

Miscibility and Complexation Behavior in Poly(ethyl methacrylate)/Poly(styrene-*co*-methacrylic acid), Poly[2-(*N,N*-dimethylamino) ethyl methacrylate]/Poly(styrene-*co*-methacrylic acid), and Poly{styrene-*co*-[2-(*N,N*-dimethylamino) ethyl methacrylate]}/Poly(styrene-*co*-methacrylic acid) Systems

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Received 1 June 2004; accepted 6 February 2005

DOI 10.1002/app.22087

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This contribution presents a study of the hydrogen-bonding interactions between poly(styrene-*co*-methacrylic acid) containing 22 mol % methacrylic acid (SMA-22) and poly(ethyl methacrylate) (PEMA), poly[2-(*N,N*-dimethylamino) ethyl methacrylate] (PMAD), or poly{styrene-*co*-[2-(*N,N*-dimethylamino) ethyl methacrylate]} containing 3, 12, or 21 mol % 2-(*N,N*-dimethylamino) ethyl methacrylate (SMAD-3, SMAD-12, or SMAD-21) by viscometry and differential scanning calorimetry (DSC). On the basis of the analysis of DSC thermograms and viscometric measurements, polymer miscibility was observed with the PEMA/SMA-22 system. This miscibility was due to hydrogen-bonding specific interactions between carbonyl groups of PEMA and carboxylic groups of SMA-22. The SMAD-3/SMA-22 system was immiscible, whereas complexation was observed with PMAD/SMA-

22, SMAD-21/SMA-22, and SMAD-12/SMA-22 mixtures in butan-2-one. This complexation was due to stronger interactions between poly(styrene-*co*-methacrylic acid) and the 2-(*N,N*-dimethylamino) ethyl methacrylate groups of PMAD or SMAD copolymers, as evidenced by viscometry and DSC. A similar phenomenon was observed for PMAD/SMA-22 and SMAD-21/SMA-22 mixtures in tetrahydrofuran. For the SMAD-12/SMA-22 system in this solvent, such behavior was noted only in the presence of an excess of the copolymer SMAD-12. This study showed that the minimum amount of interacting species required for the interpolymer complexation was higher in tetrahydrofuran than in butan-2-one. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 658–664, 2005

Key words: blends; immiscibility; miscibility

INTRODUCTION

Polystyrene is immiscible with high-molecular-weight poly(alkyl methacrylate)s.^{1–3} The introduction of groups capable of developing specific interactions between the polymers in a blend is a method for increasing the miscibility of the polymers. In a previous study,⁴ we have shown from the polymer–polymer interaction parameter, as determined by inverse gas chromatography, that poly(styrene-*co*-acrylic acid) containing 20 mol % acrylic acid units is miscible in all proportions with poly(ethyl methacrylate) (PEMA) and poly(ethyl methacrylate-*co*-4-vinylpyridine); it has also been reported^{5,6} that poly(styrene-*co*-methacrylic acid) containing 8, 12, 24, or 29 mol % methacrylic acid units in poly(styrene-*co*-methacrylic acid) (SMA) copolymers is immiscible with poly(butyl methacrylate). On the other hand,⁶ poly(styrene-*co*-

methacrylic acid) containing 12, 24, or 29 mol % methacrylic acid units in SMA copolymers and poly-(butyl methacrylate-*co*-4-vinylpyridine) with different compositions of 4-vinylpyridine are miscible. Several studies have shown that, depending on the nature of the solvent, polymer complexes are formed when the densities of interacting species within the polymers are increased.^{7–16} Goh et al.¹⁷ reported that poly[2-(*N,N*-dimethylamino) ethyl methacrylate] (PMAD) and poly(vinyl phenol) (PVPh) formed interpolymer complexes in solvents such as methanol, ethanol, and butan-2-one. They also found that the carbonyl oxygen atom and the nitrogen atom were about equally favored as proton-accepting sites for the hydroxyl groups of PVPh. The contribution of the nitrogen to interactions induced by hydrogen bonding in this binary system was confirmed with X-ray photoelectron spectroscopy.

In this work, the miscibility or complexation of poly(styrene-*co*-methacrylic acid) with PEMA, PMAD, and poly{styrene-*co*-[2-(*N,N*-dimethylamino) ethyl methacrylate]} was studied by viscometry and differential scanning calorimetry (DSC).

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TABLE I
Characteristics of the Polymers and Copolymers

Polymer	Styrene composition (mol %)	T_g (K)	Intrinsic viscosity (dL/g)		K_h	
			Butanone	THF	Butanone	THF
PMAD	—	292	1.200	1.577	0.479	0.322
PEMA	—	345	1.373	1.528	0.251	0.283
SMA-22	78	410	0.378	0.801	0.623	0.228
SMAD-3	97	375	0.403	0.965	0.402	0.352
SMAD-12	88	365	0.558	0.988	0.578	0.442
SMAD-21	79	357	0.556	0.915	0.349	0.528

EXPERIMENTAL

Materials

Styrene, methacrylic acid, ethyl methacrylate, and 2-(*N,N*-dimethylamino) ethyl methacrylate (MAD) were distilled at a reduced pressure before use. Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol.

PMAD and PEMA were prepared by the free-radical polymerization of the corresponding monomers at a low conversion with AIBN as the initiator. Random copolymers of different compositions of MAD with styrene (SMAD) and methacrylic acid with styrene (SMA) were prepared under the same conditions used for the homopolymers, and the conversion was kept low. The styrene contents in the SMAD and SMA copolymers were determined by UV spectroscopy and elemental analysis. Table I displays the characteristics of these polymers.

Viscosity measurements

Measurements of the reduced viscosities of the polymer blend solutions were conducted as a function of the composition with an Ubbelohde viscometer at 25°C. The original concentration of the component polymers was kept at 0.1 g/dL. The polymeric solutions were used 24 h after the dissolution of the polymers to achieve thermodynamic equilibrium, and the reduced viscosities were measured 10 min after the introduction of the polymer solutions to the viscometer. When the polymer solutions remained clear, the viscosity still could be measured, but when the mixed solutions became turbid because of precipitation, the viscosity was measured after the filtration of the precipitates. For this latter case, the apparent viscosities were then measured. In this work, we studied PEMA/SMA-22, PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 binary systems with butan-2-one and tetrahydrofuran (THF) as solvents. The intrinsic viscosities of the different polymers and copolymers were determined in these two solvents in the usual way from the Huggins equation. The obtained values are shown in Table I.

Glass-transition temperature (T_g) measurements

Blends of different ratios of PEMA/SMA-22, PMAD/SMA-22, SMAD-3/SMA-22, SMAD-12/SMA-22, and SMAD-21/SMA-22 were prepared by the codissolution of the polymers in butan-2-one. Films were generated from polymeric solutions with the evaporation of the solvent in pure polymers or blends.

For complexes, the precipitates were separated and dried in a vacuum oven. A Mettler-Toledo star differential scanning calorimeter (Schwerzenbach, Switzerland) was used to determine the T_g values of the polymers, copolymers, and their blends or complexes. All measurements were carried out at a heating rate of 20 K/min under a nitrogen blanket.

RESULTS AND DISCUSSION

Viscometry analysis

Viscometry is one of the techniques among others widely used to study interpolymer complexation in solution due to hydrogen-bonding specific interactions. When such complexation occurs, caused by an increase in the interpolymer hydrogen-bonding density, the viscosity decreases as a result of a contraction of the component polymer chains.

The nature of the solvent,^{18–24} the composition,^{25,26} and the density of the functional groups of one or both polymers^{12,26–30} affect the formation of interpolymer complexes.

The study of the complexation was carried out at a concentration lower than the critical concentrations (C)* of both polymers of the mixture, estimated by Simha³¹ as the reverse of the intrinsic viscosity.

On the basis of the calculated critical concentrations, the total concentration of the polymer solutions was fixed at 0.1 g/dL. This concentration was obviously lower than the critical concentration of each polymer.

Figures 1 and 2 show the variation of the reduced viscosities of PEMA/SMA-22 solutions and the apparent reduced viscosities of PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 binary systems as a function of the feed weight fraction of the SAM-22 copolymer in butan-2-one and THF, respectively. The

latter weight fraction is indeed slightly different from the actual one, as also reported by several authors.^{22,23,32} The general trend of the variation of the apparent viscosity versus the weight fraction is, however, practically the same. The PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 systems formed precipitates, and their apparent viscosities were measured just after the filtration of the polymeric solutions.

The linear variation of the reduced viscosity as a function of the weight fraction of the SMA-22 copolymer, observed with PEMA/SMA-22 solutions prepared in butan-2-one, may be considered evidence of the miscibility of this blend being essentially due to sufficient specific interactions induced by hydrogen bonding that occurred between the ester groups of PEMA and the acidic groups of SMA-22, as evidenced by Fourier transform infrared (FTIR) spectroscopy mainly from the appearance of a new band at 3272 cm^{-1} characteristic of these interactions.³³

The marked negative deviation from the linear average viscosity of the respective components in all feed compositions observed with PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 mixtures prepared in butan-2-one is considered evidence of the formation of interpolymer complexes being due to stronger interconstituent attractive interactions. The most important negative deviation was observed with the PMAD/SMA-22 system. As the density of interacting groups decreased, the negative deviation of the apparent reduced viscosity was less pronounced, as shown in Figures 1 and 2.

The PEMA/SMA-22 binary system was miscible, whereas the PMAD/SMA-22 and SMAD/SMA-22

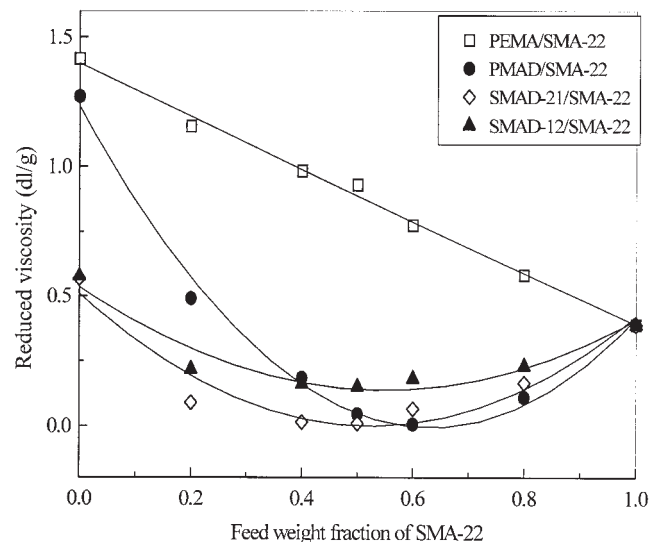


Figure 1 Reduced viscosity of PEMA/SMA-22, PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 solutions in butan-2-one as a function of the feed weight fraction of SMA-22 at 25°C.

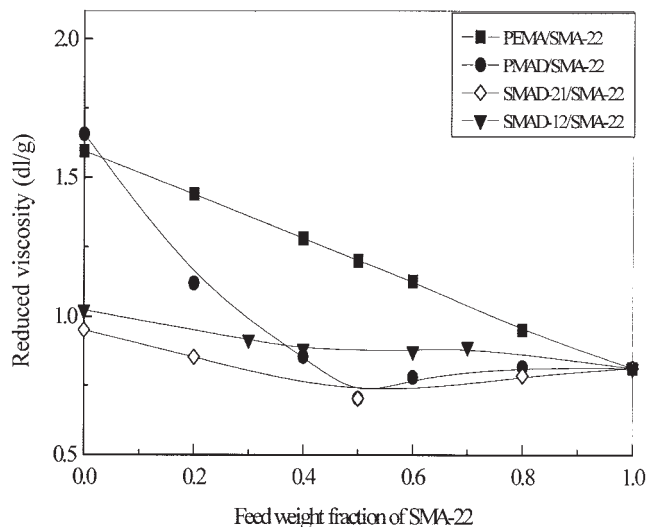


Figure 2 Reduced viscosity of PEMA/SMA-22, PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 solutions in THF as a function of the feed weight fraction of SMA-22 at 25°C.

ones formed complexes in butan-2-one. This was mainly due to the additional contribution of the nitrogen atom of the comonomer MAD in specific interactions by hydrogen bonding that could develop between PMAD or SMAD basic copolymers with the SMA-22 acidic copolymer. These interactions were also evidenced by FTIR.³³ Similar results were observed by Jiang and coworkers^{2,34,35} in their study of poly(styrene-*co*-vinylphenol) with poly(styrene-*co*-vinylpyridine) and poly(styrene-*co*-vinyl benzoic acid) with poly(*n*-butyl methacrylate-*co*-4-vinylpyridine).

A negative deviation in all feed compositions was also observed with the PMAD/SMA-22 and SMAD-21/SMA-22 systems in THF, whereas with the SMAD-12/SMA-22 system, such a deviation was observed only in the presence of an excess of the basic copolymer. A linear variation of the reduced viscosity as a function of the weight fraction was observed for the compositions rich in the acidic copolymer. Figure 2 displays these observations.

It is well known that THF has a strong ability to form hydrogen bonding with proton-donating polymers.^{2,24,36} It can develop associations with the SMA-22 acidic copolymer. This is confirmed by the Huggins constant (K_H) of the SMA-22 copolymer listed in Table I. Besides the self associations within the SMA-22 copolymer, such polymer-solvent interactions will affect those that may occur between the constituents of the mixture. Furthermore, the introduction of 12 mol % of the basic comonomer MAD within the copolymer SMAD was insufficient to induce complexation in the rich region of the acidic copolymer.

The minima of the curves of the apparent reduced viscosities correspond to the most stable composition

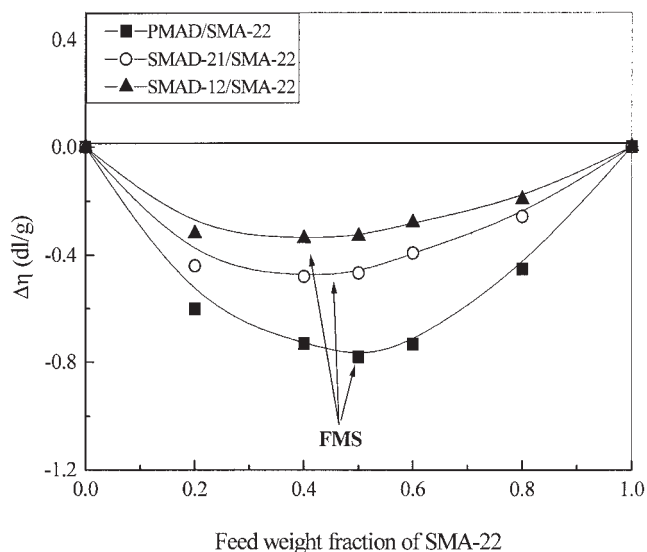


Figure 3 Variation of $\Delta\eta$ of PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 systems in butan-2-one as a function of the feed weight fraction of the acidic copolymer at 25°C.

of the complex or the complex stoichiometry called *fixed mean stoichiometry* (FMS).³⁷ The FMS of polymeric systems varies generally with the quantity of functional groups within the copolymers and gradually approaches a 1/1 ratio when the amount of functional groups increases.^{35,38}

The difference between the viscosities measured experimentally and those calculated from the arithmetic average, denoted $\Delta\eta$, is represented as a function of the feed weight fraction of the acidic copolymer SMA-22 in butan-2-one and THF for PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 systems (Figs. 3 and 4).

These curves show that most of the viscosity loss occurred when an important quantity of the proton-acceptor copolymer SMAD (12 or 21) was added to a small quantity of the proton-donor copolymer because the FMS was located in the rich region of the basic copolymer SMAD. This is explained by the fact that complex aggregates formed a loose structure with free styrene units of the SMA-22 acidic copolymer.

The value of the FMS for these systems in butan-2-one and THF varied with the content of MAD in the SMAD copolymer and equaled the ratio (1/1) for the PMAD/SMA-22 one.

DSC analysis

DSC is in general the most convenient technique for determining the miscibility of polymer blends. Before the DSC analyses, we carried out qualitative tests and observed one homogeneous phase when SMA-22 was mixed in a common solvent with PEMA and transpar-

ent films after solvent evaporation. One T_g , intermediate between the T_g 's of the two pure polymers PEMA and SMA-22, was observed from the DSC thermograms of blends of different compositions. This confirmed the miscibility of this pair of polymers.

SMA-22 was, however, found to form interpolymer complexes with PMAD, SMAD-21, and SMAD-12, as shown by the formation of precipitates just after the mixing of the two polymers in a common solvent. A single T_g , sometimes higher than the T_g 's of the two components of the mixture, was observed with these systems. Figure 5 presents a curve of T_g versus the weight fraction of SMA-22 for PEMA/SMA-22, whereas Figure 6 displays T_g versus the feed weight fraction of SMA-22 for PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 systems.

As shown by these figures, there are two kinds of curves. When the MAD content in SMAD is 12 mol %, the curve of T_g versus the feed composition appears sigmoidal with respect to the linear average line. However, the T_g 's of the blends or complexes are all above the linear average line when the MAD content in SMAD is 21 mol % or higher, as with the SMAD-21/SMA-22 or PMAD/SMA-22 and PEMA/SMA-22 systems.

The decrease of the content of the basic comonomer MAD from 12 to 3 mol % within the SMAD copolymer led to the immiscibility of SMAD-3/SMA-22 blends. Phase separation occurred when these two polymers were mixed in a common solvent, and opaque films were obtained after solvent evaporation. As displayed in Figure 7, two T_g 's close to those of the pure constituents and independent of the composition were observed with these blends. Despite the eventual attrac-

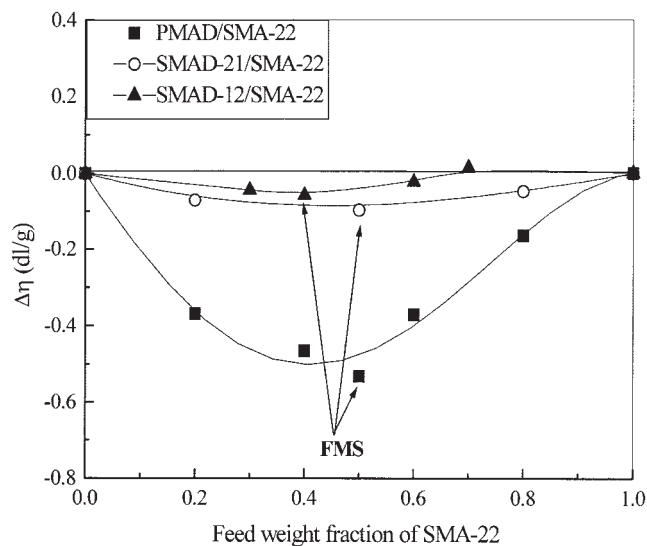


Figure 4 Variation of $\Delta\eta$ of PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 systems in THF as a function of the feed weight fraction of the acidic copolymer at 25°C.

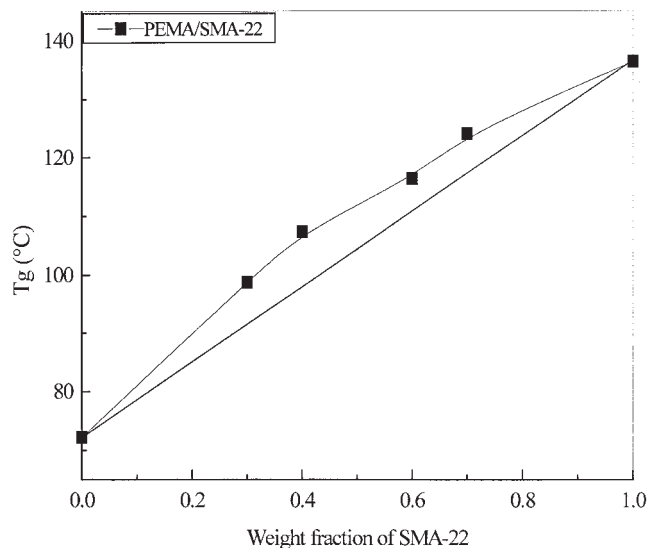


Figure 5 T_g of the PEMA/SMA-22 system in butan-2-one as a function of the weight fraction of the acidic copolymer SMA-22.

tive interactions between the two comonomers methacrylic acid (MA) and MAD, they were insufficient to overcome the acid–acid self-associations in the SMA-22 copolymer.

The miscibility of the PEMA/SMA-22 system was analyzed with the T_g –composition curve presented in Figure 5.

The positive deviation of T_g from the weight average of the T_g 's of the pure components can be attributed mainly to the specific polymer–polymer interactions (carboxylic acid–ester) that occurred between the components of the blends. These specific interac-

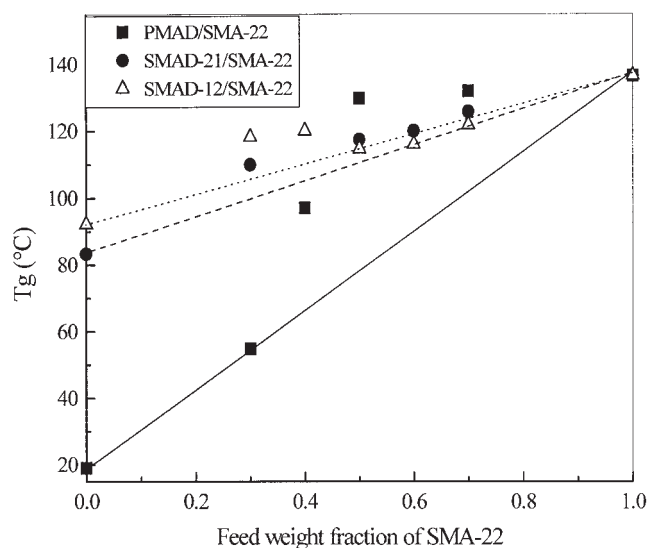


Figure 6 T_g of the PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 systems in butan-2-one as a function of the feed weight fraction of the acidic copolymer SMA-22.

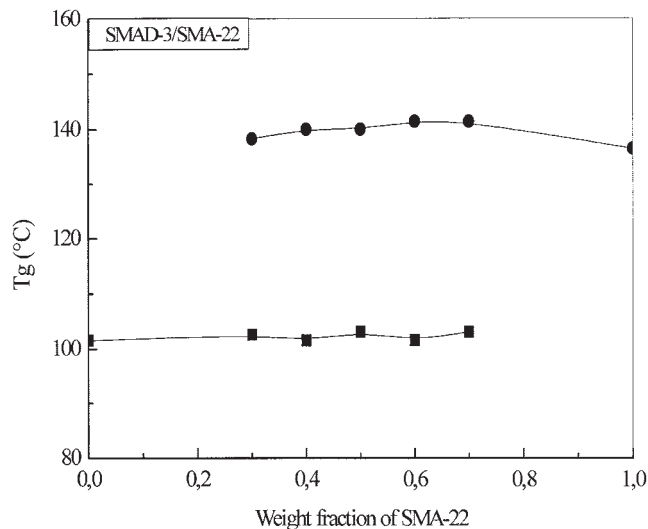


Figure 7 T_g of the SMAD-3/SMA-22 system in butan-2-one as a function of the weight fraction of the acidic copolymer SMA-22.

tions were estimated from the constant q obtained from the Kwei³⁹ equation as follows:

$$T_{gM} = \frac{W_1 T_{g1} + K W_2 T_{g2}}{W_1 + K W_2} + q W_1 W_2 \quad (1)$$

where W_1 and W_2 are the weight fractions of the two components of the blend; T_{g1} , T_{g2} , and T_{gM} are the glass-transition temperatures of the two polymers and their mixture, respectively; and q reflects the extent of intermolecular specific interactions between the two polymers. The greater this parameter is, the more important the specific interactions are. The q parameter should not be considered as simply reflecting the strength of the interactions in blends. According to Painter et al.,⁴⁰ this parameter depends on the balance between the processes of self-association and interassociation in the blend. K is an adjustable parameter. For systems with strong interactions, K is 1, and the Kwei equation takes the following form:

$$T_{gM} = W_1 T_{g1} + W_2 T_{g2} + q W_1 W_2 \quad (2)$$

The Kwei constant value for the PEMA/SMA-22 system is 32.

Because the actual weight fractions of SMA-22 in the complexes were not determined, the estimation of the Kwei constant q from the curve of T_g versus the feed composition was slightly different.

We note, however, that the most positive deviation in T_g versus the feed composition was observed with the PMAD/SMA-22 system. Besides the ester–carboxylic acid interactions that could occur with both the PEMA/SMA-22 and PMAD/SMA-22 systems, there

were amine–carboxylic acid ones in the PMAD/SMA-22 system. These results confirmed the contribution of the nitrogen atom of PMAD in the hydrogen-bonding specific interactions. The DSC results are in agreement with those obtained from the viscometric study, in which a negative deviation of the apparent reduced viscosity versus the weight fraction of SMA-22 was observed with the PMAD/SMA-22 system but not with the PEMA/SMA-22 one.

The transition from the PMAD/SMA-22 system to the SMAD-21/SMA-22 and SMAD-12/SMA-22 ones reduced the positive deviation. This was due to the styrene effect, which was inert toward hydrogen-bonding specific interactions.

The most positive deviation in the curve of T_g versus the feed composition observed with the SMAD-21/SMA-22 system was noted in a region of an excess of the basic copolymer. This result is in agreement with the viscometric study, in which the most stable complex was observed in the presence of an excess of the basic copolymer.

The curve of T_g versus the feed composition had a sigmoidal shape for the SMAD-12/SMA-22 system. It showed a positive deviation from the weight average of T_g 's of the pure components in the region of higher content of the basic copolymer SMAD-12, whereas it revealed a slightly negative deviation in the presence of an excess of the acidic copolymer SMA-22. In the presence of an excess of the acidic copolymer, carboxylic groups in each chain of SMA-22 had sufficient strength to form complexes with the basic copolymer SMAD-12. However, the quantity of SMAD-12 was insufficient to complex all chains of the acidic copolymer existing in the polymeric mixture. Therefore, in the formed complexes, an important fraction of the carboxylic groups of SMA-22 was self-associated as dimers, and only some groups were interassociated. In this case, the structure of the formed complex was not very compact. This phenomenon resulted in T_g 's lower than the weight average of the two T_g 's of the pure components. When the SMAD-12 basic copolymer quantity was in excess, an important fraction of dimers was consumed in the acid–base associations, and so T_g 's were higher than the weight average of the two T_g 's of the pure components.

To confirm the existence of specific interactions within PEMA/SMA-22, PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 binary systems, the approach of Schneider and coworkers^{41–44}, given by eq. (3), was used:

$$\frac{T_{gM} - T_{g1}}{(T_{g2} - T_{g1})W_{2C}} = (1 + K_1) - (K_1 + K_2)W_{2C} + K_2W_{2C}^2 \quad (3)$$

with

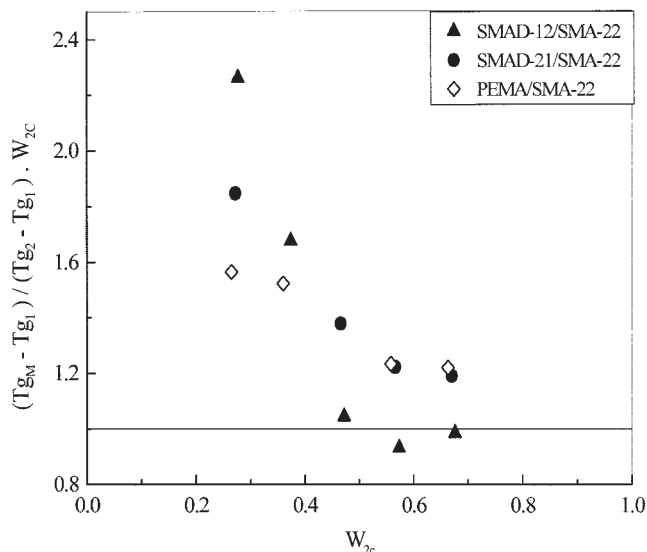


Figure 8 Variation of $(T_{gM} - T_{g1}) / (T_{g2} - T_{g1})W_{2C}$ for PEMA/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 systems as a function of W_{2C} of SMA-22.

$$W_{2C} = \frac{KW_2}{W_1 + KW_2}$$

and

$$K = \frac{\rho_1 T_{g1}}{\rho_2 T_{g2}}$$

where W_{2C} is the corrected weight fraction of component 2 with the higher T_g ; ρ_1 and ρ_2 are the densities of polymers 1 and 2, respectively; and K_1 and K_2 are constants proportional to the intensity of the molecular interactions.

In the absence of specific interactions, the values of K_1 and K_2 equal zero, and the equation becomes

$$\frac{T_{gM} - T_{g1}}{(T_{g2} - T_{g1})W_{2C}} = 1 \quad (4)$$

Any positive deviation from the horizontal line is considered evidence of the presence of specific interactions within these systems.

The variation of $(T_{gM} - T_{g1}) / (T_{g2} - T_{g1})W_{2C}$ as a function of W_{2C} of SMA-22 for the PEMA/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 systems is presented in Figure 8.

This figure shows a positive deviation in all composition for PEMA/SMA-22 and SMAD-21/SMA-22, confirming the presence of specific interactions within these binary systems, whereas a small negative deviation can be observed in the presence of an excess of the acidic copolymer. This may be due to the self-associations within the acidic copolymer SMA-22.

CONCLUSIONS

As a contribution to the study of immiscibility–miscibility–complexation transitions in polymer blends induced by hydrogen bonding, PEMA/SMA-22, PMAD/SMA-22, and SMAD (3, 12, and 21)/SMA-22 blends were studied by viscometry and DSC. A viscometric study revealed that the PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 systems formed interpolymer hydrogen-bonding complexes in butan-2-one solutions. The same phenomena were observed for PMAD/SMA-22 and SMAD-21/SMA-22 in THF. As for the SMAD-12/SMA-22 system in this solvent, such behavior was noted in the presence of an excess of the basic copolymer SMAD-12, whereas the PEMA/SMA-22 blend did not form complexes in these two solvents. The minimum content required for the interpolymer complexation was higher in THF than in butan-2-one. The FMS value progressively increased with the MAD composition in the SMAD copolymers. A 1/1 complex was obtained for the PMAD/SMA-22 system.

DSC studies showed the immiscibility of the SMAD-3/SMA-22 system. This technique did not permit us to distinguish miscible blends from interpolymer complexes in the PEMA/SMA-22, PMAD/SMA-22, SMAD-21/SMA-22, and SMAD-12/SMA-22 binary systems. Stronger interactions, however, occurred within the PMAD/SMA-22 system.

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