Studies on the Thermal Properties of PVC : Polystyrene Alloy

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Synopsis

The effect of composition on the thermal properties of poly(vinyl chloride) (PVC)–polystyrene (PSt) alloy was investigated. Using the DSC, it was observed that the glass transition temperature (T_g) and melting point (T_m) as well as the enthalpic change at melting (ΔH) were altered with respect to their theoretical values. An attempt is made to explain these facts.

INTRODUCTION

The great interest in this nature of work stems from the fact that blending reduces compositional nonuniformity.[1] Further, these materials very often exhibit a synergism in properties achievable only by formation of polymer alloys, which are either polyblends, block, or graft copolymers. A review of the available literature indicates that the bulk of the effort in this area is concerned with the mechanical, physical, chemical, and optical properties of these alloys.[1-4] For example, in Ref. 4, it was reported that there is reduction of elastic properties of PVC melts, coupled with improvements on certain optical and physical properties on blending with PSt. Our survey shows that very little has been reported, if any, on the thermal characteristics of PVC–PSt alloys. These two common plastics are extensively used due to their special properties such as, stability to heat, relatively high T_g and T_m, etc.[5]

In this study we report on the influence of composition on the T_g and T_m of PVC–PSt blend. Theoretical models predicting these thermal transitions were compared to the experimental results. In addition, the ΔH values of this system were determined and interpreted.

MATERIALS AND METHODS

The following materials were used as received: PVC powder and PSt granules from Dow Chemical Co., New York, and tetrahydrofuran (THF), ethanol, and mercury from B.D.H., Ltd., Poole, U.K.

Blend Preparation

Blend of PVC with PSt was obtained by coprecipitation of both polymers from solutions in THF with ethanol as nonsolvent. The alloy was dried at 40°C.

PVC and PSt (20 g/dm^3) were separately made in THF. Aliquots (50 cm^3) of the PVC were taken in 10 250-cm^3 flasks. Varying quantities (0–200 cm^3) of

PSt solution were added to each of the flasks. Each mixture was shaken for 10 min, after which it was slowly poured into an excess of ethanol contained in a beaker, with brisk stirring. The precipitate was filtered and dried.

Thermal Analysis

The glass transition temperatures and the melting points were determined on a Metler differential scanning calorimeter, DSC TA 3000. Integration of the melting point endotherm to give ΔH values was done automatically. Measurements were carried out in an air atmosphere over a temperature range from 10 to 400°C and at a heating rate of 10°C/min. Samples of about 5 mg were encapsulated in an aluminium pan. Another empty pan formed the reference. The DSC was calibrated with a standard indium pellet supplied by the manufacturer.

RESULTS AND DISCUSSION

T_g. As is evident in Figure 1, blending of PVC with PSt results in a material where T_g is higher than that of the calculated values. At lower and higher mole fractions of PSt, the increases in T_g are moderate. A dramatic increase is observed around the 1:1 mole ratio. Further, it is found that in all cases the blend has just one T_g, which is evidence of compatibility of the two polymers over the composition ranges.[6]

These observations no doubt show that there are either chemical or physical interactions between these two polymers. Interaction would entail the interlocking of the chains of the composites. This is expected to affect thermomechanical properties including T_g and T_m. Thus these observations are hardly surprising. The relatively very high T_g's at about 1:1 mole ratio means enhanced interaction at these points. It may be necessary to recall a
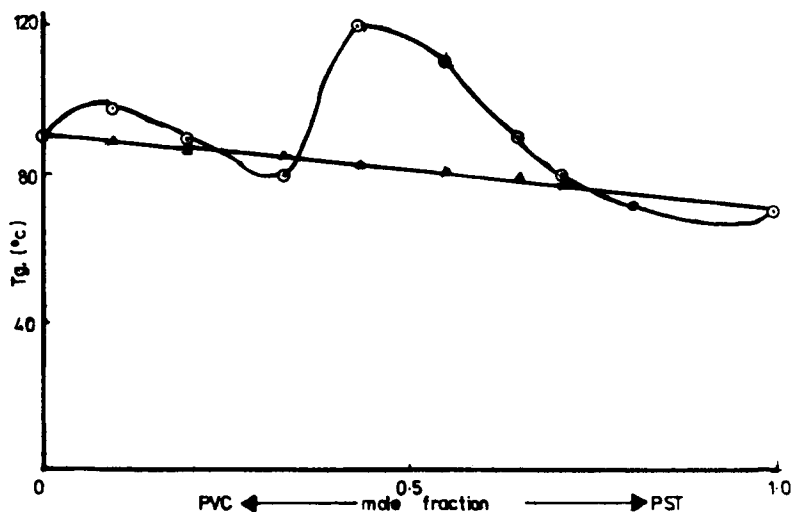

Fig. 1. Effect of blending on glass–transition temperature: (⊙) observed; (▲) calculated.

similar report by Frisch et al.[7] who investigated the T_g's of poly(propylene oxide)–polystyrene blends.

The following empirical equation after Neilson[8] has been used to show the dependence of T_g (or T_m) on composition in random copolymers and blend systems:

$$T_g \text{ (theoretical)} = w_1\left(T_{g1}\right) + w_2\left(T_{g2}\right),$$

where w_1, T_{g1} T_{g2}, and w_2 refer, respectively, to the T_g's and weight fractions of the composites. As earlier stated, a comparison of the predicted T_g's using the above equation with the corresponding T_g's observed indicates the latter to be higher around the 1 : 1 ratio. Beyond this region, however, quite an opposite picture is the case.

In a related study, Frisch et al.[7] expressed the amount of lowering of the T_g in terms of σ, which is defined by the equation

$$\frac{T_g - T_g \text{ (copolymer)}}{T_g \text{ (copolymer)}} = \frac{-\sigma}{1 + \sigma}$$

According to these authors, if significant phase mixing occurs, σ would be expected to be positive or zero [i.e., $T_g \leq T_g$ (copolymer)]. Applying this to our system, it is clear that, in the main, there was phase mixing which reached a peak around the 1 : 1 composition.

T_m. It is clear in Figure 2 that, for a large proportion of the PSt mole fraction, T_m observed is higher than T_m calculated, with a maximum deviation occurring around equimolar concentration as in the case of T_g. For lower mole
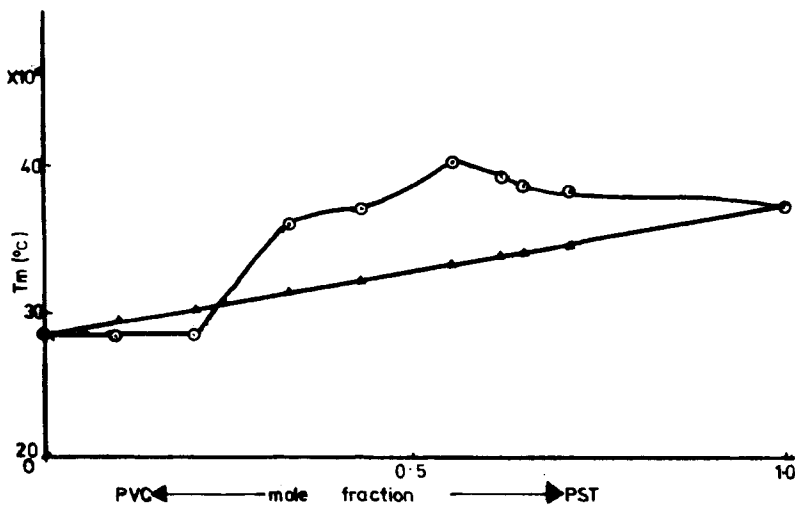

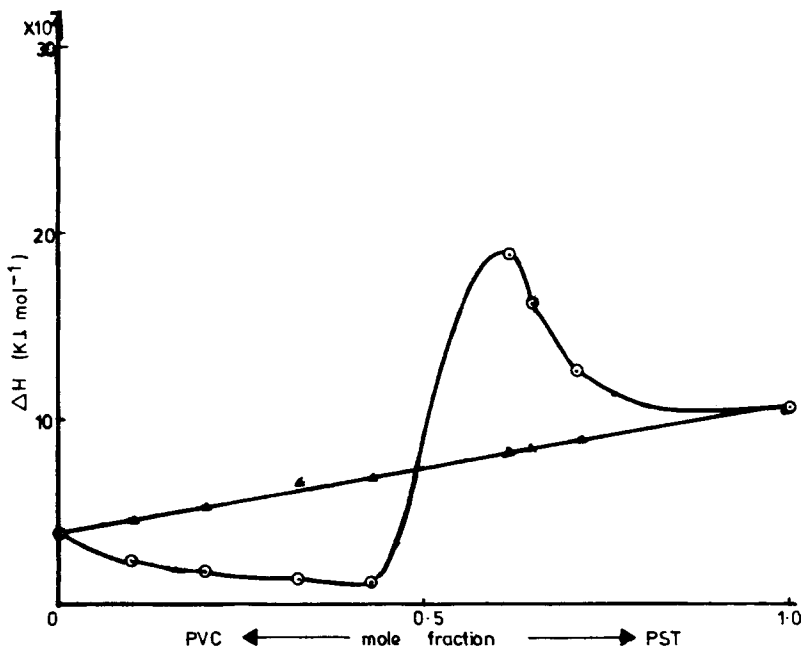Fig. 2. Effect of blending on the melting point of polymers: (○) observed; (▲) calculated.

Fig. 3.   Effect of blending on enthalpy: (⊙) observed; (▲) calculated.

fractions PSt, the observed values of T_m are smaller than those of the theoretical. The latter observation must be due to the plasticization effect of PSt on the system largely composed of PVC. Perhaps the same argument explains the tailing off of the T_m values at very high PSt contents. Plasticization effect or lowering of T_m by impurities is attributable, among other things, to increase in free volume.

ΔH. An interesting case is recorded in Figure 3 as enthalpic values at melting are observed with changes in the blend composition. At about equimolar ratio, the ΔH observed approximates that of the theoretical. Below the 1 : 1 ratio ΔH observed is lower than those of the calculated values, while the reverse is the case at higher PSt contents. These facts are difficult to explain. A plausible reason might be that at low PSt contents free volume is greatly increased whereas with more PSt it is decreased substantially. This must be due to the inherent free volumes of the two polymers.

CONCLUSIONS

The following conclusions may be drawn from the foregoing studies: PVC and PSt form compatible mixtures at all compositions, as a result of good phase mixing. Blending raises both the T_g and T_m of the composite as compared to their theoretical values. Maximum deviations of these thermomechanical properties from their predicted values occur around equimolar compositions.

References

1. T. Zeher and G. G. Costas, *Principles of Polymer Processing*, Wiley, New York, 1976, p. 196.
2. H. Mark, *J. Macromol. Sci. (Chem.)*, **A15**(6) 1065–1073 (1981).
3. J. M. Schultz and J. S. Lin, *J. Polym. Sci. (Chem.)*, **A4**(19), 620 (1981).
4. J. S. Orville, *The Science and Technology of Polymer Films*, Wiley, New York, 1971, vol. II, p. 200.
5. Elias Hans-George, *Macromolecules*, Wiley, New York, 1977, p. 878.
6. A. Aref-Azar, J. N. Hay, and B. Maroden, *J. Polym. Sci. (Chem.)* **A3**(18), 638 (1980).
7. H. L. Frisch, K. C. Frisch, and D. Klempner, *Polym. Eng. Sci.*, **14**, 646 (1974).
8. L. E. Nielson, *Mechanical Properties of Polymers*, Reinhold, New York, 1963.