Effect of Tacticity of Poly(Methyl Methacrylate) on the Miscibility with Poly(Vinyl Acetate)

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ABSTRACT: The results of the miscibility between the chemically similar polymers poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) published so far show inconsistent statements concerning miscibility. The problems may be due to differences in molecular weights, tacticity, and preparation methods of the polymers. This investigation was carried out by using either chloroform or tetrahydrofuran (THF) as solvent to prepare the blends, because to our knowledge, nobody has reported any tacticity effect of PMMA on the miscibility with PVAc. Therefore, in this article, different tactic PMMAs were used to mix with PVAc and their miscibility was studied calorimetrically. The results showed little effect of solvent and tacticity. PMMA and PVAc were determined to be almost completely immiscible because of the observation of two T_g's. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 35–39, 2004

Key words: tacticity; miscibility; poly(methyl methacrylate); poly(vinyl acetate); binary blends

INTRODUCTION

In polymer–polymer mixtures, the entropy of mixing is usually very small; miscibility generally requires specific interactions such as hydrogen bonding, donor–acceptor interaction, etc., resulting in a negative free energy of mixing.[1] However, some miscible pairs are known to have no supposedly specific interactions operative. In these systems, the chemical structures are so similar that the free-volume contribution is very small; therefore, small positive exchange interaction energy allows the net free energy of mixing to be negative. A polyacrylate and a polyester (when their repeating units contain the same number of carbon atoms) belonging to this category were found to be miscible.[2]

The miscibility of the blends of poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc) has been widely studied. A very interesting effect was found by Ichihara and coworkers,[3] who prepared transparent PMMA/PVAc blends by a freeze-drying technique. In differential scanning calorimetry (DSC) experiments, these blends exhibited only single glass transition, a characteristic indication of miscible polymer blends. However, after annealing the blends at 400 K, two glass transition temperatures (T_g's) were detected corresponding to the T_g of the homopoly-

mers. The authors explained this by demixing of the frozen nonequilibrium state at temperatures higher than the T_g's of PMMA and PVAc. The same blends were prepared by Schneier[4] by mixing the polymers in the melt and in the absence of a solvent. PMMA was the major constituent of the blend. Data obtained from dynamic mechanical and DSC experiments show that, when they are mixed under given Brabender mix conditions, the blends exhibit properties characteristic of miscible polymer pairs. However, if the mix conditions are altered, a two-phase system is evidenced. Schenk et al.[5] prepared the PMMA/PVAc blends from solutions of benzene. They used nuclear magnetic resonance technique to study the miscibility of the same blends. Heterogeneity was detected and the results of immiscibility was also confirmed by DSC studies. The PMMA/PVAc blends in chloroform cast at 50°C were prepared by Song and Long.[6] They studied the blends by using DSC and IR techniques. PMMA is miscible with PVAc at all compositions. Based on IR spectra, conformational changes were detected in the miscible blends.

The influence of solvent and temperature on the miscibility of PMMA and PVAc was investigated by Muniz et al.[7] Experiments using DSC and viscometry were performed. The miscibility of the cast PMMA/PVAc blends (not definitely in equilibrium thermodynamic state) was observed to depend on the solvent. The miscible blends are miscible in chloroform at 30 and 50°C, whereas in *N,N*-dimethyl formamide (DMF) at the same temperatures, the blends are immiscible. In toluene, the miscibility depends on the tempera-

ture: the blends are miscible at 30°C and immiscible at 50°C.

In view of conflicting data, the present studies are intended to give some insight into miscibility in solid blend systems of PMMA and PVAc prepared from solutions of chloroform or tetrahydrofuran (THF) by using calorimetry. Although FTIR can give information on the miscibility and the processes of phase separation of the blends, calorimetry was used as the main investigation tool. Because the T_g difference between PMMA and PVAc is over 30°C, calorimetry proved to be effective in determining miscibility. According to the results of Ichihara et al.,[3] sample annealing procedures are also important. Therefore, the blends were cast at room temperature but annealed at 126–130°C to make the blends approach closely to the equilibrium state. To the best of our knowledge, nobody has reported the effect of tacticity of PMMA on the miscibility with PVAc. Thus in addition to the solvent effect, this investigation is also tried to determine the tacticity effect of PMMA on its miscibility with PVAc.

EXPERIMENTAL

Materials

Isotactic, atactic, and syndiotactic PMMAs (designated as iPMMA, aPMMA, and sPMMA in this study) were purchased from Polysciences, Inc. (Warrington, PA). According to supplier information, the molecular weights (M_w's) of iPMMA, aPMMA, and sPMMA are the same, about 100,000 g/mol. The mesodiad fractions of PMMA were previously computed.[8] The m and r fractions of iPMMA, aPMMA, and sPMMA were 68.7 and 31.3%, 33.8 and 66.2%, and 9.3 and 90.7%, respectively. The error of estimation was 5–8%. Molecular weight distributions of iPMMA, aPMMA, and sPMMA were not measured but the effect is believed to be minimal when compared with the effect of tacticity. PVAc used for this study was obtained from Scientific Polymer Products, Inc. (Ontario, NY). The M_w value for PVAc is approximately 100,000 g/mol.

Film preparation

Thin films of PVAc and its blends with tactic PMMA in three different weight ratios (∼ 3/1, 1/1, 1/3) were made by solution casting. Chloroform and THF were used as solvent for all the blend compositions. Chloroform and THF are A.C.S. reagents purchased from Fisher Scientific (Fair Lawn, NJ). All the solutions were cast onto glass plates and covered with petri dishes for slow evaporation overnight. Then the films were placed inside a vacuum oven for the removal of solvent. The final drying steps for all the films took place at temperatures of 126–130°C for about 16 h. The

films appeared to be transparent before annealing at 126–130°C. Then the films were slowly cooled to room temperature by air to make as-cast samples. The films were opaque after cooling. The as-cast samples were later used for DSC study.

Differential scanning calorimetry

T_g's of the polymer blends were determined by a DuPont 2000 thermal analyzer (DuPont NEN, Wilmington, DE) coupled with a mechanical cooling system. Experiments were often performed in two consecutive scans from 10 to 200°C in the ambient environment of nitrogen gas at a flow rate of 90–110 mL/min. At the end of the first thermal scan, the samples stayed at 200°C for 1 min. The samples were then cooled to 10°C at a cooling rate of 20°C/min and were scanned the second time. A heating rate of 20°C/min was used in each scan. The inflection point of the specific jump of a thermal scan was taken as the glass transition temperature. The glass transition temperatures determined from the first and second thermal scans were designated as T_{gsc} and T_{gfc}, respectively. Therefore, T_{gsc} is the T_g of the slowly cooled (as-cast) films and T_{gfc} is that of the fast cooled films. The glass transition temperature regions (ΔT_g) were calculated as differences between the onset and end points of T_{gfc}. The cooling rate was proven to be fast enough to produce virtually the same results as quenching.

RESULTS

Glass transition temperatures

The thermal scans of the chloroform-cast PMMA/PVAc blends are omitted for presentation. However, the calculated T_{gsc} and T_{gfc} values are listed in Table I. There is not much difference between T_{gsc} and T_{gfc} values. Because the T_{gfc} values are considered to be free of the effect of thermal history, they are used in the following discussion. The T_{gfc} values of chloroform-cast PMMA/PVAc blends were plotted in Figure 1. All the three blends (iPMMA/PVAc, aPMMA/PVAc, and sPMMA/PVAc) exhibited two T_g's. These two T_g values correspond very close to T_g's of the component polymers. Therefore, it can be concluded that PMMA was found to be nearly immiscible with PVAc regardless of tacticity.

For the use of THF as solvent, very similar results (as listed in Table II) were obtained for the same blends. The difference between the T_{gsc} and T_{gfc} is negligible. The T_{gfc} values of the THF-cast blends were plotted and shown in Figure 2. Two T_g's corresponding well to the T_g's of the homopolymers indicates that PMMA and PVAc are immiscible independent of tacticity.

TABLE I
Thermal Characteristics of Chloroform-Cast PMMA/PVAc Blends

	T_{gsc} (°C)	T_{gfc} (°C)	ΔT_g (°C)
iPMMA/PVAc			
(1) 100/0	68.1	77.2	15
(2) 74.6/25.4	45.5, 68.3	44.8, 76.3	8, 17
(3) 49.8/50.2	45.4, 69.4	43.3, 73.7	10, 14
(4) 24.7/75.3	n.d.[a]	44.9, 76.3	10, 13
aPMMA/PVAc			
(1) 100/0	103.8	105.9	13
(2) 74.4/25.6	44.8, 100.5	42.8, 102.9	9, 12
(3) 50.0/50.0	46.0, 100.7	44.2, 103.6	9, 13
(4) 25.2/74.8	46.0, 97.1	44.5, 103.6	8, 13
sPMMA/PVAc			
(1) 100/0	n.d.	129.6	19
(2) 75.0/25.0	45.5, 128.0	42.5, 127.3	11, 11
(3) 50.1/49.9	45.0, 127.6	42.1, 128.4	10, 11
(4) 25.5/74.5	n.d.	45.0, 126.0	10, 11
(5) 0/100	46.6	44.7	6

[a] n.d., not detected.

TABLE II
Thermal Characteristics of THF-Cast PMMA/PVAc Blends

	T_{gsc} (°C)	T_{gfc} (°C)	ΔT_g (°C)
iPMMA/PVAc			
(1) 100/0	71.0	77.3	17
(2) 74.7/25.3	45.3, 69.0	45.0, 75.8	11, 17
(3) 50.1/49.9	44.9, 73.7	44.0, 74.7	8, 18
(4) 25.4/74.6	46.2, 70.5	44.2, 76.4	9, 13
aPMMA/PVAc			
(1) 100/0	106.5	106.0	12
(2) 74.5/25.5	39.0, 104.0	43.0, 104.0	10, 12
(3) 50.5/49.5	41.8, 103.2	44.1, 103.1	10, 13
(4) 24.9/75.1	n.d.[a]	45.3, 105.2	10, 12
sPMMA/PVAc			
(1) 100/0	130.1	130.2	12
(2) 74.7/25.3	46.2, 127.3	42.8, 127.7	11, 13
(3) 49.8/50.2	42.0, 130.0	43.6, 127.6	10, 12
(4) 24.7/75.3	43.4, 127.0	45.8, 126.4	11, 15
(5) 0/100	n.d.	43.4	10

[a] n.d., not detected.

Phase compositions of PMMA/PVAc blends

Because two T_{gfc}'s were detected in most of the studied blends, PMMA-rich and PVAc-rich phases were rightfully assumed. Estimations of the compositions of these two phases were attempted and illustrated as the following: If the T_g of PVAc-rich phase is equal to or slightly lower than that of PVAc, the composition is considered to be 0% PMMA. If T_g is located between PMMA and PVAc, its composition was estimated from the Fox equation,[9] shown below as

$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \qquad (1)$$

where w_1 and w_2 represent the weight fractions of the components, and T_g, T_{g1}, and T_{g2} are the T_g's of the

blend and components 1 and 2, respectively. Although the Fox equation was derived for and is often used in miscible blends, attempts made here for immiscible blends were a qualitative estimation. Equation (1) can be rearranged to

$$w_1' = T_{g1}(T_{g1,b} - T_{g2})/[T_{g1,b}(T_{g1} - T_{g2})] \qquad (2)$$

where w_1' is the apparent weight fraction of PMMA in the PMMA-rich phase, and $T_{g1,b}$ is the observed T_g of PMMA-rich phase. Similarly, eq. (1) can also be rearranged to

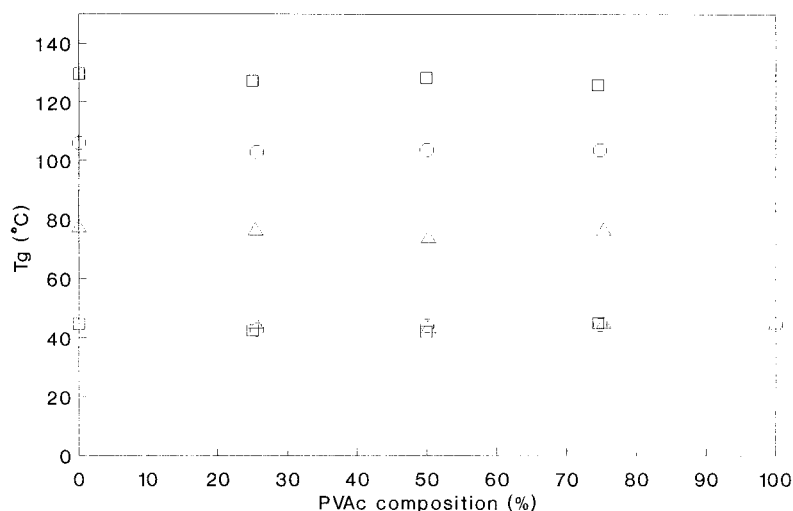$$w_1'' = T_{g1}(T_{g2,b} - T_{g2})/[T_{g2,b}(T_{g1} - T_{g2})] \qquad (3)$$

Figure 1 Glass transition temperatures of chloroform-cast PMMA/PVAc blends. △, iPMMA; ○, aPMMA; □, sPMMA.

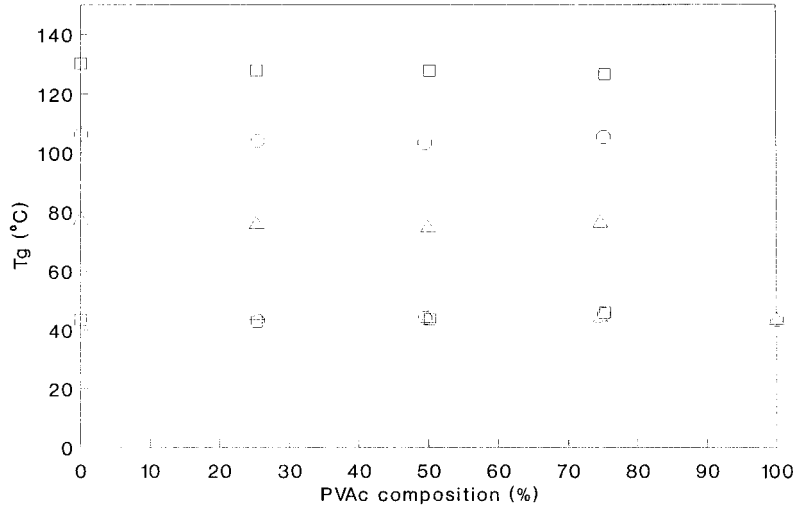**Figure 2**   Glass transition temperatures of THF-cast PMMA/PVAc blends. △, iPMMA; ○, aPMMA; □, sPMMA.

where w_1'' is the apparent weight fraction of PMMA in the PVAc-rich phase, and $T_{g2,b}$ is the observed T_g of PVAc-rich phase.

Applying eqs. (2) and (3) to the T_{gfc} values of PMMA/PVAc blends, the apparent weight fractions of PMMA in the PMMA-rich phase (w_1') and in the PVAc-rich phase (w_1'') were calculated. The results are tabulated in Tables III and IV for chloroform-cast and THF-cast blends, respectively.

For chloroform-cast PMMA/PVAc blends, PMMA and PVAc were found to be completely or nearly immiscible based on phase composition estimation. Among the three PMMAs, iPMMA showed marginally partial miscibility with PVAc. For THF-cast blends, the situation is slightly different. Mutual solubility between PMMA and PVAc was a little higher. Also among the three PMMAs, iPMMA was found to show the highest partial miscibility with PVAc than the other two PMMAs.

The overall weight fraction of PMMA-rich phase (W') and PVAc-rich phase (W'') is calculated by the following material balance equations

$$W_{1T} = w_1' W' + w_1'' W'' \qquad (4)$$

$$W_{2T} = w_2' W' + w_2' W'' \qquad (5)$$

where W_{1T} and W_{2T} are the overall weight fraction of PMMA and PVAc for blending, respectively, and w_1' and w_2' are obtained from eqs. (2) and (3), respectively. The W' and W'' values were calculated and are also listed in Tables III and IV for reference. For chloroform-cast blends shown in Table III, the calculations show that aPMMA is completely immiscible with PVAc. For iPMMA (or sPMMA)/PVAc blends, PVAc shows marginally low solubility in PMMA and the solubility of PMMA in PVAc is close to zero. Mutual solubility between PMMA and PVAc is slightly im-

TABLE III
Phase Compositions of Chloroform-Cast PMMA/PVAc Blends

iPMMA/PVAc	iPMMA-rich phase	PVAc-rich phase
[W_{1T} (%)/W_{2T} (%)]	w_1' (%) [W' (%)]	w_1'' (%) [W'' (%)]
74.6/25.4	97 (76.8)	0.3 (23.2)
49.8/50.2	100 (49.8)	0 (50.2)
24.7/75.3	97 (24.9)	0.7 (75.1)
aPMMA/PVAc	aPMMA-rich phase	PVAc-rich phase
[W_{1T} (%)/W_{2T} (%)]	w_1' (%) [W' (%)]	w_1'' (%) [W'' (%)]
74.4/25.6	100 (74.4)	0 (25.6)
50.0/50.0	100 (50.0)	0 (50.0)
25.2/74.8	100 (25.2)	0 (74.8)
sPMMA/PVAc	sPMMA-rich phase	PVAc-rich phase
[W_{1T} (%)/W_{2T} (%)]	W_1' (%) [W' (%)]	w_1'' (%) [W'' (%)]
75.0/25.0	100 (75.0)	0 (25.0)
50.1/49.9	100 (50.1)	0 (49.9)
25.5/74.5	97 (26.0)	0.4 (74.0)

TABLE IV
Phase Compositions of THF-Cast PMMA/PVAc Blends

iPMMA/PVAc	iPMMA-rich phase	PVAc-rich phase
[W_{1T} (%)/W_{2T} (%)]	W_1' (%) [W' (%)]	W_1'' (%) [W'' (%)]
74.7/25.3	96 (76.6)	5 (23.4)
50.1/49.9	93 (52.9)	2 (47.1)
25.4/74.6	98 (23.6)	3 (76.4)
aPMMA/PVAc	aPMMA-rich phase	PVAc-rich phase
[W_{1T} (%)/W_{2T} (%)]	w_1' (%) [W' (%)]	w_1'' (%) [W'' (%)]
74.5/25.5	100 (74.5)	0 (25.5)
50.5/49.5	96 (52.1)	1 (47.9)
24.9/75.1	99 (22.0)	4 (78.0)
sPMMA/PVAc	sPMMA-rich phase	PVAc-rich phase
[W_{1T} (%)/W_{2T} (%)]	w_1' (%) [W' (%)]	w_1'' (%) [W'' (%)]
74.7/25.3	100 (74.7)	0 (25.3)
49.8/50.2	98 (50.7)	0.3 (49.3)
24.7/75.3	97 (23.1)	3 (76.9)

proved (as shown in Table IV) in THF-cast blends in comparison with chloroform-cast ones. Based on the calculations, the mutual solubility between iPMMA and PVAc is the highest among the three tactic blends.

CONCLUSION

Based upon the results of the prepared blends, casting solvent and tacticity of PMMA have little effect on the miscibility of PMMA with PVAc. PMMA was found to be almost completely immiscible with PVAc. Through the calculation of phase compositions of two immiscible phases, the blends prepared from THF show a little more partial miscibility than the ones cast from chloroform. Among the three tactic PMMAs, iPMMA was found to show the highest mutual solubility with PVAc when the blends were cast from THF.

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