

Miscibility of Methylmethacrylate-co-methacrylic Acid Polymer with Magnesium, Zinc, and Manganese Sulfonated Polystyrene Ionomers

Cemil ALKAN¹, Nebahat YURTSEVEN², Leyla ARAS^{2*}

¹ *Gaziosmanpaşa University, Department of Chemistry,
60240, Tokat-TURKEY*

² *Middle East Technical University, Department of Chemistry,
06581, Ankara-TURKEY
e-mail: leylaras@metu.edu.tr*

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The miscibility of methyl methacrylate-co-methacrylic acid polymer (MMA-MAA) with metal neutralized sulfonated polystyrene ionomers was investigated by viscometry, differential scanning calorimetry (DSC), and Fourier transform infrared radiation spectroscopy (FTIR) techniques. Polystyrene (PS) was sulfonated by acetic anhydride and sulfuric acid and the sulfonation degree was found to be 2.6 mole percent, and 2.6 mole percent sulfonated polystyrene was neutralized by Mg, Zn, and Mn salts. The miscibility behavior of the blends of MMA-MAA with Mg neutralized 2.6 mole% sulfonated polystyrene (2.6MgSPS), Mn neutralized 2.6mole% sulfonated polystyrene (2.6MnSPS), and Zn neutralized 2.6 mole% sulfonated polystyrene (2.6ZnSPS) was investigated by dilute solution viscometry. The results showed that 2.6MgSPS blends were miscible with MMA-MAA in all compositions, 2.6ZnSPS blends were all immiscible, and 2.6MnSPS blends were immiscible at certain compositions. Even though the DSC thermograms of samples were taken in the solid state, they showed consistency with the results of dilute solution viscometry with a few exceptions. DSC results indicated that 2.6ZnSPS was immiscible with MMA-MAA as 2.6MnSPS and 2.6ZnSPS blends were immiscible at certain compositions. FTIR studies of miscible and immiscible blends revealed the existence of specific interactions between carbonyl oxygen of MMA-MAA copolymer and neutralizing cation of the sulfonated polystyrene.

Key Words: Methylmethacrylate-methacrylic acid polymer, sulfonated polystyrene ionomers, viscometry, compatibility.

Introduction

Polymers are considered miscible when specific attractive interactions among the functional groups of the macromolecules occur. The specific interactions include donor-acceptor, dipole-dipole, hydrogen-bonding, ion-ion, acid-base, and ion-dipole interactions. The techniques used for the detection of polymer-polymer

*Corresponding author

miscibility can be of several kinds, such as DSC, neutron scattering, morphology studies by optical and electron microscopy, dynamic mechanical measurements, IR spectroscopy, ultrasound and viscometry¹⁻⁵.

Random ionomers are macromolecules containing a small percentage of ionic groups placed randomly and covalently attached to a non-polar backbone. The ionic species in the salts of lightly sulfonated polystyrene associate due to electrostatic attraction. The ion content is the source of the interaction in blends. Many authors have attempted to estimate the compatibility for polystyrene-based ionomers with several other kinds of polymers or copolymers⁶⁻⁹. Tomita et al. showed that poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is miscible with a wide range of styrene-based ionomers, provided that the functionalization level or PPO content is low⁷. Lu et al., on the other hand, concluded their work by showing that lightly sulfonated polystyrene ionomers are miscible with bisphenol A polycarbonate not by specific interactions but by copolymer effect⁸. Yurtseven et al.¹⁰ estimated the compatibility of Na neutralized sulfonated polystyrene ionomers/methylmethacrylate-co-methacrylic acid polymer and sulfonated polystyrene ionomers/methylmethacrylate-co-methacrylic acid polymer systems and their conclusion is that the Na ion somewhat increased the miscibility.

The phase behavior of the 2.6MgSPS/MMA-MAA, 2.6MnSPS/MMA-MAA, and 2.6ZnSPS/MMA-MAA systems has been analyzed using the viscometric methods¹¹⁻¹⁷ proposed by Krigbaum and Wall, and Sun et al.

The compatibility of solutions was characterized by a viscometry technique by using the Krigbaum and Wall parameter¹⁴, Δb . Basically viscometry hinges on the classical Huggins equation that expresses the specific viscosity (η_{sp}) of the polymer as a function of the concentration C (1)

$$\eta_{sp}/C = [\eta] + K[\eta]^2 C \quad (1)$$

where $[\eta]$ is the intrinsic viscosity, K is the Huggins coefficient, and $K[\eta]^2$ is the interaction term and is represented by b after this point. The specific viscosity, $\eta_{sp,m}$, of a mixed polymer solution was expressed as (2)

$$\eta_{sp,m} = [\eta_1]C_1 + [\eta_2]C_2 + b_{11}C_1^2 + b_{22}C_2^2 + 2b_{12}C_1C_2 \quad (2)$$

where $[\eta_1]$ and $[\eta_2]$ are the intrinsic viscosities of components 1 and 2, C_1 and C_2 are the concentrations in mixed polymer solutions, b_{11} and b_{22} are self-interaction parameters that are the slopes of viscosity number versus concentration relationships of pure components, respectively, and b_{12} is the interaction coefficient for the mixture. For mathematical convenience, Krigbaum and Wall¹⁴ defined the interspecific interaction coefficient b_{12}^* as

$$b_{12}^* = (b_{11}b_{22})^{0.5} \quad (3)$$

However, the definition of the inter-specific interaction coefficient according to equation 3 is not valid for systems that have negative values for b_{11} and b_{22} . Therefore, the modification by Williamson and Wright¹⁶, equation 4, is used to evaluate b_{12}^* , which can be expressed as (4)

$$b_{12}^* = (b_{11} + b_{22})/2 \quad (4)$$

According to Krigbaum and Wall¹⁴, information on the interaction between polymer molecules 1 and 2 should be obtainable from a comparison of experimental b_{12} and theoretical b_{12}^* values. Here the compatibility of the polymer mixture is characterized by a parameter Δb , which is expressed as (5)

$$\Delta b = b_{12} - b_{12}^* \quad (5)$$

where b_{12}^* is calculated from equation 3 or 4. Negative values of Δb are found for solutions of incompatible polymer systems, whereas positive values of Δb refer to attractive interactions. Observed intrinsic viscosity values are higher than the calculated values for compatible systems.

According to Sun et al.,¹⁷ for a ternary system of components, polymer A, polymer B, and the solvent, the Huggins coefficient K contains 3 interaction parameters.

1. Hydrodynamic interactions between polymer pairs (6)

$$K_1 = \frac{K_A[\eta_A]^2 w_A^2 + K_B[\eta_B]^2 w_B^2 + 2(K_A K_B)^{1/2} [\eta_A][\eta_B] w_A w_B}{([\eta_A] w_A + [\eta_B] w_B)^2} \quad (6)$$

2. Formation of double molecules, which presupposes actual contact (7)

$$K_2 = \frac{k}{[\eta]} ([\eta]_2 - [\eta]_1) \quad (7)$$

k is a constant and can be neglected for nonpolar solvents. $[\eta]_1$ and $[\eta]_2$ are intrinsic viscosities for single and double molecules.

3. Intermolecular attraction and repulsion $K_3 = \alpha$. Then

$$K = K_1 + K_2 + K_3 \cong K_1 + \alpha \quad (8)$$

K_2 is neglected in the absence of strong specific forces of attraction between molecules that would encourage aggregation, and at sufficiently low concentrations, then α becomes (9)

$$\alpha = K - K_1 \quad (9)$$

$\alpha > 0$ shows miscibility and $\alpha < 0$ shows immiscibility.

MMA-MAA is a copolymer composed of 66.6% methylmethacrylate and 33.3% methacrylic acid repeating units in the backbone and it is used in pharmaceutical formulations as a film coating agent, binders, direct compression excipients, and gel bases. To satisfy the growing needs for new materials with specific properties such as engineering materials, new polymers have been synthesized and chemical modifications in conventional polymers have been proposed. However, the economical way to obtain new polymeric material is blending. The final properties of a polymeric blend depend on the combination of components and mainly on the miscibility of the polymers. In some cases, by synergistic effects, the blend can present better properties than the pure component. The objective of this research was to investigate miscibility between the MMA-MAA and metal neutralized sulfonated PS ionomers by viscosity and DSC and to determine the interaction between functional groups of the components.

Experimental

MMA-MAA copolymer with a number average molecular weight of 135,000 was obtained from Röhm Pharma with a ratio of carboxylate groups of 1:2 (i.e. 33% MMA). Sulfonated polystyrene ionomer was synthesized from polystyrene and neutralized in our laboratory¹⁰.

Mg, Zn, and Mn neutralized ionomers were prepared by dissolving 2.6SPS and appropriate amounts of corresponding metal acetate [$\text{Mg}(\text{CH}_3\text{COO})_2$, $\text{Zn}(\text{CH}_3\text{COO})_2$, and $\text{Mn}(\text{CH}_3\text{COO})_2$] in tetrahydrofuran (THF). The solutions were then mixed for 1 h at room temperature. The ionomers were back titrated to confirm complete neutralization. The polymer blends of sulfonated PS with MMA-MAA were prepared by the solution blending method in 3 different weight fractions of the sulfonated PS component (25%, 50%, 75%). For each composition, appropriate amounts of ionomers and MMA-MAA copolymer were dissolved in suitable solvents and ionomer solution was added to the MMA-MAA solution dropwise. Viscosity measurements were obtained with an Ubbelohde viscometer in a constant temperature water bath at 25 °C using dioxane as a solvent. A blend concentration of 0.5 g/dL was not exceeded in viscosity measurements.

The standard deviation in the calculations of the Δb values was approximately 0.001-0.007. To calculate b values for each system, a linear regression method was used. According to these results the coefficient of correlation “r” values for each system varied between 0.9969 and 0.9999, which is quite good for linear regression. DSC thermograms of the blends were obtained with a Perkin-Elmer DSC -4 using a heating rate of 20 °C min^{-1} . A Nicolet 510 type FTIR was used for taking the FTIR spectra of the samples.

Results and Discussion

Miscibility Analysis

2.6MgSPS/MMA-MAA system: The viscosity numbers of 2.6MgSPS, MMA-MAA copolymer, and their 25/75, 50/50, and 75/25 w/w blend compositions are plotted in Figure 1. The blend compositions, experimental intrinsic viscosities, b, Δb , and α values are also presented in Table 1. The positive values of Δb and α shows miscibility for each composition.

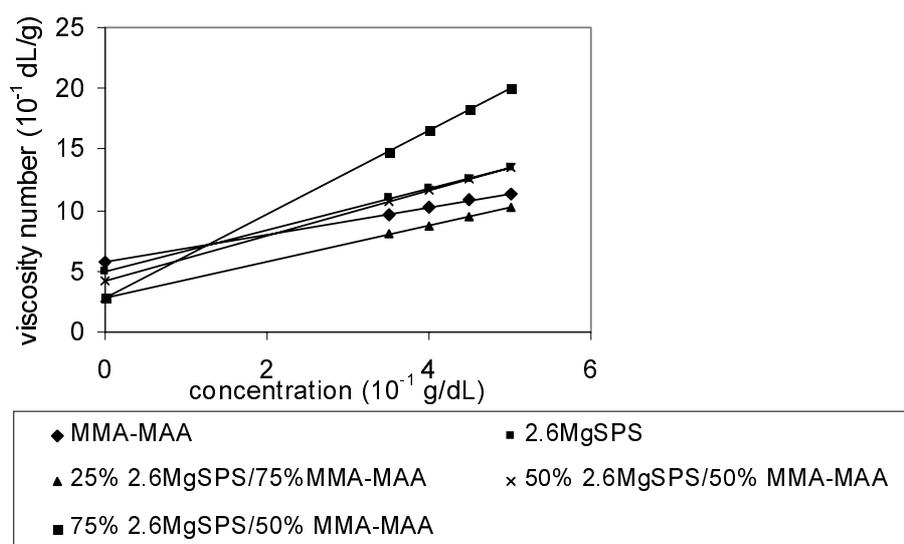


Figure 1. Viscosity number versus concentration relationship for 2.6MgSPS/MMA-MAA blends.

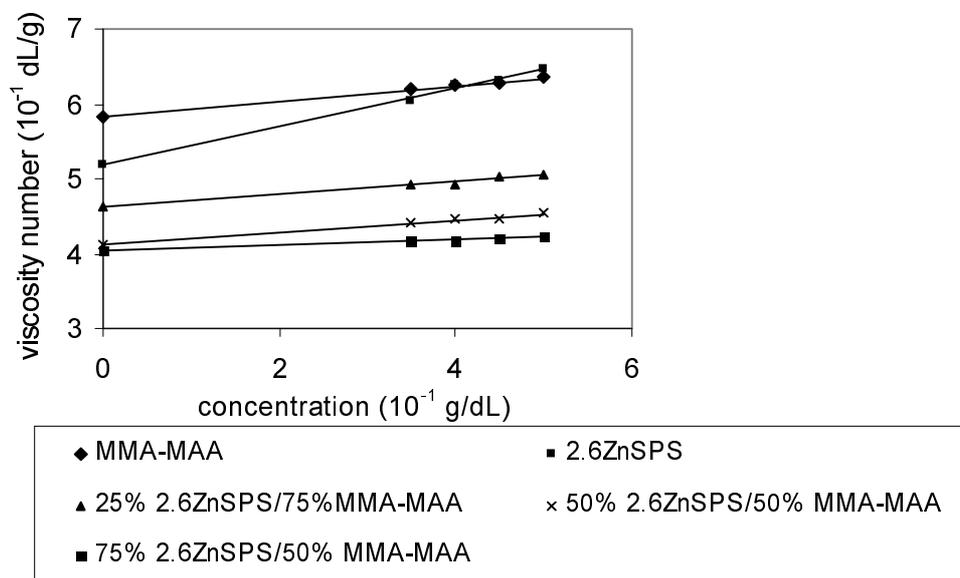
Table 1. Viscometric data and T_g values for the 2.6MgSPS/MMA-MAA system in 1,4-dioxane at 25 °C.

2.6MgSPS composition (w/w)	$[\eta]$ (dL/g)	b	Δb	α	T _g (°C)
0.00	0.580	0.111	-	-	176
0.25	0.282	0.148	0.060	1.468	105, 165
0.50	0.419	0.187	0.022	0.596	107
0.75	0.282	0.343	0.503	3.752	108
1.00	0.504	0.169	-	-	104

b is interaction term found experimentally, Δb is Krigbaum and Wall interaction parameter, and α is Sun interaction parameter.

T_g values agree well with viscosity except for the 25% 2.6MgSPS composition. For all compositions the glass transition temperatures are close to the T_g of 2.6MgSPS. The 2 T_g values for the 2.6MgSPS/MMA-MAA system show the immiscibility of the components in their solid states. Yet, 165 °C may be due to a reduction in T_g of pure MMA-MAA copolymer due to a very low miscibility.

2.6ZnSPS/MMA-MAA system: According to the viscosity analysis, the 2.6ZnSPS/MMA-MAA system is completely immiscible. All Δb values given in Table 2 are negative for all 3 compositions, implying repulsive interactions between the components. Furthermore, immiscibility is confirmed by α parameters and decreases in the slopes of the curves represented in Figure 2. The 2 T_g values in the system belong to pure components and confirm immiscibility. An increasing 2.6ZnSPS percentage in the blend increases the negative Δb value, which corresponds to increasing amounts of repulsive interactions.

**Figure 2.** Viscosity number versus concentration relationship for 2.6ZnSPS/MMA-MAA blends.

2.6MnSPS/MMA-MAA system: The viscosity number versus concentration plots for the individual components and their 25/75, 50/50, and 75/25 weight percent compositions are plotted in Figure 3. The data tabulated from Figure 3 are represented in Table 3, and negative Δb values for 25/75 and 50/50 w/w compositions agree with the plots and with the T_g values. This implies repulsive interactions between

the blend components. When the blend compositions increase to 75/25 w/w, the blend showed positive miscibility parameters and single T_g , which supports attractive interactions. α parameters show complete miscibility by having positive values for all compositions, i.e. Δb and α are only in agreement for the 75/25 w/w blend in this blend system.

Table 2. Viscometric data for the 2.6ZnSPS/MMA-MAA system in 1,4-dioxane at 25 °C.

2.6ZnSPS composition (w/w)	$[\eta]$ (dL/g)	b	Δb	α	T_g (°C)
0.00	0.580	0.111	-	-	176
0.25	0.461	0.090	-0.152	-0.018	111, 174
0.50	0.407	0.094	-0.176	-0.014	113, 176
0.75	0.401	0.043	-0.463	-0.477	114, 174
1.00	0.518	0.253	-	-	110

b is interaction term found experimentally, Δb is Krigbaum and Wall interaction parameter, and α is Sun interaction parameter.

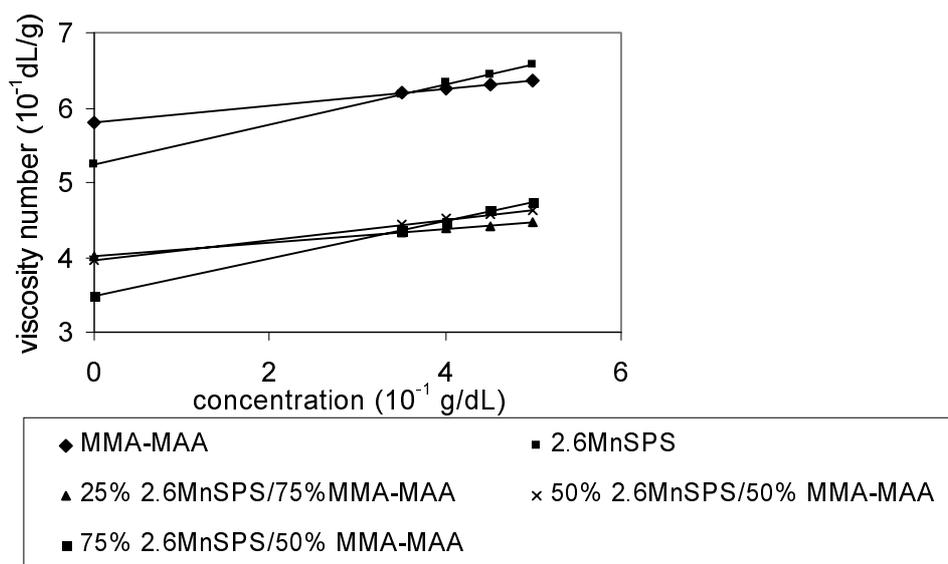


Figure 3. Viscosity number versus concentration relationship for 2.6MnSPS/MMA- MAA blends.

Table 3. Viscometric data for the 2.6MnSPS/MMA-MAA system in 1,4-dioxane at 25 °C.

2.6ZnSPS composition (w/w)	$[\eta]$ (dL/g)	b	Δb	α	T_g (°C)
0.00	0.580	0.111	-	-	176
0.25	0.402	0.088	-0.164	0.0970	119, 175
0.50	0.395	0.137	-0.072	0.0285	111, 179
0.75	0.348	0.247	0.051	1.275	108
1.00	0.524	0.267	-	-	104

b is interaction term found experimentally, Δb is Krigbaum and Wall interaction parameter, and α is Sun interaction parameter.

Fourier Transform Infrared Radiation (FTIR) Spectroscopy Analysis

FTIR spectroscopy is a powerful technique to investigate specific interactions in polymer blends. Figures 4-6 show the FTIR absorption spectra for the pure components and their corresponding blends.

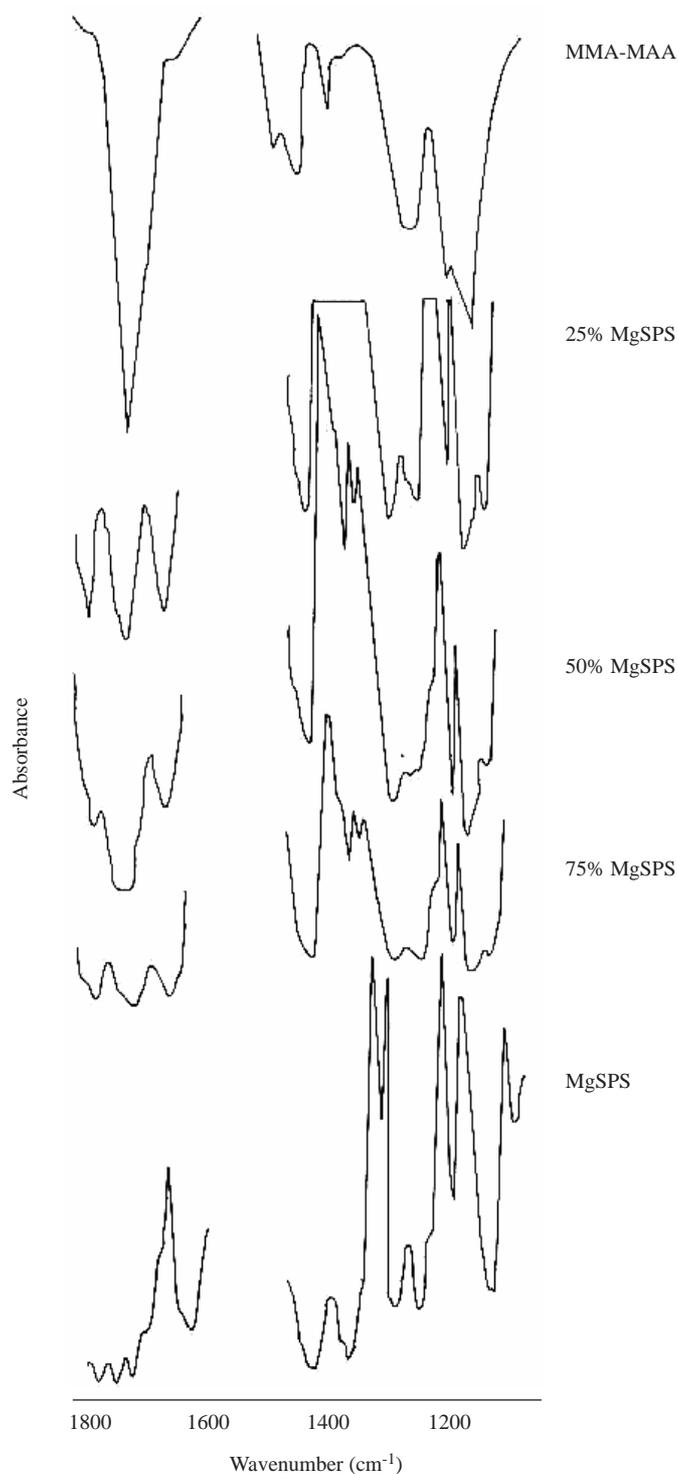


Figure 4. FTIR absorption spectra for the 2.6MgSPS/MMA-MAA system.

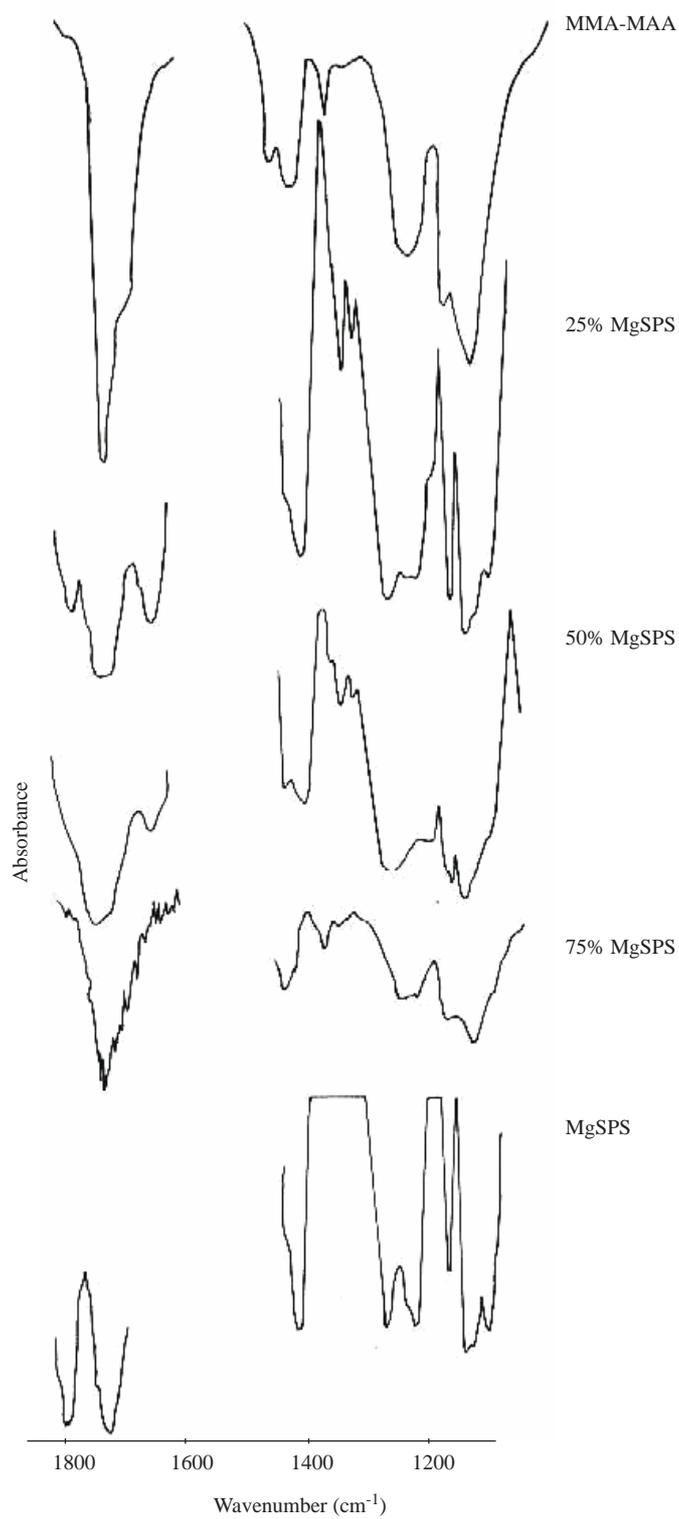


Figure 5. FTIR absorption spectra for the 2.6ZnSPS/MMA-MAA system.

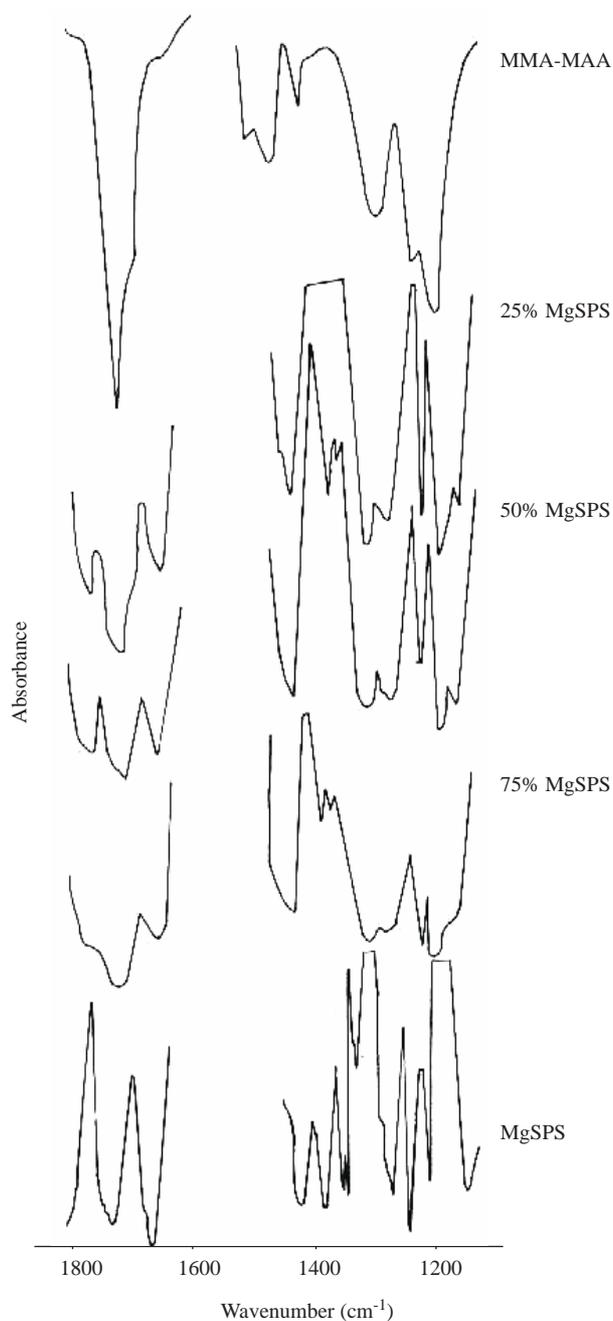


Figure 6. FTIR absorption spectra for the 2.6MnSPS/MMA-MAA system.

The following remarks are based on the FTIR spectroscopy:

Polystyrene was sulfonated successfully and this is supported by O=S=O stretching peaks at around 1160 cm^{-1} .

Metal neutralization of sulfonated PS ionomers is also successful due to the disappearance of $\text{S}(=\text{O}_2)\text{OH}$ stretching shoulder at around 1200 cm^{-1} .

It is apparent in all the spectra that the carbonyl stretching peak for pure MMA-MAA copolymer at about 1730 cm^{-1} is deformed by the addition of the metal neutralized sulfonated polystyrene ionomers' second component¹⁸.

Conclusion

The values of Δb and α for 2.6MgSPS/MMA-MAA blend systems are all positive. This suggests that these blends are miscible under equilibrium conditions regardless of the blend compositions. They also show a single T_g value in the solid state, supporting the Δb and α values, except for the 2.6MgSPS/MMA-MAA; 25/75 w/w blend.

For the 2.6ZnSPS/MMA-MAA blend system, Δb and α values are negative, showing that this blend system is immiscible independent of composition. The 2-phase behavior of this system is also reflected by the 2 T_g values for all the blends.

2.6MnSPS/MMA-MAA blends showed partial miscibility and immiscibility depending on the composition of the system. However, α values support compatibility for all blend compositions, while T_g values agree with Δb parameters. FTIR spectra reflected characteristic interactions between the groups of the 2 components.

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