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Miscibility of poly(vinyl chloride) with terpoly(α-methylstyrene–acrylonitrile–methyl methacrylate)

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Abstract

The miscibility of poly(vinyl chloride)/terpoly(α-methylstyrene–acrylonitrile–methyl methacrylate) (PVC/MS-AN-MMA) blend was investigated by differential scanning calorimetry. The parameters of thermal transitions and phase behaviour of the blend were determined. Using the criterion that miscible blend exhibits one glass transition temperature T_g, the miscibility of the blends with 0–40 and with more than 80 mass% of MS–AN–MMA was found. The dependence of glass transition temperature on the composition was well described by the Couchman, Gordon–Taylor and Fox equations. The blends with 50–80 mass% of MS–AN–MMA were partially miscible. The apparent mass fraction of PVC and MS–AN–MMA in the PVC-rich and MS–AN–MMA-rich phases was estimated. The phase diagram of PVC/MS–AN–MMA blend indicated miscibility upon heating.

INTRODUCTION

Blends of poly(vinyl chloride) (PVC) with styrene copolymers have significant technological importance. For example, copoly(styrene–acrylonitrile) (SAN), copoly(α-methylstyrene–acrylonitrile) (MSAN) or their terpolymers are efficient modifiers of the heat deflection temperature of PVC. This temperature, the Vicat softening point, is 80–85°C for PVC, and can be lower in the presence of additives. The softening point can be raised by adding miscible polymers which have a glass transition temperature considerably higher than the glass transition temperature of PVC. The extent of the increase in the softening temperature depends on the ratio in which the components are blended.

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There are many conflicting reports in the literature concerning the miscibility of polymer blends. These discrepancies may be the result of numerous factors, such as whether the miscibility depends on the composition of copolymers, on the procedure and the temperature of the blend preparation, on the polymer–polymer diffusion and on the effect of solvent [1].

The solvent preparation methods used, due to the rapid elimination of the polymers from homogeneous solutions, cause the two polymers to become kinetically trapped in a homogeneous, but non-equilibrium mixture below T_g. The reverse phenomenon is also possible when certain solvent casting methods lead to phase separated samples of the miscible polymer pairs. The latter seems to have its origin in the polymer–solvent interaction [2].

The characteristics of PVC/SAN, PVC/MSAN, PVC/PMMA blends as well as of SAN/PMMA blend have been the subject of numerous studies [1–11]. PVC is miscible with SAN having an AN composition from 11.5 to 26 mass% [1]. PVC/PMMA blends are miscible at low PMMA contents [3,4]. PMMA and SAN are miscible if the SAN content ranges from 9.4 to 34.4 mass% of AN [5]. The miscibility window of PMMA/MSAN exists for an AN content from 8.6 to 42.3 vol.% [6,7]. Following the analysis of SAN copolymers it seems likely that strong intramolacular repulsion between styrene (methylstyrene) and acrylonitrile units has a dominant effect on the miscibility of polymer/SAN blends [1,7,9].

DSC scans of ternary PVC/SAN/MMA blends exhibit two glass transitions temperatures, which clearly indicates the presence of two phases [3]. The characteristics of the PVC blends with terpolymers S–AN–MMA or MS–AN–MMA are insufficiently investigated [10]. The latter system is the subject of the research of this paper. The report presents a study of thermal transition and phase behaviour of PVC/MS–AN–MMA blend.

EXPERIMENTAL

The materials used in this study were commercially available PVC ($\bar{M}_w = 93\,000$) and MS–AN–MMA (32.2 mass% AN and 8.1 mass% MMA, determined by NMR).

PVC/MS–AN–MMA blends with the composition 100/0, 95/5, 90/10, 80/20–10/90, 5/95 and 0/100 were prepared by dissolving both PVC and MS–AN–MMA in tetrahydrofuran (THF) to a total concentration of 2.5 mass%. The blends were precipitated into an excess of methanol (12:1), dried at room temperature for 24 h and then in a vacuum oven at 330 K for 72 h.

The glass transition temperatures of the blends were determined by differential scanning calorimetry (Perkin–Elmer DSC-4 with TADS microprocessor) under a nitrogen atmosphere with a sample size of 12–15 mg. A heating rate of 20 K min^{-1} was used. Each sample was first heated from room temperature to 423 K, annealed for 1 min at 423 K, then rapidly cooled (320 K min^{-1}) to 298 K. The transition behaviour was recorded during the second heating. The glass transition temperature (T_g) was defined as the midpoint of the shift in heat capacity. The width of the glass transition region (ΔT) is the region between the intersections of the lower and upper extrapolated baselines with tangent to the inflection point of T_g.

The phase separation was investigated according to the following procedure. The blends were heated at the rate of 20 K min^{-1} and then held at the selected annealing temperature for 15 min. This period of time was selected in order to avoid degradation and yet allow enough time for the equilibrium to establish. Then the samples were quenched at the rate of 320 K min^{-1} to 298 K. The subsequent scanning revealed one or two glass transitions, depending upon whether or not the phase separation temperature had been exceeded.

RESULTS AND DISCUSSION

DSC thermograms of PVC/MS–AN–MMA blends are shown in Fig. 1. The blends containing 0–40 and more than 80 mass% of MS–AN–MMA

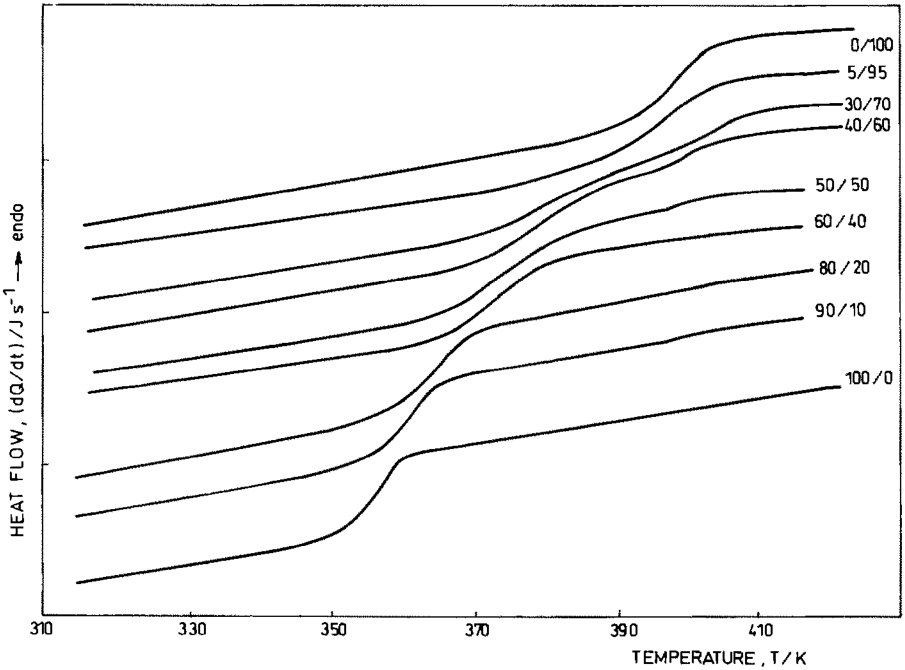

Fig. 1. Normalized DSC thermograms of PVC/MS–AN–MMA blends.

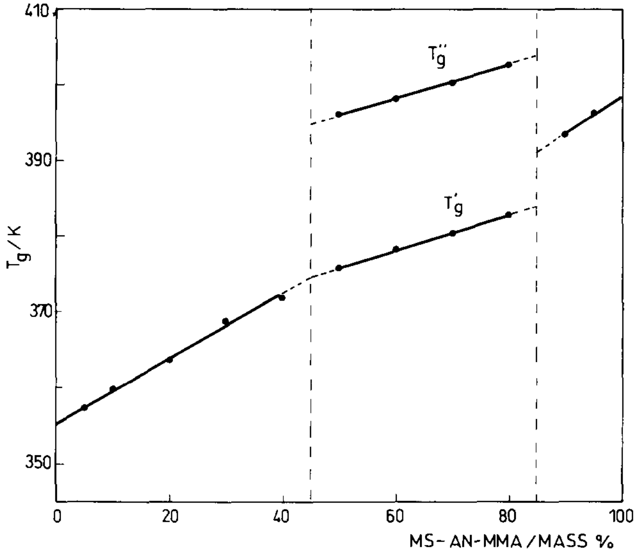

Fig. 2. Dependence of glass transition temperature on composition of PVC/MS–AN–MMA blend: T_g' is the glass transition of the PVC-rich phase and T_g'' the glass transition of the MS–AN–MMA-rich phase.

are miscible, while the ones having 50–80 mass% of MS–AN–MMA are partially miscible, since they have two glass transition temperatures, different from the glass transition temperature of the pure components. The first glass transition (T_g') is attributed to the the PVC-rich phase and the second glass transition (T_g'') is attributed to the MS–AN–MMA-rich phase (Fig. 2). Both glass transition temperatures increased linearly with mass fraction of MS–AN–MMA.

The T_g'' of 30/70 and 20/80 blends are higher than the glass transition temperature of the 0/100 sample but lower then the glass transition temperature of the original MS–AN–MMA (Table 1). Since T_g is related to the chain mobility it can be concluded that PVC reduces the mobility of MS–AN–MMA chains in the blend. It is also possible that the affinity of residual THF is much greater with PVC than with MS–AN–MMA. In this case THF is preferentially associated with PVC. Consequently the T_g of the blend with very low PVC content will be nearer to T_g of the original polymer.

The width of the glass transition ΔT may be used to estimate the miscibility of polymers in the blends for which $T_{g2} - T_{g1} \leq 20$ K is valid. According to data in literature [11] the ΔT of pure polymers is 6 K, of miscible blends 10 K, and it is equal to or higher than 32 K for immiscible blends. As shown in Table 1, the width of the glass transition of PVC/MS–AN–MMA blends, which is up to 14 K for the miscible blends and 16–32 K for immiscible, increases with the increase in mass fraction of MS–AN–MMA.

TABLE 1

Glass transitions parameters of PVC/MS–AN–MMA blend

PVC/MS–AN–MMA in mass%	T_g/K		ΔT/K	ΔC_p/J g^{-1} K^{-1}	
PVC[a]	357.3		8.0	0.297	
100/0	355.3		7.9	0.311	
95/5	357.3		9.0	0.306	
90/10	359.9		9.8	0.303	
80/20	363.7		10.3	0.301	
70/30	368.9		12.5	0.300	
60/40	371.9		14.0	0.278	
	T'_g	T''_g		$\Delta C'_p$	$\Delta C''_p$
50/50	375.7	396.3	16.7	0.278	0.064
40/60	378.2	398.2	18.6	0.255	0.089
30/70	380.4	400.2	32.2	0.185	0.148
20/80	382.7	402.7	16.7	0.144	0.178
10/90	393.3		14.1	0.303	
5/95	396.1		13.1	0.317	
0/100	398.5		11.8	0.322	
MS–AN–MMA[a]	404.3		7.2	0.312	

[a] Original polymer.

The dependence of the glass transition temperature on the composition of miscible polymer blends can usually be described by several empirical equations [12–15]. The Couchman eqn. (1) was applied in this study as well as the Gordon–Taylor (2) and Fox (3) equations.

$$T_g = \frac{W_1\,\Delta C_{p1}\ln T_{g1} + W_2\,\Delta C_{p2}\ln T_{g2}}{W_1\,\Delta C_{p1} + W_2\,\Delta C_{p2}} \tag{1}$$

$$T_g = \frac{W_1 T_{g1} + k W_2 T_{g2}}{W_1 + k W_2} \tag{2}$$

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{3}$$

where T_g is the glass transition temperature of the blend; T_{gi} and W_i are the glass transition temperatures and weight ratio of the component polymer i, respectively; ΔC_{pi} is the difference in molar heat capacity at T_{gi}. The Gordon–Taylor adjustable parameter k describes the deviation of the measured T_g values from the additivity law, for which $k = 1$ is valid. If $k < 1$ the T_g is lower than expected and the chain mobility in the blend is enhanced. If $k > 1$ strong interaction is suggested [16].

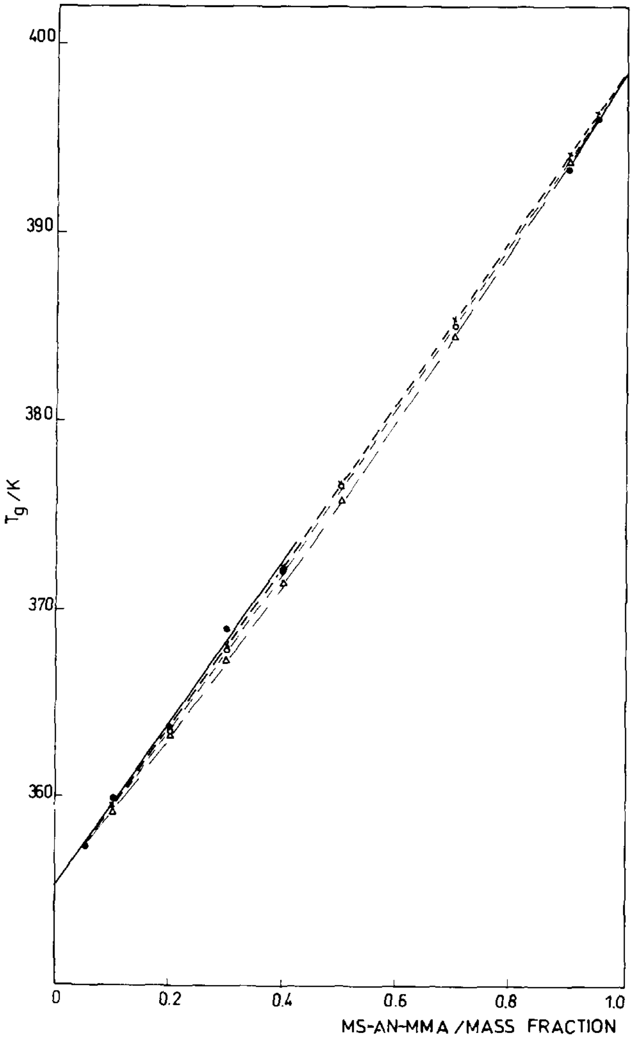

Fig. 3. Comparison of experimental (●) and calculated glass transition temperatures according to Couchman (×), Gordon–Taylor (O) and Fox (△).

Figure 3 demonstrates the fit of the experimental T_g data of the miscible PVC/MS–AN–MMA compositions with the above three equations. It is seen that all three relations can appropriately describe the T_g behaviour of PVC/MS–AN–MMA miscible compositions. The adjustable parameter $k = 0.953$ is determined by regression analysis from the linearized Gordon–Taylor equation

$$(T_2 - T_g)/(T_g - T_{g1}) = 1/k[(1 - W_2)/W_2] \tag{4}$$

According to Lin et al. [14] the Gordon–Taylor equation successfully describes the behaviour of miscible blends in the range of k values 0.8–1.2.

Applying eqns. (1)–(3) to the DSC results, the phase compositions for partially miscible PVC/MS–AN–MMA blends were determined. By rearranging these relations the eqns. (5)–(7) were derived, from which the apparent mass fractions of PVC and MS–AN–MMA dissolved in the PVC-rich and MS–AN–MMA-rich phases were estimated.

Couchman equation

$$W_1' = \frac{\Delta C_{p2}(\ln T_g' - \ln T_{g2})}{\Delta C_{p1}(\ln T_{g1} - \ln T_g') + \Delta C_{p2}(\ln T_g' - \ln T_{g2})} \tag{5}$$

Gordon–Taylor equation

$$W_1' = \frac{-k(T_g' - T_{g2})}{(T_g' - T_{g1}) - k(T_g' - T_{g2})} \tag{6}$$

Fox equation

$$W_1' = \frac{T_{g1}(T_g' - T_{g2})}{T_g'(T_{g1} - T_{g2})} \tag{7}$$

where W_1' is the apparent mass fraction of polymer 1 in the polymer 1-rich phase, and T_g' is the observed glass transition of polymer 1-rich phase; $W_2' = 1 - W_1'$.

The results are shown in Table 2. The mass fraction of MS–AN–MMA dissolved in the PVC rich phase is higher than the mass fraction of PVC component dissolved in the MS–AN–MMA rich phase. These results suggest that the limits of miscibility are not symmetrical. PVC has a greater tendency to accept MS–AN–MMA copolymer than MS–AN–MMA to accept PVC. These results also confirm the previously presented hy-

TABLE 2

Apparent mass fraction of PVC and MS–AN–MMA in the PVC-rich and MS–AN–MMA-rich phases of partially miscible blends PVC/MS–AN–MMA 50/50 and 40/60

Calculated according to	50/50				40/60			
	PVC-rich [a]		MS–AN–MMA-rich		PVC-rich		MS–AN–MMA-rich	
	W_1'	W_2'	W_1''	W_2''	W_1'	W_2'	W_1''	W_2''
Couchman	0.522	0.478	0.050	0.950	0.464	0.536	0.007	0.993
Gordon–Taylor	0.516	0.484	0.053	0.947	0.458	0.542	0.007	0.993
Fox	0.499	0.501	0.046	0.954	0.441	0.559	0.006	0.994

[a] Single primes and double primes denote the PVC-rich phase and MS–AN–MMA rich phase, respectively. Subscripts 1 and 2 denote PVC and MS–AN–MMA component, respectively.

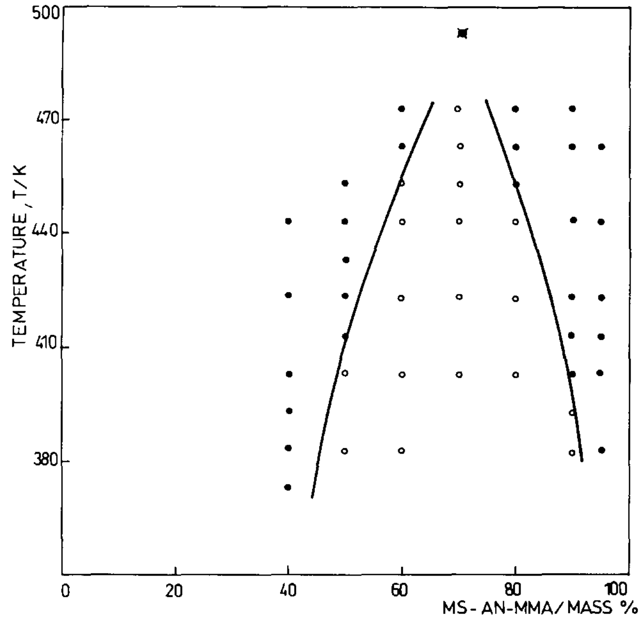

Fig. 4. Phase diagram of PVC/MS–AN–MMA blends: (●)-one phase, (○)-two phases, (⊠)-degraded sample.

pothesis about the influence of specific interactions between PVC and residual solvent on T_g'' of the blends 30/70 and 20/80.

The phase diagram of PVC/MS–AN–MMA blend indicates the upper critical solution temperature (UCST) behaviour, as shown in Fig. 4. The phase separated compositions exhibit miscibility upon heating. The blends with 50–90% MS–AN–MMA show phase separation at 383 K. The region of immiscibility gets narrower with the increase in temperature so that only the compositions with about 70% MS–AN–MMA are immiscible at 463 K. On annealing, the blends degraded at 493 K.

CONCLUSION

Investigation of the miscibility of PVC with terpolymer MS–AN–MMA by means of differential scanning calorimetry showed that the blends with 0–40 mass% and more than 80 mass% of MS–AN–MMA were miscible, while the blends with 50–80 mass% of MA–AN–MMA were partially miscible. The glass transition behaviour of miscible compositions can be well described by the Gordon–Taylor equation with parameter $k = 0{\cdot}953$, as well as by the Couchman and Fox equations. In partially miscible compositions PVC has a greater tendency to accept MS–AN–MMA than MS–AN–MMA to accept PVC. The phase diagram of PVC/MS–AN–MMA blend indicates that the phase separation compositions exhibit miscibility upon heating.

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