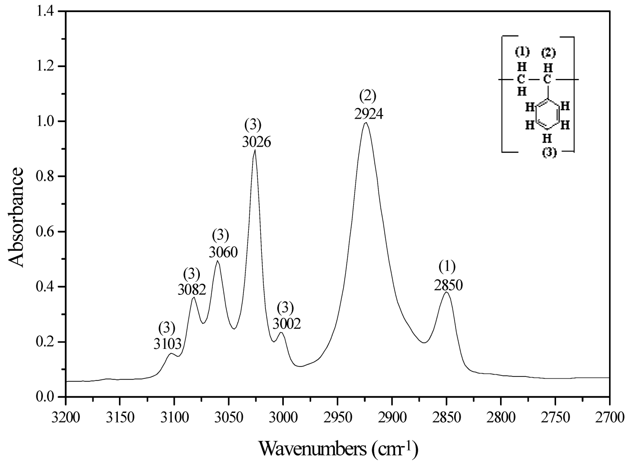

Fig. 1. Infrared spectra of pure PS at high-frequency in the 3200–2700 cm^{-1} regions measured at room temperature.

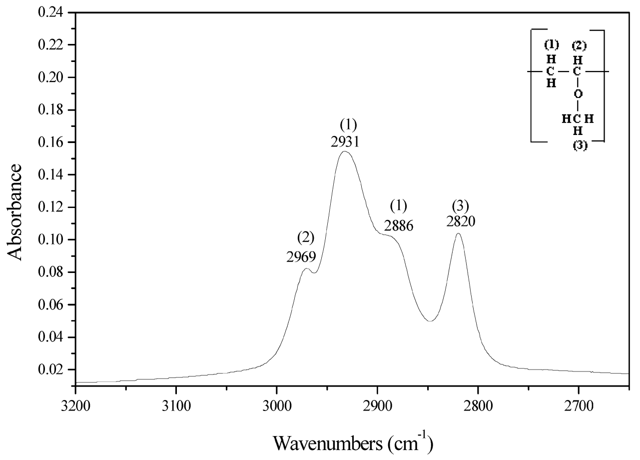

Fig. 2. Infrared spectra of PVME at high-frequency in the 3200–2700 cm^{-1} regions measured at room temperature.

groups on the main PS chain, respectively. The high-frequency spectra of PVME consist of four absorption bands. The bands with peak positions at 2886, 2931, and 2971 cm^{-1} are due to the C–H stretching vibration of the CH_2 and CH_3 groups on the main-chain, respectively. The band at 2820 cm^{-1} is the C–H stretching of the CH_3 group of the methoxyside chain, as shown in Fig. 2. In this region, three peaks were found most sensitive to the changes in the composition of PS/PVME blends. These are band at 2820 in PVME, and in PS the bands appearing at 2850 and 2924 cm^{-1}.

Fig. 3 shows FTIR spectrum of 50/50 (w/w) PS/PVME system. The seven absorption bands of PS and the four bands of PVME in the high-frequency region combine to give 10 bands with the PS and PVME bands at 2926 cm^{-1} superimposed. However, it was observed that the band which is assigned C–H stretching of CH group on the main PS chain at 2924 cm^{-1} in pure PS shifts slightly to higher frequency when PS blends with PVME. This difference in peak position can be expected from simple addition of two closely spaced broad peaks of different absorbance and cannot be interpreted as a result of some interaction. As shown in Fig. 4 (the spectrum of a (50:50) PS/PVME and SPS/PVME blends at room temperature) this band is found at 2926 cm^{-1} in both sulfonated and unsulfonated blends.

Fig. 5 shows the spectrum of PVME: a strong doublet at 1085 and 1107 cm^{-1} with a shoulder at 1132 cm^{-1}. The bands in 1100 cm^{-1} have been usually assigned to the C–O stretching mode, but could also contain contributions from CH_3 rocking and C–C stretching modes [8,9]. It is seen that the intensity of the 1085 cm^{-1} band is greater than that of the 1107 cm^{-1} components in all the blends with the contribution of 1069 cm^{-1} of C–H in-plane bending vibration of PS ring. As the PVME content in the blend increases, the 1107 cm^{-1} band becomes more prominent in comparison to the 1085 cm^{-1} band. The SPS/PVME blend also shows similar changes to that of PS/PVME blend except the appearance of sulfonation peaks at 1229, 1043, and 1011 cm^{-1}.

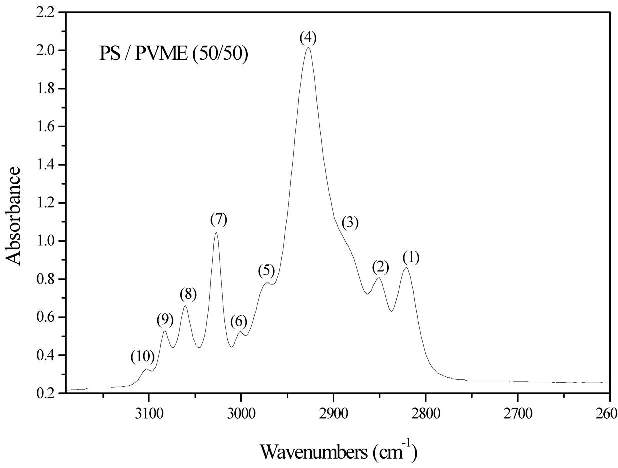

Fig. 3. Infrared spectra of 50:50 (w/w) PS/PVME blends at room temperature in high frequency from 3200 to 2600 cm^{-1} regions. Peak frequencies (1)–(10) are 2820, 2850, 2886, 2926, 2971, 3001, 3026, 3060, 3082, and 3103 cm^{-1}, respectively.

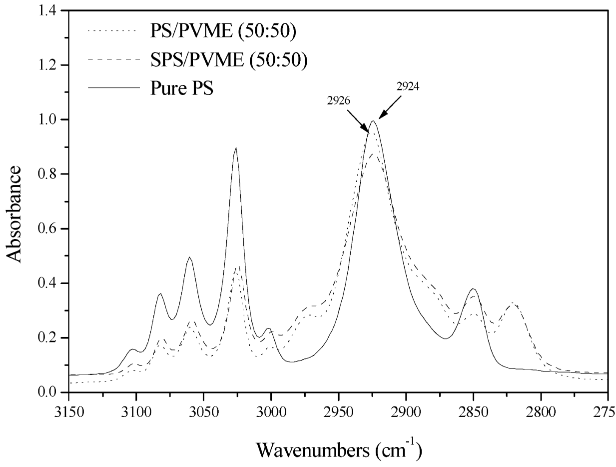

Fig. 4. Infrared spectra (2750–3150 cm^{-1}) of PS and 50/50 PS/PVME, SPS/PVME blends at room temperature.

Hsu et al. [3] reported that PVME has a strong doublet at 1085 and 1107 cm^{-1} with a shoulder at 1132 cm^{-1}, and the relative intensity of this doublet varies considerably when the blend sample is cooled or heated. Thus, they concluded that the relative intensity of this doublet was sensitive to the miscibility of the PS/PVME blends, and that the intensity of this 1085 cm^{-1} peak was greater than that of the 1107 cm^{-1} peak for the miscible blend. This conclusion contradicts our interpretation of IR spectra obtained by a more accurate data analysis and also the results obtained by quasielastic neutron scattering [5].

It can be seen from Fig. 5 that the contribution from PS peak is small. In addition, the absorbance (peak height) is critically dependent on sample geometry, spectrometer throughput and temperature. Accurate subtraction can only be done if the baseline, specimen thickness and peak broadening are known. None of this procedure has been

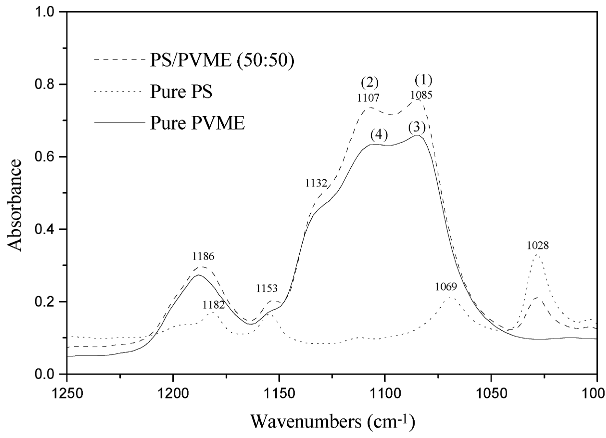

Fig. 5. Infrared spectra (1000–1250 cm^{-1}) of PS, PVME and 50/50 PS/PVME blends measured at room temperature. Band: 1, 1085 cm^{-1}, absorbance 0.760; 2, 1107 cm^{-1}, absorbance 0.728; 3, 1085 cm^{-1}, absorbance 0.655; 4, 1107, absorbance 0.635.

reported by Lu et al. [3]. These authors also do not explain how molecular interaction will affect peak height. After a careful study of the behaviour of these peaks and subtraction of PVME and PS peaks, the conclusion was, that this evidence [3] for molecular interaction is unreliable.

To understand the role played by intermolecular interactions in the miscibility and phase behaviour of PS/PVME blends, it is crucial to examine the nature of interaction of homopolymers and blends at different temperatures. We were also particularly interested in whether such measurements can be used to distinguish between thermal behaviour of spectral changes observed on homopolymers and miscibility effects of PS/PVME blends. Spectra for different temperatures are plotted together, to see the spectral shift and peak broadening. Some peaks show no shift or broadening, others shift and broaden simultaneously. Only the peak at 758 cm^{-1} (Fig. 8) shows pure shift to lower wave numbers. The peak at 699 cm^{-1} is very intense and can be measured accurately for very thin samples only, but the shift is clearly visible. The peak height is also temperature-dependent and some peaks increase with temperature, while others decrease. This is most clearly observed for peaks at 1107 and 1085 cm^{-1}.

Figs. 6 and 7 show the C–O stretching vibration of COCH$_3$ group in pure PVME and (50:50) PS/PVME blend, respectively. The relative intensity of the doublet at 1107 and 1085 cm^{-1} of PVME shows changes with temperature, but this change is similar to that observed in pure PVME as well as in blends. Their relative intensities changed substantially with temperature, but the position of these two bands did not change neither in pure PVME nor when blended with PS. The 1107 cm^{-1} component dominates at high temperatures, whereas the 1085 cm^{-1} component dominates at low temperature, as reported previously [2,3, 10]. The spectral shift can also be plotted and shows similar behaviour for both pure PVME and the blend. The only shift observed for all temperatures is the 758 cm^{-1} peak, which is about 1.5 cm^{-1} higher for the blend than for PS for all temperatures (see Fig. 8). This is the only positive reliable result, which indicates molecular interaction.

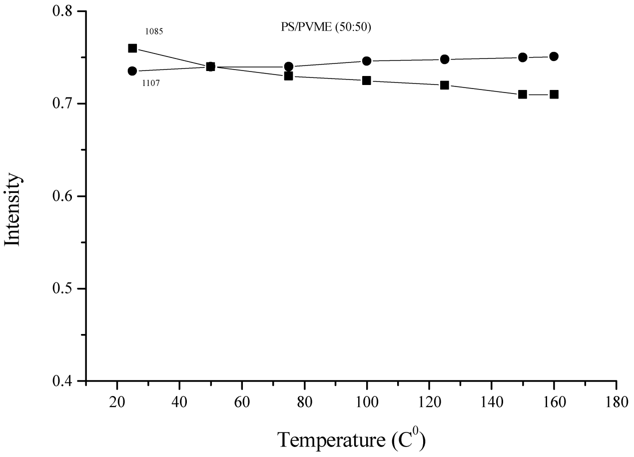

Fig. 7. Relative intensity of doublet of 1100 cm^{-1} regions in PS/PVME (50:50) blends recorded from room temperature to 160 °C.

Our results are in good agreement with quantitative analysis of local dynamic effect of the ether CH$_3$ group in PVME and the ester methyl group in PMMA, investigated as a function of temperature and blend composition using quasielastic neutron scattering by Arrighi et al. [5]. They observed that the local dynamic of the ether CH$_3$ group of PVME in blends with PS is very similar to the pure polymer, whereas a strong influence due to blending was detected in the SCPE/PMMA blend. They concluded that the absence of any dynamic effect on the methyl group rotation in PS/ PVME blend is considered to be a consequence of the dynamics of the PS units compared to that of SCPE in the SCPE/PMMA blend. They added that the weaker interaction between PS and PVME might be responsible for the differences observed in the two blends. These results indicate that the miscibility observed in DSC [7] experiments is not due to an interaction involving the ether lone-pair electrons of PVME and the phenyl ring of PS. If any specific interactions involving the C–O group are present,

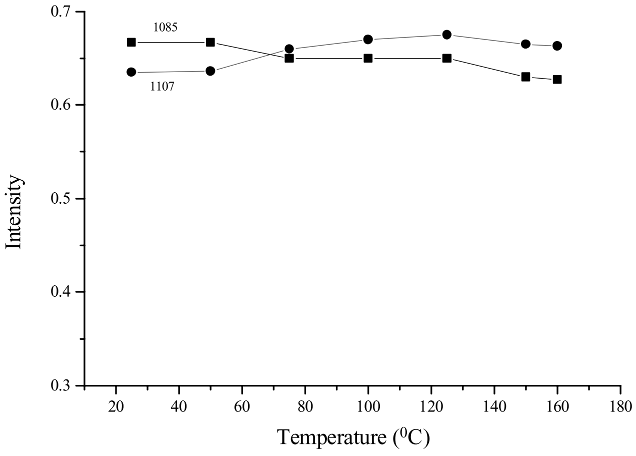

Fig. 6. Relative intensity of doublet of 1100 cm^{-1} regions in pure PVME recorded from room temperature to 160 °C.

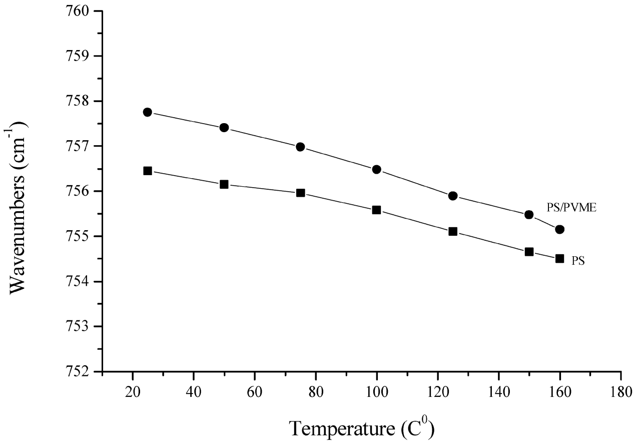

Fig. 8. The frequency of the C–H out-of-plane phenyl ring of PS in blend with PVME at different temperatures.

they will be at best extremely weak. However, spectroscopic perturbations arising from interchain forces are simply too small to be observed with a high degree of confidence. The sulfonation of PS clearly show changes in FTIR spectra which means that FTIR spectroscopy is very sensitive to small chemical changes in the molecular structure. On the other hand, the blends of SPS and PS with PVME show no differences in FTIR spectra. All the spectral changes reported in the literature have been shown in this work to be related to the temperature dependence of spectra of homopolymers. This means that molecular dynamics rather than atomic vibration is affected by blending. In other words the molecular interactions responsible for changes in T_g (glass transition) are occurring on a molecular rather than on an atomic scale.

4. Summary

Miscibility and specific interactions in blends of PS and SPS with PVME have been investigated by Fourier transform infrared spectroscopy. FTIR spectroscopy failed to identify any perturbation of the ether lone-pair electron of PVME and the benzene ring vibration of PS as a result of blending the PS and PVME. It was found that the peak assigned to the C–O stretching mode of PVME at $1100\ \mathrm{cm}^{-1}$ shows similar behaviour for both pure PVME and the blend. The same local dynamic effect of the ether CH_3 group in PVME and PS/PVME blend composition has been reported as a function of temperature using QENS [5]. Therefore, the spectral changes in polymer blends as described in the literature can be explained by temperature changes in pure homopolymers. The FTIR spectra of SPS/PVME blends indicate that sulfonate groups on PS affect polymer miscibility through changes in configuration of molecules, rather than through direct interaction with PVME, as suggested in the literature.

References

[1] Olabisi O, Robeson LM, Shaw MT. Polymer–polymer miscibility. New York: Academic Press; 1971.
[2] Garcia D. J Polym Sci, Polym Phys Ed 1984;22:1773.
[3] Lu FJ, Benedetti E, Hsu SL. Macromolecules 1983;16:1525.
[4] Larbi BCF, Leloup S, Halary JL, Monnerie L. Polym Commun 1986;27:23.
[5] Arrighi V, Higgins JS. Macromolecules 1995;28:4622.
[6] Bhutto AA. Ph.D. thesis, Brunel University, London, 1999.
[7] Bhutto AA. Sci. Int. (Lahore), 2003;15(2)113–117.
[8] Snyder RG, Zerbi G. Spectrochim Acta 1967;23A:391.
[9] Colthup NB, Wiberly SE. Introduction to infrared and raman spectroscopy. New York: Academic Press; 1990.
[10] Kang D-P, Chang SH, Won JC. J Polym Sci, Polym Chem 1989;27:1401.