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Modulated differential scanning calorimetry: 1. A study of the glass transition behaviour of blends of poly(methyl methacrylate) and poly(styrene-*co*-acrylonitrile)

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The glass transition and the effect of specific interactions on this transition process in a binary polymer blend of poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-acrylonitrile) (SAN), which have very similar glass transition temperatures, have been investigated by means of modulated differential scanning calorimetry. The blends investigated were miscible blends of PMMA and SAN and a physical mixture of the two constituent polymers. Using the differential of heat capacity *versus* temperature signal, the technique has been shown to be able to resolve the two glass transitions so long as their difference is not less than about 5°C. The value of heat capacity of the miscible blend does not satisfy simple linear addition of the heat capacities of the two component polymers over the glass transition region. It is believed that this enhancement of heat capacity in the glass transition region results from specific interactions between segments of the two polymers.

(Keywords: polymer blends; glass transition; modulated d.s.c.)

INTRODUCTION

Polymer–polymer miscibility is usually characterized[1] by investigating the optical appearance, morphology, glass transition temperature or crystalline melting behaviour of the mixture. A blend of two amorphous polymers with different refractive indices will be judged to be miscible if it is optically clear. Measurement of the glass transition temperature T_g, which marks the characteristic transition of the amorphous region of a polymer or blend from a glassy state to a rubbery state, is the most convenient and popular way of investigating the miscibility or immiscibility of pairs of polymers. In a miscible blend only one T_g will be observed, but if the polymer constituents in the blend are immiscible, then two T_gs will be recorded.

T_g is commonly measured by differential scanning calorimetry (d.s.c.), but the use of T_g determination for studying blend miscibility has its own limitations. As is known, the glass transition region covers at least a 15–20°C range. Thus, if the difference of the glass transition temperatures between the two polymers is within 15°C, it has been almost impossible to detect the extent of mixing by d.s.c.

In fact, the glass transition is a thermokinetic phenomenon with no true order parameter[2]. The glass transition is not a true phase transition, but is a process in which frozen chain segments are unfrozen. The glass transition results from chain segment motions, which result in a glass transition spectrum. The polymer system may be divided into many subsystems $1,2,3\ldots,n$ corresponding to different segment lengths. The glass transition temperature is T_{g1} for subsystem 1, T_{g2} for subsystem $2,\ldots,T_{gn}$ for subsystem n, and the overall glass transition is a consequence of all the different segmental motions. Thus, the glass transition may be considered to arise from a continuous function of subsystems. The heat capacity does not change suddenly in the transition region, i.e. its differential is not a delta-function of temperature, but can be a continuous function, so that the differential signal of heat capacity will be sensitive to the glass transition process.

Recently, a new thermal analysis technique has been invented[3], known as modulated d.s.c. (m.d.s.c.). In a

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Table 1 Characterization data

Polymer	AN (wt%)	M_w ($\times 10^{-5}$)	M_w/M_n	T_g (°C)
PMMA	–	1.98	2.03	101
SAN18	17.3	1.65	2.00	91
SAN25	23.9	1.62	1.89	106

m.d.s.c. experiment, the linear heating ramp used in conventional d.s.c. is modulated sinusoidally. For further details, see the review by Reading[4]. For the purposes of this study, one of the principal advantages of m.d.s.c. is that, with the right experimental parameters, the value of the heat capacity at the glass transition can be determined independently of any enthalpic effects due to relaxation events, thus making the interpretation of the results much less equivocal. Other advantages include better precision, resolution and sensitivity.

In this paper, using the differential signal of heat capacity, we describe the analysis of the glass transitions of two types of polymer blend (a miscible blend and a physical mixture of the constituent polymers) prepared using two polymers with very similar T_g values, and we comment on the effect of inter-segmental specific interactions.

EXPERIMENTAL

Sample preparation

Poly(methyl methacrylate) (PMMA) and poly(styrene-*co*-acrylonitrile) (SAN) were obtained from Aldrich. The characterization data for these polymers used are given in *Table 1*. The average molecular weights and the polydispersities were determined by g.p.c. (Waters, model 510) relative to polystyrene standards. The AN contents of the SAN copolymers were determined by ^{1}H n.m.r. spectroscopy (JEOL FX-100). The PMMA and SAN samples are both amorphous polymers and blends of this pair of polymers are reported[5] to be miscible. Samples for miscibility measurements were prepared by solvent casting of 5 wt% chloroform solution onto glass plates. After evaporation of the solvent at room temperature, the films were dried under vacuum at 80°C for 2 weeks. Physical mixtures of the two polymers were also prepared by cutting cast sheets of PMMA and SAN into small pieces and mixing them by hand at room temperature.

Instrumentation

The m.d.s.c. instrument was supplied by TA Instruments. An oscillation amplitude of 0.8°C and an oscillation period of 60 s were used throughout this investigation. A heating rate of 3°C min^{-1} was used. To obtain accurate results, additional calibration for heat capacity was performed. The heat capacity calibration was made by running a standard sapphire sample over a wide temperature range and comparing the determined heat capacities with the literature values[6] at the temperatures of interest. The melting peak temperature and cell constant were calibrated using an empty pan and a standard indium sample.

RESULTS AND DISCUSSION

Figures 1 and *2* show heat flow and heat capacity data for the miscible blend and for the physical mixture of the PMMA/SAN18 system. From these data, it was not possible to draw any conclusions about miscibility because only one glass transition was observed for both the miscible blend and the physical mixture. The difference of T_gs between the two constituent polymers is only about 10°C. However, it is clear from the derivative of heat capacity *versus* temperature data, shown in *Figure 3* for both the miscible blend and the physical mixture, that there are differences. The physical mixture

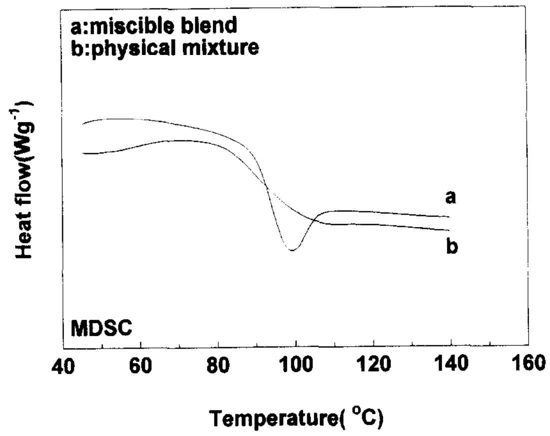

Figure 1 Variation of heat flow with temperature for (a) the miscible blend and (b) the physical mixture (PMMA/SAN18=50/50 (wt/wt))

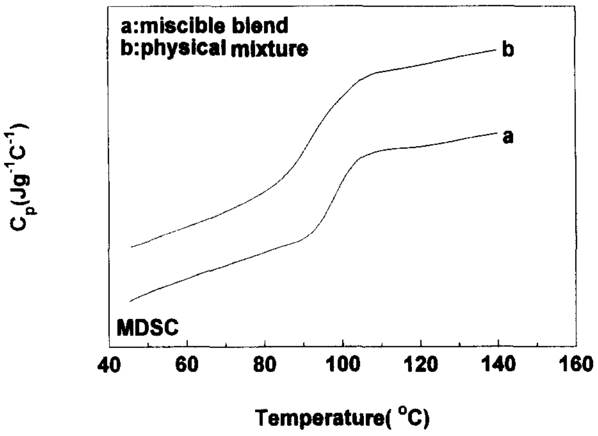

Figure 2 Variation of heat capacity for (a) the miscible blend and (b) the physical mixture from *Figure 1*. The data are deliberately shifted vertically for clarity

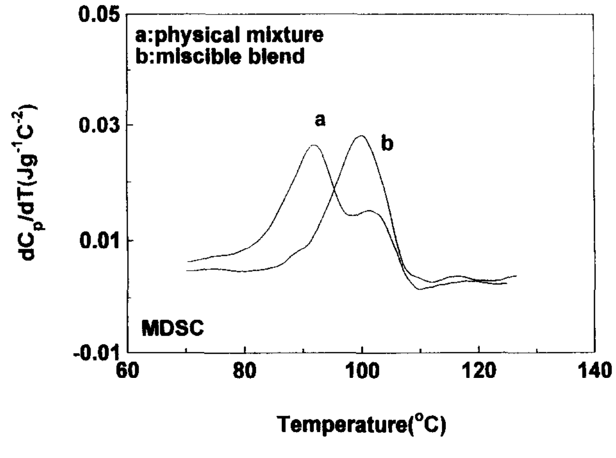

Figure 3 Comparison of the differential of heat capacity *versus* temperature for the miscible blend and the physical mixture (PMMA/SAN18 = 50/50)

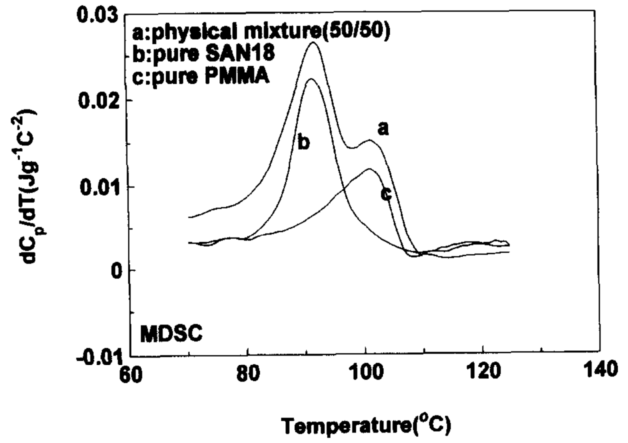

Figure 4 The differential of heat capacity *versus* temperature for the physical mixture (PMMA/SAN18 at 50/50 (wt/wt) composition) and for the component polymers

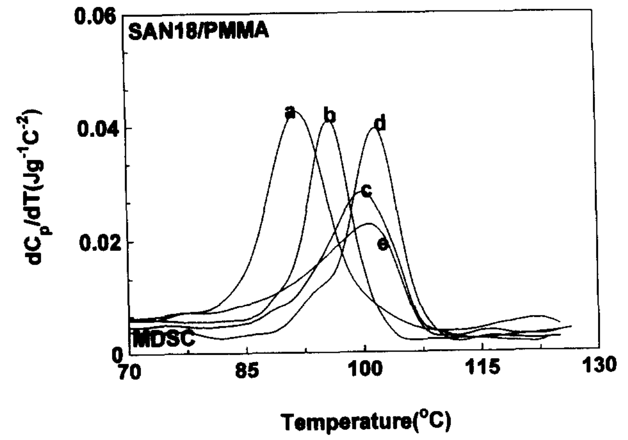

Figure 5 Variation of the differential of heat capacity with composition for the miscible blends of PMMA and SAN18: (a) 0 wt% PMMA; (b) 25 wt% PMMA; (c) 50 wt% PMMA; (d) 75 wt% PMMA; (e) 100 wt% PMMA

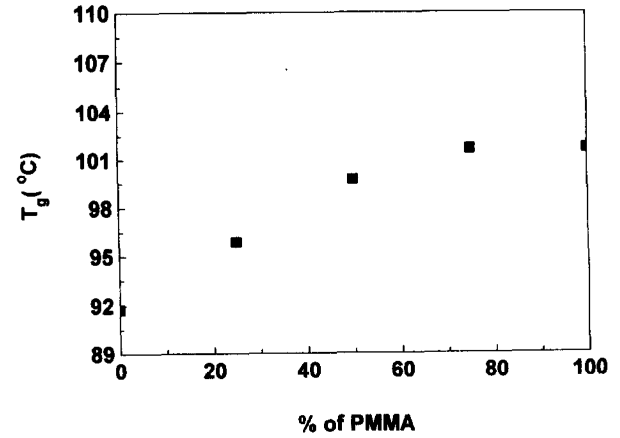

Figure 6 Plot of the glass transition temperature *versus* composition. Data from *Figure 5*

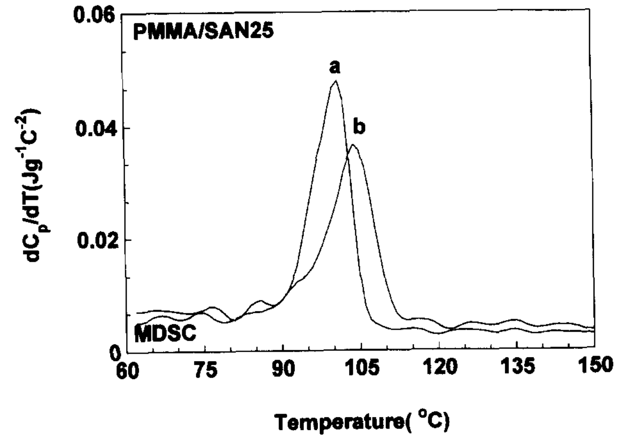

Figure 7 Comparison of (a) the miscible blend with (b) the physical mixture (PMMA/SAN25 = 50/50)

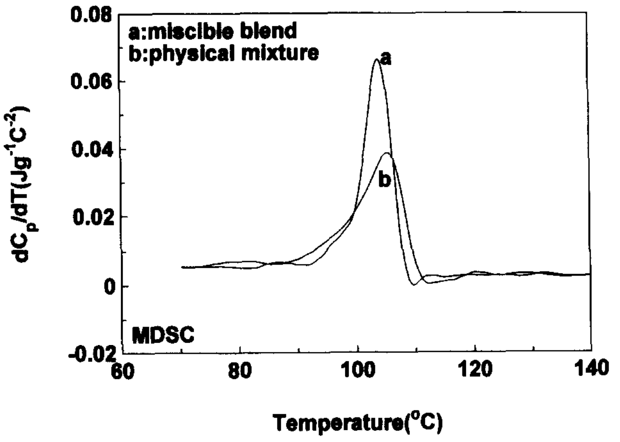

Figure 8 Comparison of (a) the miscible blend with (b) the physical mixture (PMMA/SAN25 = 25/75)

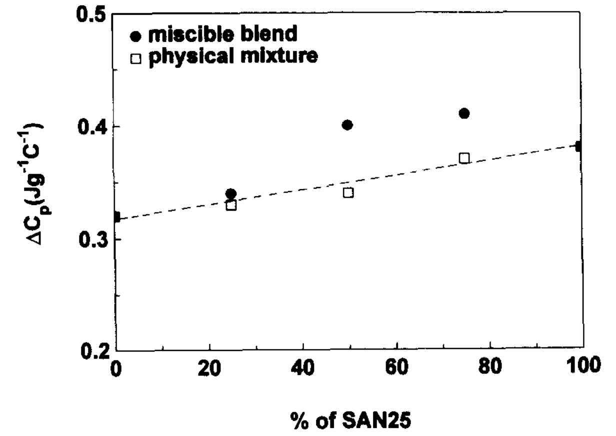

Figure 9 Variation of heat capacity with composition for the miscible blends and the physical mixtures

shows two transition peaks. From the plots shown in *Figure 4*, the differential of heat capacity *versus* temperature (over the glass transition region) characteristic of the physical mixture appears to be the result of a simple linear addition of the differential heat capacities of the constituent polymers. In *Figure 5*, the differential of heat capacity *versus* temperature, over the glass transition region, is plotted for some PMMA/SAN18 miscible blends with weight ratios ranging from 0 : 100 to 100 : 0, while in *Figure 6* the glass transition temperatures are plotted *versus* composition. This shows the positive deviation from linearity often observed[5] for miscible blends and ascribed to specific interactions between segments.

Figures 7 and *8* show the results for the miscible blend and the physical mixture based on the PMMA/SAN25 combination at two compositions. The single peak behaviour of the differential of heat capacity is very clear for the, by definition, phase-separated physical mixture. The difference of the T_gs of PMMA and SAN25 is approximately 5°C. This indicates that it may be difficult to detect immiscibility in blend systems if the difference of T_gs is around this value. However, other experimental conditions, not yet investigated, might yield success.

The effect of specific interactions, in miscible blends, on the heat capacity in the glass transition region can be inferred from the plots illustrated in *Figure 9*. These show the increment in heat capacity (over the glass transition region) *versus* composition ratio in the case of the miscible blend and the physical mixture of PMMA/SAN25. Although the linear trend observed for the physical mixture might be expected because of the linear additivity rule, the non-linear trend observed for the miscible blend could be explained by specific interactions, which change the supramolecular structure. Prud'homme *et al.*[7] proposed how chain entanglements, in addition to specific interactions, may play an important role in the orientation behaviour of miscible polymer blends. The specific interactions may lead to isolated chain segments being oriented in polymer blends. Hsu *et al.*[8,9] compared the orientation of miscible and immiscible poly(vinyl methyl ether)/polystyrene (PVME/PS) blends. They found that the PS chains had a higher orientation in the mixed state than in the immiscible mixture, which was explained as being the result of a greater interconnectivity of the chains in the former case. Li *et al.*[10] also reported that poly(ϵ-caprolactone) orientation was observed in miscible matrices, but not in immiscible SAN matrices, and indicated that the miscibility leads to the orientation and maintenance of orientation of isolated segments in blends.

The volume of mixing decreases because of specific interactions[11]. In the PMMA/SAN system, it may be predicted that some chain segments will become stiffer and that there will be an enhancement of the interconnectivity with some chain segment motions being cooperative during the glass transition.

Figure 9 shows that for the miscible blends the heat capacity does not satisfy a simple linear additivity rule, possibly because of these specific interactions. The increment of heat capacity over the glass transition can be determined by the following equation:

$$\Delta C_p = \int_{C_p(i)}^{C_p(e)} [\mathrm{d}C_p(T)/\mathrm{d}T]\,\mathrm{d}T$$

C_P(i) and C_p(e) are the initial and final values of heat capacity in the glass transition region. The results show that the values of ΔC_p of the miscible system are larger than for the physical mixtures.

CONCLUSIONS

The extent of mixing in polymer blends can, to considerable advantage, be studied over the glass transition region by using the m.d.s.c. differential of heat capacity *versus* temperature signal. Experimental analysis of physical mixtures has shown that differences in transition temperatures of the constituent polymers as small as about 10°C can be readily resolved.

The increment of heat capacity over the transition region in miscible blends was found not to follow a linear additivity rule. The enhancement of heat capacity in the miscible system may result from specific interactions, with the glass transition involving cooperative motions of segments.

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