

Blends of poly(2-hydroxyethyl methacrylate)/ (styrene-*co*-dialkyl itaconates) and poly(*N*-vinyl-2-pyrrolidone)/(styrene-*co*-dialkyl itaconates)

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Summary

Blends containing poly(*N*-vinyl-2-pyrrolidone) (PVP) and poly(hydroxyethyl methacrylate) (PHEMA) with (styrene-*co*-dimethyl itaconate) (Sty-*co*-DMI) and (styrene-*co*-diethylitaconate) (Sty-*co*-DEI) copolymers of three different compositions were studied. One T_g value over the whole range of compositions is observed for the majority of the blends, what is indicative of compatibility. The Gordon-Taylor k_{GT} and the Couchman k_C parameters were determined for all the blends in order to compare the strength of the interactions. The effect of the side chain structure of the copolymer on the miscibility of these blends is analyzed.

Introduction

Polymer blends containing copolymers are of considerable interest, both academic and industrial, because it has been demonstrated that systems consisting of a homopolymer (1, 2) and a copolymer or two different copolymers (3-5) can be miscible over a range of copolymer compositions. The effect of specific interactions in such systems, which could be the responsible of the miscibility is not clear. The driving force for miscibility is attributed to unfavourable interaction between the monomer pairs comprising the copolymer (2, 6) which outweighs the aggregate effect of all the other interactions involved, the so called "repulsion effect" between the covalently bonded comonomer units of the copolymers (7-9). The balance of the segmental interactions has been formalized using the modified Flory-Huggins expression for the free energy of mixing in which the interaction parameter χ_{12} is replaced by an expandable term χ_{blend} (10, 11).

In previous papers (12-15) we have reported the miscibility behaviour in blends composed of poly(mono and dialkylitaconates), with poly(thiocarbonates), poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(vinylpyridines) (PVPy) and poly(methacrylates). Miscibility, interpolymer complex formation and phase separation were reported, depending on the polymer side chain structure. Hydrogen bond formation through the free carboxyl groups is one of the main factors that affects the miscibility and complex formation in such systems.

Poly(2-hydroxyethyl methacrylate) (PHEMA) can strongly interact with acceptor polymers by hydrogen bonds, PVP interacts strongly with polymers of very different structures (12-16) and polystyrene is miscible with a number of polymers (10,11).

The aim of the present work is the study of the miscibility behaviour in blends of (PHEMA)/(Styrene-*co*-dialkyl itaconates) (Sty-*co*-DAI) and PVP/(Sty-*co*-DAI) in order to study the effect of the polymer structure on miscibility using a common copolymer with polymers which can interact by different ways.

Experimental

Monomers, polymers and copolymers preparation

Commercial PVP samples weight-average molecular weight M_w : 24000 (PVP₂₄) and (PHEMA) M_w : 300.000 from Aldrich were used. Dimethyl itaconate (DMI) and diethyl itaconate (DEI), were synthesized by reaction of itaconic acid with the corresponding alcohols in toluene using *p*-toluensulphonic acid as previously reported (16,17).

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Copolymerization of styrene with DMI and DEI were carried out in bulk at 345-350 °K (depending on the diitaconate used) under nitrogen, using α, α' -azobisisobutyronitrile (AIBN) as initiator. The monomer feed ratio was varied in a series of copolymerizations of both comonomers. Polymerization time was varied from 15 to 30 min and the conversion of monomer to polymer was about 10%. Purification of the copolymers was achieved by reprecipitation with diethylether in THF solutions, before vacuum drying at r.t. Two sets of copolymers of three different compositions were selected. The copolymer compositions were determined by Fourier Transform Infrared (F.T.I.R.) measurements in KBr using a Bruker IFS 25 spectrophotometer and a calibration curve, following the intensity of the carbonyl groups of itaconate moieties.

Preparation of the blends

Blends of different compositions were prepared by solutions casting using chloroform and then evaporated at room temperature and vacuum dried at 298° K for 72 h. The polymer concentration in the solution was about 2% (w/w).

DSC Measurements

The glass transition temperatures (T_g) of the different polymers, copolymers and blends were measured with a Mettler TA-3000 system equipped with a TC-A 10 Processor with a DSC-20 cell. Polymer samples were dried under reduced pressure in a vacuum oven prior measurements. Dry nitrogen was used as purge gas and thermograms were measured in the range 308° K to 453° K, at a scan rate of 10 K/min.

Results and discussion

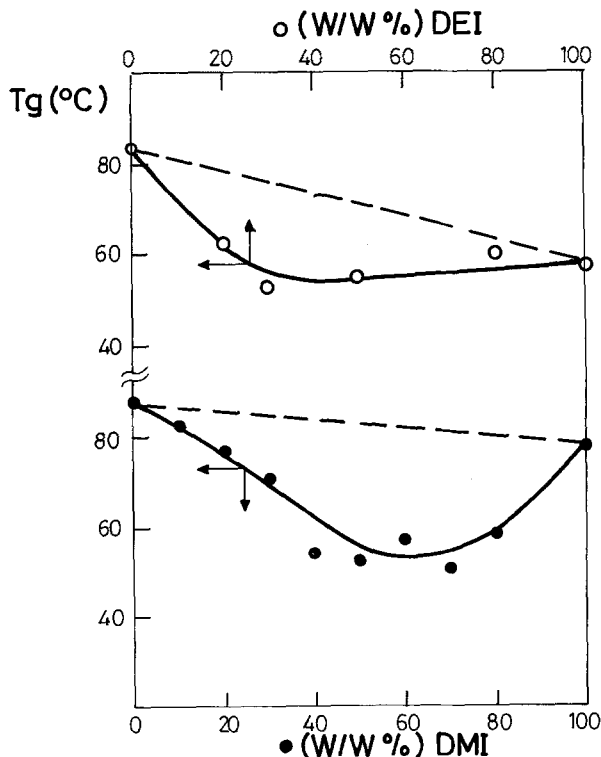


Figure 1. Variation of the glass transition temperature, T_g , with the copolymer composition for copolymers of (Sty-co-DMI) (●) and (Sty-co-DEI) (○).

Statistical copolymers of styrene-co-dimethyl itaconate (Sty-co-DMI) and styrene-co-diethyl itaconate (Sty-co-DEI) of different chemical compositions at constant weight average molecular weights were prepared by solution polymerization in benzene. Purification was achieved by repeated precipitation in methanol. The dependence of the Tg of the copolymers on the chemical composition is shown in Figure 1. Tg varies in a monotonous way with copolymer composition.

To mathematically describe the correlation between the Tg and copolymer composition, the equations of Gordon-Taylor (18) and Couchman (19) were used; the k_{GT} and k_C , i.e., the constants of the corresponding equations were determined. These constants are adjusting parameters related to the degree of curvature of the Tg-composition plots. The k_{GT} and k_C values for both theoretical treatments obtained for these copolymers are, respectively: 0.32 and 0.34 for (Sty-co-DMI) and 0.039 and 0.035 for (Sty-co-DEI) respectively. Good agreement between both theoretical procedures is found. k_{GT} and k_C values would indicate strong interaction between the comonomers.

Statistical copolymers of three different comonomer chemical compositions and labelled as 20, 50 and 80 wt % of styrene were selected. The exact styrene compositions are 18.5, 47.0 and 82.0 wt % for copolymers containing DMI and 18.0, 49.5 and 79.0 wt % for copolymers containing DEI. In order to analyze their thermal behaviour when blended with PVP and PHEMA the Tg-composition diagrams were established.

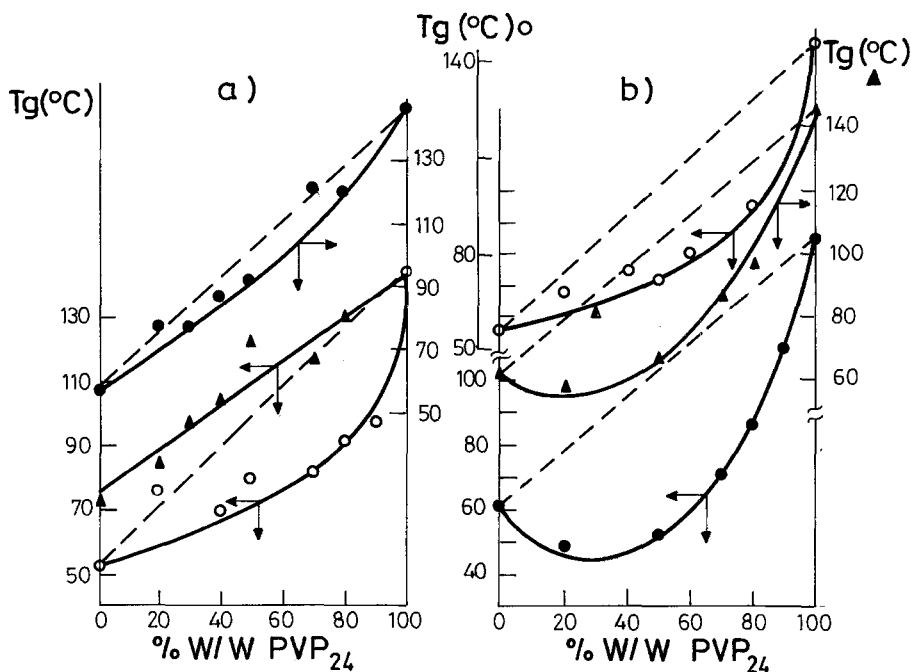


Figure 2. Variation of the glass transition temperature, Tg, for blends containing PVP₂₄ and a) (Sty-co-DMI): 20 wt % Sty. (●), 50 wt % Sty.(○), 80 wt % Sty. (▲). b) (Sty-co-DEI): 20 wt % Sty. (●), 50 wt % Sty.(○), 80 wt % Sty. (▲).

Figure 2-a shows the dependence of Tg on composition for blends of (Sty-co-DMI) with PVP₂₄ and using the copolymers of the three different compositions mentioned above. Figure 2-b shows the same plots for blends containing different (Sty-co-DEI)

copolymers with PVP₂₄. There is distinct evidence of only a single glass transition for each of the different blend compositions. These T_g values are intermediate between the T_g of PVP₂₄ and the corresponding copolymer, irrespective of the copolymer composition involved. Therefore, miscibility over the whole range of composition can be assumed. A continuous variation in the T_g is observed but the degree of curvature of the plots is different. For blends with the copolymer rich in polystyrene the variation of T_g with composition is almost a straight line and for blends containing the copolymer richer in DMI the concavity is less pronounced. In contrast, blends containing the copolymer of 50% composition show large concavity. In the case of blends of PVP₂₄ and Sty-co-DEI, the degree of curvature is very pronounced and similar in all the systems studied. Nevertheless in Figure 2, it is possible to observe that the degree of curvature is in general larger than in blends containing (Sty-co-DMI). A qualitative analysis could interpret these results as a consequence of possible steric hindrance of the side chain structure on the strength of the interaction. In fact, the presence of the ethyl lateral group in the diethyl itaconate comonomer could affect in some way the interaction because of the slight difference in the bulkiness between methyl and ethyl groups.

In order to represent the T_g-composition variation of the blends, one of the most used equations is that of Gordon-Taylor (18), to quantify the strength of the interaction in the case of copolymers. The k_{GT} parameter can be taken as a semiquantitative measure of the strength of the interaction between the components of the blend as Belorgey and Prud'homme have pointed out (20). Another equation that can be used for similar purpose is that of Couchman (19) applied in this case to the polymer blend.

Table 1. Constants of the Gordon-Taylor (k_{GT}) and Couchman (k_C) equations for blends of (Sty-co-DAI)/PVP₂₄ and (Sty-co-DAI)/PHEMA

Copolymer	Copolymer Composition (wt%) Styrene	k_{GT}	k_C
(Sty-co-DMI)/PVP ₂₄	20	0.62	0.96
(Sty-co-DMI)/PVP ₂₄	50	0.14	0.13
(Sty-co-DMI)/PVP ₂₄	80	0.65	0.85
(Sty-co-DEI)/PVP ₂₄	20	0.13	0.20
(Sty-co-DEI)/PVP ₂₄	50	0.17	0.24
(Sty-co-DEI)/PVP ₂₄	80	0.19	0.30
(Sty-co-DMI)/PHEMA	20	0.35	0.45
(Sty-co-DMI)/PHEMA	50	0.46	0.63
(Sty-co-DMI)/PHEMA	80	0.18	0.25
(Sty-co-DEI)/PHEMA	20	0.33	0.34
(Sty-co-DEI)/PHEMA	50	0.63	0.79
(Sty-co-DEI)/PHEMA	80	0.83	1.00

The concavity in the T_g-composition plots is observed even in polymer-polymer blends which present strong interactions (12,21-25). The analysis of the degree of interaction between the components of the blends, can be carried out by comparison of the k_{GT} and k_C parameters for the different systems studied. Table 1 summarizes these values for all the systems studied. According to the experimental results previously reported for different kind of miscible polymers blends, the degree of concavity in the T_g-composition plots can be considered as inversely proportional to the strength of the interaction between the two polymers in the mixture (20).

Figure 3 represents the T_g-composition plots for blends containing (Sty-co-DMI) (Figure 3-a) and (Sty-co-DEI) (Figure 3-b) with PHEMA. One T_g value is observed for all the blends and the monotonous variation of T_g shows a slightly deviation from the linearity, which can be interpreted as a miscible polymer blend with a strong interaction between blend components. The shape of the curves could be attributed to a stronger interaction, relative to the plots shown in Figure 2, i.e., the degree of curvature is less pronounced. This means that

the degree of compatibility in these systems is larger than those containing PVP₂₄. This fact could be attributed to specific interactions between PHEMA and the copolymer. Blends containing copolymers with higher styrene content seem to be more compatible than those with low styrene content, which should be reflected in the k_{GT} and k_C values. In fact, blends of (Sty-co-DEI) (80% Sty) with PHEMA are completely miscible and the thermal behaviour is ideal (straight line in Tg-Composition plots). PHEMA interacts strongly by hydrogen bonding with acceptor polymers, therefore, from this point of view, PHEMA interacts with (Sty-co-DMI) and (Sty-co-DEI) stronger than PVP₂₄ through the -OH groups. Effectively, plots shown in Figure 3 are similar to that for an ideal blend, miscible over the whole range of compositions, for all the copolymers of the three different compositions.

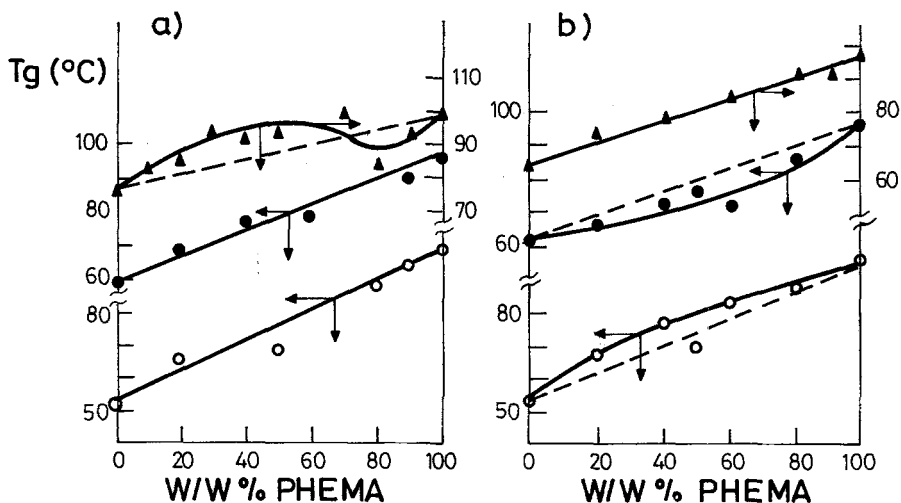


Figure 3. Variation of the glass transition temperature, Tg, for blends containing PHEMA and a) (Sty-co-DMI): 20 wt % Sty. (●), 50 wt % Sty. (○), 80 wt % Sty. (▲). b) (Sty-co-DEI): 20 wt % Sty. (●), 50 wt % Sty. (○), 80 wt % Sty. (▲).

The k_{GT} and k_C values obtained from these plots are summarized in Table 1. They show that it is possible to notice differences between these systems. According to these results, the interaction in blends containing Sty-co-DAI/ PVP₂₄ is less pronounced, which can be attributed to the absence of a specific interaction, taken into account that the affinity between PS, PVP and PDAI should not be important. In the case of blends containing Sty-co-DAI/ PHEMA, miscibility could be attributed to hydrogen bonding and therefore the interaction between the components is stronger.

It is possible to conclude that copolymers of styrene and dialkyl itaconates with PVP and PHEMA are miscible over the whole composition range. The different behaviour shown by systems containing PHEMA can be attributed to specific interactions such as hydrogen bonds.

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