

Miscibility of poly(p-vinyl phenol) with polymethacrylates

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Summary

Poly(p-vinyl phenol) is miscible with poly(methyl methacrylate), poly(ethyl methacrylate), poly(n-propyl methacrylate), poly(isopropyl methacrylate), and poly(tetrahydrofurfuryl methacrylate), but is immiscible with poly(n-butyl methacrylate). Except for poly(p-vinyl phenol)/poly(methyl methacrylate) blends, the other miscible blends show pronounced positive deviations in their glass transition temperatures. The T_g -composition curves of the five miscible blend systems can be described by the Gordon-Taylor and the Kwei equations.

Introduction

Hydroxyl-containing polymers such as poly(hydroxyether of bisphenol-A) (1-6), poly(styrene-co-allyl alcohol) (7,8), poly(p-vinyl phenol) (9-13), poly(styrene-co-p-vinyl phenol) (14), poly(styrene-co-p-(hexafluoro-2-hydroxyl isopropyl)styrene) (14-18), and novalac resins (19-21) are miscible with a large variety of polymers which contain proton acceptor groups. Hydrogen-bonding interactions in many of these blends have been detected by Fourier transform infrared (FTIR) spectroscopy.

Poly(p-vinyl phenol) (PVPh) is miscible with poly(vinyl acetate), poly(ethylene-co-vinyl acetate), poly(ϵ -caprolactone), poly(β -propiolactone), poly(vinyl methyl ketone), poly(ethylene oxide), poly(vinyl pyrrolidone), and poly(2-ethyl-2-oxazoline) (9-13). The miscibility of PVPh with some polymethacrylates is reported in this communication.

Experimental

The following polymers were used in this study: PVPh (Polysciences, $M_n = 1500-7000$), poly(methyl methacrylate) (PMMA) (Du Pont Elvacite 2010, $M_w = 120,000$), poly(ethyl methacrylate) (PEMA) (Du Pont Elvacite 2042, $M_w = 310,000$), poly(n-propyl methacrylate) (PnPMA) (prepared by bulk polymerization at 60°C for 18 h using 0.3% by weight of AIBN as initiator, $[\eta] = 1.17$ dL/g in 2-butanone at 30°C), poly(isopropyl methacrylate) (PiPMA) (Scientific Polymer Products, Inc., $[\eta] = 0.33$ dL/g in 2-butanone at 30°C), poly(n-butyl methacrylate) (PnBMA) (Du Pont Elvacite 2044, $M_w = 288,000$) and poly(tetrahydrofurfuryl methacrylate) (PTHFMA) (Scientific Polymer Products, Inc., $[\eta] = 0.31$ dL/g in toluene at 30°C).

All the blends except PVPh/PTHFMA blends were cast from 2-butanone. The 2-butanone solutions of PVPh/PTHFMA blends showed turbidity. However, the tetrahydrofuran (THF) solutions of PVPh/PTHFMA blends were clear and hence they were cast from THF. As PVPh is hydrophilic (11,22), attempt

was made to exclude moisture during the preparation of the blends. Polymer solution was poured into an aluminium pan and then placed in a desiccator. The lid of the desiccator was partially opened such that solvent evaporated slowly over a period of about 24 h. The blends were then dried in a vacuum oven at 120°C for at least 48 h.

T_g 's of the polymers and blends were measured using a Perkin-Elmer DSC-4 differential scanning calorimeter. A heating rate of 20°C/min was used and T_g was taken at the initial onset of the change of slope in the heat capacity plot.

All the miscible blends were examined for the existence of lower critical solution temperatures (LCST) using the method as described previously (23).

Results and discussion

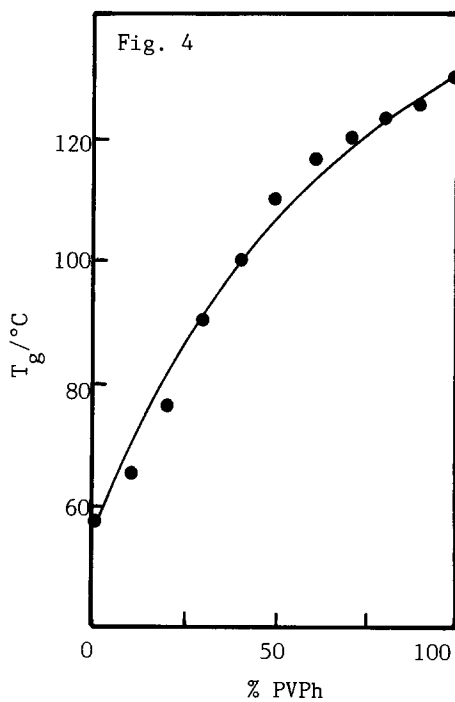
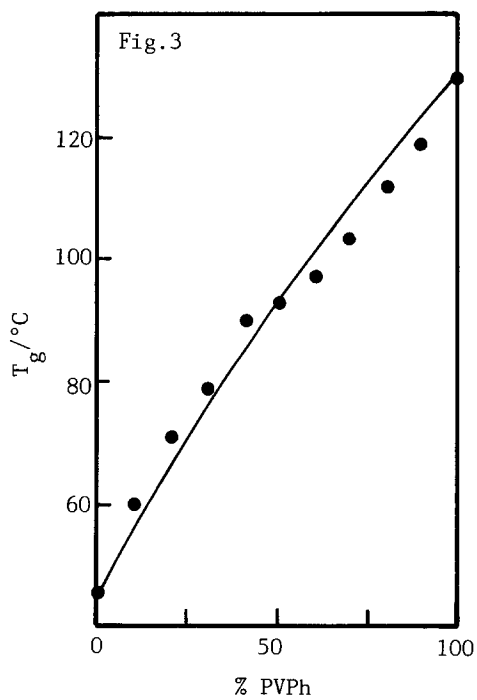
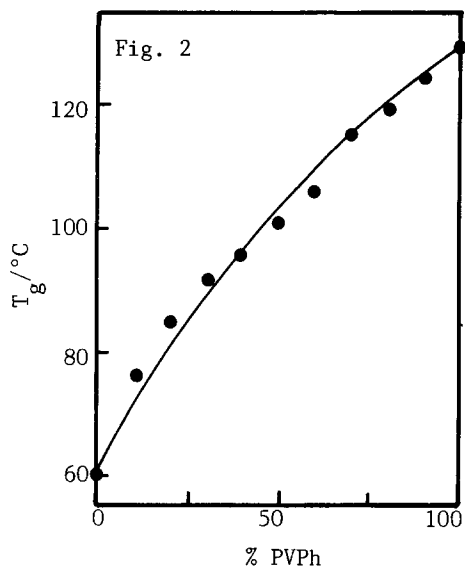
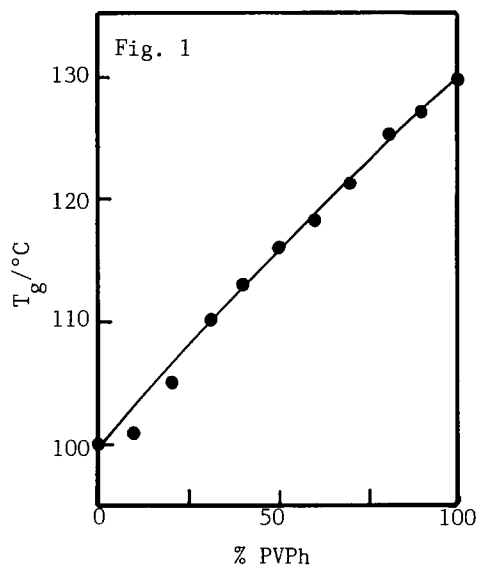
All the blends of PVPh with PMMA, PEMA, PnPMA, PiPMA and PTHFMA were transparent and with a brownish tinge due to PVPh. Each blend showed only one composition-dependent T_g , indicating its single-phase nature. The T_g -composition curves for the five miscible blend systems are shown in Figures 1 to 5. Phase separation of these blends could not be induced by heating up to 300°C. However, the PVPh/PnBMA blends were heterogeneous. The immiscibility of this blend system was further confirmed by T_g measurements which showed the existence of two T_g 's in each blend. Fahrenholtz and Kwei (19) reported that PVPh was immiscible with PMMA and poly(styrene-co-acrylonitrile) (SAN). We confirmed the immiscibility of PVPh with SAN, but we found that PVPh was miscible with PMMA.

The miscibility of homologous polymethacrylates with various polymers such as poly(vinylidene fluoride) (PVDF) (24), poly(vinyl chloride) (PVC) (25,26), SAN (27) and poly(α -methyl styrene-co-acrylonitrile) (MSAN) (28) have been reported. The lower members of the polymethacrylates are readily miscible with these polymers, but the higher members are not. Based on the cloud point measurements (24,27,28) and inverse gas chromatographic studies (25,26), it was found that as the size of the pendant alkyl group increased, the interaction between the polymethacrylate and the other polymer became less intense and eventually the blend became immiscible.

Coleman and co-workers (9-12) have shown that there are hydrogen-bonding interactions involving the PVPh hydroxyl groups and either the carbonyl or the ether oxygen moieties of the other polymers in PVPh-containing miscible blends. In the present case, the formation of a miscible PVPh/polymethacrylate blend is likely a result of hydrogen-bonding interactions as well.

It is interesting to note that while PnBMA is immiscible with PVPh, PTHFMA is miscible with PVPh in spite of the bulkiness of the tetrahydrofurfuryl group. We have earlier reported that PTHFMA is miscible with SAN, MSAN, PVC, phenoxy and poly(styrene-co-allyl alcohol) (29,30). The unusually good miscibility of PTHFMA as compared with the other higher members of the polymethacrylates can be attributed to the presence of two interacting moieties, namely, the carbonyl group and the ether oxygen in the tetrahydrofuran ring in PTHFMA.

As shown in Figure 1, the T_g of a PVPh/PMMA blend is approximately a weighted-average value of the T_g 's of the component polymers. For the other miscible blend systems, T_g 's of the blends are higher than the weighted-average values as shown in Figures 2 to 5. Such positive



Figures 1 to 4. T_g -composition curves of blends.

(1) PVPh/PMMA (2) PVPh/PEMA (3) PVPh/PnPMA (4) PVPh/PTHFMA.

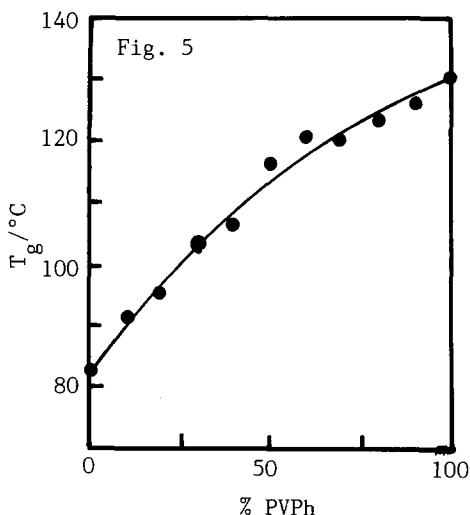


Figure 5.
T_g-composition curve of
PVPh/PiPMA blends.

deviations of T_g have been observed for miscible blends showing hydrogen-bonding (13,14,17,20,21) and electron donor-acceptor (31) interactions. The positive deviation of T_g is commonly taken as an indication of very strong intermolecular interactions which reduce the mobility of the polymer chains. T_g's of blends showing positive deviations can be described by the Gordon-Taylor equation (32)

$$T_g = (w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2)$$

and the Kwei equation (20)

$$T_g = (w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2) + q w_1 w_2$$

where T_g, T_{g1} and T_{g2} are the glass transition temperatures of the blend, polymer 1 and polymer 2, respectively; w₁ and w₂ are the weight fractions of polymer 1 and polymer 2 in the blend; k and q are parameters. The Kwei equation is identical to the Gordon-Taylor equation when q = 0. When k = 1 and q = 0, T_g of the blend is then a weighted-average of the T_g's of the two polymers. The k parameters in the Gordon-Taylor equation, and the k and q parameters in the Kwei equation for the five miscible blend systems are calculated by least-squares analysis to obtain the best fit of the experimental data and the results are shown in Table 1.

Table 1. Parameters in Gordon-Taylor and Kwei equations.

Blend system	Gordon-Taylor		Kwei
	k	k	q
PVPh/PMMA	1.05	1.12	4.9
PVPh/PEMA	1.68	1.05	30.1
PVPh/PnPMA	1.34	1.17	10.0
PVPh/PiPMA	1.91	1.02	30.0
PVPh/PTHFMA	2.03	1.38	30.3

Both the Gordon-Taylor equation and the Kwei equation give reasonably good fits for the five blend systems. The curves in Figures 1 to 5 are based on the Kwei equation using the k and q values in Table 1. The curves based on the Gordon-Taylor equation are not shown in these figures as they cluster closely to those based on the Kwei equation.

The k values from the Gordon-Taylor equation (33,34) and the q values from the Kwei equation (20,21,31) have been used to estimate the strength of intermolecular interaction. When such an approach is used for the present work, several interesting points arise. First of all, PMMA, the first member of the polymethacrylates, then appears to interact less intensely with PVPh as compared with the other polymethacrylates. This is in contrast to the other blend systems in which PMMA is found to interact most intensely with the other polymers as mentioned earlier. Secondly, PiPMA appears to interact more intensely with PVPh as compared with PnPMA. Thirdly, of the five polymethacrylates which are miscible with PVPh, PTHFMA appears to interact most intensely with PVPh. At this time, it is rather difficult to explain the first two points. The intense interaction between PVPh and PTHFMA could be rationalized by the presence of two interacting moieties in PTHFMA. Further study is needed to quantify the intermolecular interactions in these blends.

Acknowledgement

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