Miscibility and specific interactions in blends of poly[(styrene)-co-(cinnamic acid)] with poly(methyl methacrylate) and modified poly(methyl methacrylate)

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Abstract: The miscibility behavior of poly(styrene-co-cinnamic acid) (PSCA) with poly(methyl methacrylate) (PMMA), poly[(methyl methacrylate)-co-(4-vinylpyridine)] (PMMA4VP) and poly[(methyl methacrylate)-co-(2-vinylpyridine)] (PMMA2VP) was studied. DSC measurements indicated that PSCA23 containing 23 mol% of carboxylic acid units was miscible with PMMA, PMMA2VP and PMMA4VP as established from the observation of a single composition dependent glass transition temperature. Miscibility was induced via hydrogen bonding as evidenced by IR frequency shifts of the hydroxyl stretching vibrations of the acid copolymer in the blends. Interpolymer hydrogen bonding formation within the binary systems was also investigated by viscosimetric study of dilute solutions in toluene. For PMMA/PSCA5 blends the viscosity of the mixtures was close to the weight average viscosities of the individual polymer while for blend solutions of PSCA5 with PMMA2VP and PMMA4VP, the interactions were sufficiently strong to form interpolymer complexes with a decrease in viscosity in comparison to the additivity rule.

Keywords: polymer blends and alloys, miscibility, DSC, FTIR, viscosimetry

1. Introduction

Polymer blending[1–3] is a fast and common way to develop new polymeric materials with a desirable combination of properties. The main advantage of this method is simplicity of preparation and control of the properties by varying the blend compositions. Miscibility plays a decisive role in controlling the properties of the final product and generally requires the presence of intermolecular interactions. Specific interactions most often generate a negative heat of mixing and contribute favorably to the free energy of mixing. Among all the interactions examined in the literature, hydrogen bonding[4–6] seems very attractive since it quite efficiently improved the miscibility.

In this work, we first report on the compatibilization of an immiscible[7] polymer pair, polystyrene (PS) and poly(methyl methacrylate) (PMMA), by incorporating cinnamic acid (CA) groups into the PS chains capable of participating in specific interactions with unmodified PMMA. In a second time, we examine the miscibility and specific interactions in blends of poly(styrene-co-cinnamic acid) PSCA with PMMA modified by basic comonomers. 4-vinylpyridine (4VP) and 2-vinylpyridine (2VP) groups were chosen to be incorporated into the PMMA chains because there are known to be stronger hydrogen bond acceptors than the ester carbonyl of PMMA. We have introduced approximately the same number of 4VP and 2VP units into PMMA chains for comparative purpose.

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The DSC study has been used to investigate the miscibility of the polymer blends using the single composition dependent glass transition criterion. Specific interactions between the blend components have been investigated by Fourier transform infrared spectroscopy and compared to the calorimetric results. Viscosimetric technique based on the study of interactions in dilute solutions of the polymer blends has also been used as a complementary technique to prospect the effect of the position of the nitrogen atom in the pyridine ring on the interactions developed within PMMA4VP/PSCA5 and PMMA2VP/PSCA5 blends. The variation of the reduced viscosity of dilute polymer blend solutions with blend composition has been used as a criterion[8–9] of hydrogen bonding interaction formation.

2. Experimental section

2.1. Polymer synthesis and Characterizations

MMA, 2VP and 4VP monomers were distilled under reduced pressure before use. PMMA, PMMA4VP and PMMA2VP copolymers were synthesized in solution by free radical copolymerization using 2,2'-azobisisobutyronitrile (AIBN) as initiator at 60°C, under N₂ blanket. The conversions were kept less than 15% to prevent composition drift. The polymers were purified by repeated dissolution/precipitation in THF/methanol, isolated by filtration, vacuum dried at room temperature and then at 40°C for several days. The synthesis of poly(styrene-co-cinnamic acid) (PSCA) copolymers containing 5, 10, 15 and 23 mol% of cinnamic acid (CA) content has been described previously[10]. Weight-average molecular weight M_w were determined from THF solutions by size exclusion chromatography using polystyrene or poly(methyl methacrylate) standards with a Waters GPCII. The acid content in the PSCA copolymers was determined by titration of the corresponding polymer solution in benzene-methanol (20 vol% methanol) with a standardized sodium hydroxide solution. The 4VP and 2VP chromophore contents in the PMMA4VP and PMMA2VP copolymers respectively were determined by UV spectroscopy. The main molecular characteristics of the polymers are listed in Table 1.

2.2. DSC measurements

Binary blends of different weight ratios were prepared in the desired composition by dissolving the appropriate amounts of each polymer in THF, at room temperature. The resulting solution was stirred for one day to ensure thorough mixing, followed by precipitation into a large excess of petroleum ether. The resulting blend was isolated by filtration and repeatedly washed with several portions of non-solvent. The powder samples were then vacuum dried at 50°C for several days. Thermal analysis was conducted on a Perkin-Elmer DSC-7 differential scanning calorimeter previously calibrated with indium. Small quantities of the samples, 10–15 mg, were scanned at a heating rate of 20 K·min⁻¹ under N₂. The T_g was recorded as the temperature corresponding to the midpoint of the heat capacity change at the second thermal scan. All samples were preheated to 200°C and kept for 10 mn at that temperature to ensure complete removal of any trace of residual solvent.

2.3. FTIR measurements

Infrared spectroscopic measurements were recorded on a Nicolet 560 Fourier transform infrared spectrometer at a resolution of 2 cm⁻¹ and were averaged from 64 scans at minimum.

The polymer blends were prepared in different weight ratios by codissolution of required amounts of the components in a common solvent at a concentration of 1.2 g·dl⁻¹. The resulting solutions were stirred for 1 day to ensure thorough mixing and then casted onto potassium bromide discs. The samples were first dried at room temperature to reduce the evaporation rate and to avoid film cracking and then placed in a vacuum oven at 60°C for several days.

2.4. Viscosity measurements

Viscosity measurements were carried out using an AVS360 automatic Ubbelohde-type capillary viscosimeter from Schott Geräte. Intrinsic viscosities of the different copolymers listed in Table 1, were determined at 25°C in butanone by extrapolation to zero concentration of the plot of the reduced viscosity versus concentration.

Table 1. Main characteristics of the copolymers

Polymer	Composition [mol%]	η [dl·g ⁻¹]	M _w	T _g [°C]
PMMA	–	0.59	376 146	117
PMMA4VP15	14.56	0.52	216 652	125
PMMA2VP16	16.48	0.77	231 000	121
PSCA5	4.70	0.37	163 300	116
PSCA10	9.97	0.34	–	132
PSCA15	14.70	0.29	–	141
PSCA23	23.20	0.26	115 300	174

3. Results and discussion

3.1. Calorimetric analysis

All PMMA-PSCA23, PMMA2VP-PSCA23 and PMMA4VP-PSCA23 blends exhibited a single T_g , intermediate between that of the parent polymers, indicating the miscibility of these systems. T_{gs} of PSCA copolymers with CA content lower than 23 mol% are too close to those of PMMA, PMMA 2VP and PMMA4VP to investigate the miscibility of their blends by conventionnel DSC. As illustrated in Figure 1, the T_g -composition curve was S-shaped for PMMA-PSCA23 system. The strength of the interactions involved in such a case is considered being less important than in PMMA2VP/PSCA23 and PMMA4VP/PSCA23 systems presenting positive deviations from the calculated weight average T_g values. Indeed, it is well established that when interactions between blend components are strong, such as those affected by Hydrogen bonding, the experimentally determined T_g of the blends are higher than those calculated from the additivity rule

Figure 1. T_g -composition curves of blends of PSCA23 with (□)PMMA, (O)PMMA2VP and (Δ)PMMA4VP

as a result of the reduction of polymer chains mobility in the blend.

In order to estimate the strength of the intermolecular interactions developed within the PMMA2VP/PSCA23 and PMMA4VP/PSCA23 systems we used the Kwei [11] equation where the quadratic term qW_1W_2 provides an indication on the number and the strength of specific interactions within the blend:

$$T_{g(\text{blend})} = \frac{W_1T_{g1} + KW_2T_{g2}}{W_1 + KW_2} + qW_1W_2 \tag{1}$$

Where W_1 , W_2 and T_{g1} , T_{g2} are the weight fractions and the glass transition temperatures of pure components 1 and 2 respectively. K and q are fitting constants. To fit T_g data to the Kwei equation with only one adjustable parameter, it is useful to set K equal to unity. The Kwei equation can be written in a reduced version as:

$$T_g = W_1T_{g1} + W_2T_{g2} + qW_1W_2 \tag{2}$$

The best fitted curves of the Kwei equation for the experimental data are obtained for q values of 10 and 21 for PMMA2VP/PSCA23 and PMMA4VP/PSCA23 systems respectively. The higher q value obtained for PMMA4VP/PSCA23 suggests that the interpolymer interaction in this system is somewhat stronger than that in the PMMA2VP/PSCA23. This is probably due to the fact that the former suffers less steric effect than the latter since the nitrogen atom of the 2VP is too close to the backbone which limits the formation of hydrogen bonding between the acid hydrogen of PSCA23 and the nitrogen atom of the 2VP units in the PMMA2VP.

3.2. FTIR study

The assignments of various infrared bands in styrene copolymers containing carboxylic acid

groups have been published [12–13]. The dimeric form presents as found in the literature in the hydroxyl region a characteristic infrared broad band at about 3000 cm^{-1} and a satellite one which generally appears at 2650 cm^{-1} . The corresponding carbonyl groups are usually seen at 1700 cm^{-1} . Infrared band attributed to unassociated carboxylic acid groups has been detected at 1742 cm^{-1} . Free hydroxyl groups are difficult to observe in the hydroxyl region and may appear as a weak shoulder at about 3520 cm^{-1} . In the first part of the FTIR study, we focus our attention on the PSCA copolymers. In the carbonyl region, Figure 2, the PSCA copolymer spectra are dominated by the characteristic band of self association attributed to the intermolecular carboxylic acid dimer at 1703 cm^{-1} . The band at 1743 cm^{-1} is assigned to C=O stretching for the cinnamic acid units where the carbonyl groups are not hydrogen bonded. As can be seen, the relative magnitude of the non-hydrogen bonded or free carbonyl groups at 1743 cm^{-1} increases with a decrease of the CA content in the PSCA copolymer, indicating that the self association in the copolymer increases when the CA copolymer composition is raised progressively from 5 to 23 mol%. Figure 3 shows FTIR spectra of pure PSCA15 and the PMMA/PSCA15 blends in the hydroxyl region. As can be seen, a broad band that extends over the $3400\text{--}2700\text{ cm}^{-1}$ range with a maximum at about 3000 cm^{-1} occurring beneath the CH stretching modes is assigned to self-associated hydrogen

Figure 2. FTIR spectra of the PSCA copolymers in the carbonyl region

Figure 3. FTIR spectra of the PMMA/PSCA15 system in the hydroxyl region (blend composition indicated)

bonded acid groups in cyclic structures or dimeric form. The other characteristic band of self association is the broad band at about 2675 cm^{-1} , a satellite band, enhanced by Fermi resonance. Moreover, a weak band observed at 3442 cm^{-1} is attributed to carboxylic acid units that are intermolecularly hydrogen bonded to the π system of the phenyl groups in the PSCA copolymers. This band has already been observed by Paul [13] in the case of styrene/acrylic acid copolymers and Coleman [14] in the case of (styrene-co-methacrylic acid) copolymers. For illustrative purpose, the different hydroxyl bands of the PSCA spectrum illustrated in the same figure are obtained by performing a deconvolution procedure on the difference spectrum [(PSCA15)–(PS)] in order to eliminate the C–H bands. In the PMMA/PSCA15 blends, Figure 3, the broad band at about 3000 cm^{-1} corresponding to the dimeric hydroxyl groups decreases in intensity as compared to the pure PSCA15 spectrum indicating the dissociation of some of the dimeric groups. Furthermore, a new band at about 3295 cm^{-1} , can clearly be seen, and may be readily attributed to the stretching vibration of hydroxyl groups of PSCA15 copolymer hydrogen bonded to the PMMA carbonyl groups. It is then assigned to the ester-acid interaction. As illustrated in Figure 4, a little increase of the band corresponding to this interaction can also be detected for PMMA–PSCA23 blend in the 50/50 weight ratio and is

Figure 4. FTIR spectra of 50/50 weight ratio PMMA/PSCA blends with different compositions of CA content in the PSCA copolymer

related to the expected increase in the proportion of hydrogen bonds in the blend with CA content in the acid copolymer. However as the composition of acid groups in the PSCA copolymer is reduced from 15 to 10 and then to 5 mol% of CA content in the PSCA copolymer, no intermolecular hydrogen bonds between the two blend components is noticeable since this band disappears totally in the PMMA/PSCA10 and PMMA/PSCA5 blends. At these compositions, there is not a sufficient proportion of acid groups to allow formation of a measur-

able amount of interassociated hydrogen bonds between PMMA and PSCA copolymers.

The band at 3295 cm^{-1} has also been observed for both PMMA4VP/PSCA and PMMA2VP/PSCA systems when the CA content in the PSCA copolymer was 15 or 23 mol% indicating the development of the ester-acid interactions in these blends.

Furthermore, the satellite band at about 2675 cm^{-1} in the pure PSCA15 spectrum, Figure 5., shifts slightly to the low frequency side in the PMMA4VP/PSCA15 and PMMA2VP/PSCA15 blends. This displacement reflects a redistribution of a part of the self-associated acid groups to heteroassociated ones in the blends. We may therefore assign this shift to the pyridine-acid interaction between the hydroxyl groups of PSCA copolymer and the nitrogen atom of the 4VP or 2VP in the PMMA4VP or PMMA2VP copolymers respectively. One must note that this little displacement ($\Delta\nu = 60\text{ cm}^{-1}$) is consistent with the moderate q values revealed by the DSC study.

3.3. Viscosimetry study

Because of its simplicity, the viscosimetric technique has been extensively used to investigate polymer-polymer interactions in solution. It is well known that the solvent selected for the study has a great influence on the polymer-polymer interactions in solution since the formation of hydrogen bonding in polymer blend solutions is governed by the interaction between the proton donating and

Figure 5. Evolution of the satellite dimeric band of (a) PMMA2VP/PSCA15, (b) PMMA4VP/PSCA15 systems (blend composition indicated)

proton accepting polymers and that between the polymers and the solvent. In this study, we used toluene which is inert to hydrogen bonding and then may have small affect on the formation of the ester/acid interaction and/or the pyridine-acid one. However toluene was not able to dissolve PSCA copolymers with CA content higher than 5 mol%. Prior to the study of the polymer blend solutions, it was necessary to characterize the polymer blend components. The plot of the reduced viscosity of the polymer solutions were fitted through the Huggins equation and the values of the intrinsic viscosities $[\eta]$ were determined by linear regression analysis of the reduced viscosity *versus* c .

Measurements of the reduced viscosities η_{sp}/c of blend solutions were conducted as a function of blend composition with the original total concentration of $0.15 \text{ g}\cdot\text{dl}^{-1}$. This concentration value corresponds to a much lower concentration than the critical concentration C^* estimated by $C^* = 1/[\eta]$. Indeed, in absence of specific interactions within the blend, polymer coils are independent if the solution concentration is below the critical concentration. On the other hand, when the interpolymer interactions are sufficiently strong, we can observe polymer-polymer complexation which result in viscosity decrease, turbidity or even precipitation [15]. The mixed solutions in toluene of PMMA and PSCA5 were clear indicating that no strong interactions are taking place between the blend components chains. In contrast, turbid solutions were

obtained for PMMA4VP/PSCA5 and PMMA2VP/PSCA5 blends. This behaviour indicates the formation of strong interpolymer interactions in solution. In this case, the viscosities were measured after filtering the polymer blend solutions so the measured viscosities have apparent values. In Figure 6, the reduced viscosities of PMMA/PSCA5 blend solutions follow the additivity law indicating that CA content in the PSCA5 copolymer is too low to develop interactions with PMMA as suggested by the FTIR study. However, the introduction of the 4VP or 2VP units in the PMMA chains leads to negative deviations indicating that hydrogen bonding accompanies contraction of the components polymer coils in the PMMA2VP/PSCA5 and PMMA4VP/PSCA5 systems. Furthermore, the deviation observed for the PMMA4VP/PSCA5 is more important confirming that the 4VP-acid interaction is stronger than the 2VP-acid as demonstrated with the calorimetric results.

4. Conclusions

The enhancement of poly(methyl methacrylate)/polystyrene miscibility has been achieved by introducing cinnamic acid units along the polystyrene chains. The introduction of the 4VP or 2VP groups into the PMMA chains results in an increase of the interpolymer specific interactions between the PS and the PMMA as revealed by the DSC study. The FTIR spectra showed that PMMA4VP and PMMA2VP interact with PSCA through their carbonyl and pyridine units. The viscosimetric results are in good agreement with the DSC measurements which revealed that PSCA copolymer develop stronger interactions with PMMA4VP than PMMA2VP and PMMA polymers.

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Figure 6. Reduced viscosity versus blend composition of PSCA5 with ($\square$)PMMA, ($\circ$)PMMA2VP and (Δ)PMMA4VP

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