

# Role of Methods of Blending on Polymer–Polymer Compatibility

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## SYNOPSIS

The role of methods of blend preparation on polymer–polymer compatibility was investigated. Three different types of methods of blending, such as solution-casting, melt-mixing, and coprecipitation, were applied for three types of blend systems, viz., poly(vinyl chloride-co-vinyl acetate) (VYHH)/polystyrene (PS), VYHH/poly(styrene-co-acrylonitrile) (SAN), and VYHH/poly(methyl methacrylate) (PMMA) by measuring their glass transition temperatures ( $T_g$ ) by a differential scanning calorimeter (DSC). It has been found that compatibility of the polymers depends on the method of blending and compatibility also varies from one blend system to another. Among the various types of blending methods, the coprecipitation method of blending gives the best compatibility result. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Thermodynamic and kinetic studies of phase separation in polymer blends have made considerable progress.<sup>1–6</sup> However, the general perception is that most polymer pairs are immiscible as a result of a low entropy of mixing associated with the long molecular structures of polymers. This notion has changed gradually since polymer miscibility can be enhanced through some specific interactions between dissimilar polymers. Additional factors such as blending conditions were found to play an important role in the miscibility studies.<sup>7–9</sup> A number of mixing techniques were employed in the preparation of polymer blends, among which melt-mixing and solution-casting are common methods, widely practiced in industries and many laboratories. To determine whether the components are miscible, considerable care must be exercised in the preparation stage to assure that a physical equilibrium has, in fact, been achieved. Two-phase blends may result for systems that are miscible when a too high temperature is used in melt-mixing owing to a lower critical solution temperature (LCST) behavior<sup>10–12</sup>

or because of the so-called solvent effect during solution casting,<sup>13,14</sup> when in question, several different solvents should be tried<sup>15</sup> or the polymers precipitated by a nonsolvent.<sup>16</sup>

This article reports the role of the methods of blending such as solution-casting, melt-mixing, and coprecipitation on polymer–polymer compatibility using three types of blend systems, viz., VYHH/PS, VYHH/SAN, and VYHH/PMMA, by measuring their glass transition temperatures ( $T_g$ ).

## EXPERIMENTAL

### Materials

(a) Poly(vinyl chloride-co-vinyl acetate) (VYHH) was supplied by Union Carbide International Co. (USA) containing 87 wt % vinyl chloride and 13 wt % vinyl acetate with an intrinsic viscosity value (cyclohexanone at 20°C) of 0.53. (b) Poly(styrene-co-acrylonitrile) (SAN), with an acrylonitrile content of 22 by wt % from elemental analysis, was obtained from Polychem (India) Ltd. (Polylan 1000 IM-1). (c) Poly(methyl methacrylate) (PMMA) was supplied by Gujarat State Fertiliser Corp., India (Gujpol 876 G). (d) Polystyrene (PS) was supplied by Polychem (India) Ltd., (Polystron 666 P-1). (e) Octyl tin mercaptide (M/S ALA Chemicals) was used as

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a stabilizer for VYHH. (e) All solvents and nonsolvents (THF, MEK, chloroform, dichloromethane, methanol) were of reagent grade and purchased from E. Merck (India) Ltd.

### Blend Preparation

- (i) **Solution-casting.** Films of pure polymers and their blends were cast from the 4% solution in different solvents on a mercury surface at room temperature to obtain uniform thickness. Evaporation of the solvent was done slowly under a stream of nitrogen in a dust-free chamber and the resulting films were dried under reduced pressure at 100°C until the films reached constant weight. The blend solutions based on chloroform or THF were poured onto a glass slide preheated to 70°C on a hot plate.
- (ii) **Coprecipitated blend.** In this method, pure polymers and their blends were precipitated simultaneously from chloroform or the THF solution using the nonsolvent methanol; the latter, in a volume ratio of about 10 : 1 to the added chloroform or THF solution, was continuously stirred in a beaker while chloroform or the THF solution was added slowly. The precipitated powder was allowed to dry in a similar manner as described under solution-casting above.
- (iii) **Melt-mixing.** Melt-blending was accomplished by melting the coprecipitated blend prepared by the coprecipitation method at about 150–170°C for 5 min. In the case of melt-blending, octyl tin mercaptide was used as a stabilizer to avoid the thermal degradation of VYHH.

Glass transition temperatures ( $T_g$ 's) of the blends were determined with a DSC 20 Mettler TA 3000 system with a TC 10A microprocessor using a heating rate of 10°C/min. Each sample was first heated from ambient temperature to 130°C. The reported  $T_g$  values were the average values based on the second and the subsequent runs, and the difference between the onset and the final temperatures was taken as the breadth of the glass transition region.

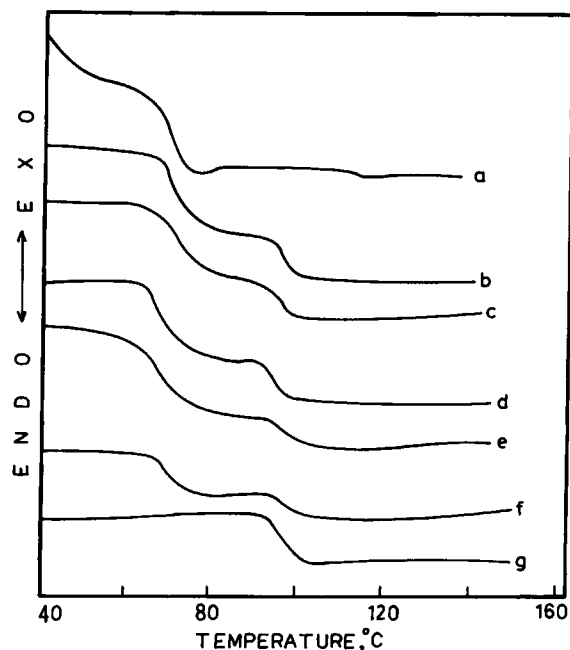
## RESULTS AND DISCUSSION

### VYHH/PS Blends

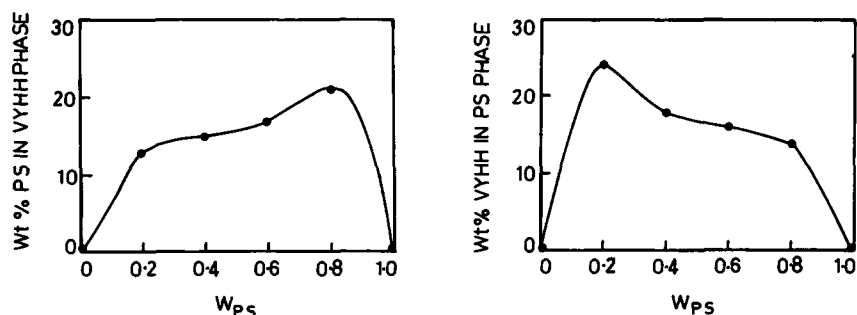
The blend films cast from chloroform, THF, MEK, and dichloromethane at ambient temperature were

opaque in contrast to the transparency of the pure polymers and showed dual  $T_g$ 's corresponding to the  $T_g$ 's of the pure polymers. Even the high-temperature casting from the above-mentioned solvents and melt-mixing blends also gave the dual  $T_g$ 's of the blends. From the above experiments, it was found that PS is immiscible with VYHH. Figure 1 shows the DSC thermograms of the solution-cast blend films at ambient and high temperature and also of the melt-mixing blends. But when the solution-blended samples were coprecipitated by methanol as a nonsolvent, the coprecipitated blends showed a slightly different pattern of the  $T_g$  behavior, i.e., the  $T_g$ 's of the lower  $T_g$  component (i.e., VYHH domains) were enhanced by 3–5°C, whereas the  $T_g$ 's of the higher  $T_g$  component (i.e., SAN domains) were lowered by 4–7°C compared with the parent polymers, indicating the partial miscibility of the two polymers.

For calculating the extent of partial miscibility of the coprecipitated blends as judged by the  $T_g$  shifts, one approach is used to assess the amount of PS dissolved in the VYHH phase and vice versa. It is assumed that the Fox equation<sup>17</sup> would describe the  $T_g$ -composition relation if PS was fully miscible



**Figure 1** DSC thermograms of incompatible blends of VYHH/PS: (a) pure VYHH; (b) blend (50 : 50) cast from THF solution at ambient temperature; (c) blend (50 : 50) cast from THF solution at elevated temperature; (d) blend (50 : 50) cast from chloroform solution at ambient temperature; (e) blend (50 : 50) cast from dichloromethane solution; (f) melt-mixed blend (50 : 50); (g) pure PS.



**Figure 2** Phase composition for immiscible blends of VYHH/PS coprecipitated from THF solution into methanol as computed from eq. (2).

with VYHH. This is an ad hoc but useful assumption since a relation with no adjustable parameters is needed for such analysis. By inverting the Fox equation:

$$1/T_g = W_{\text{VYHH}}/T_{g,\text{VYHH}} + (1 - W_{\text{VYHH}})/T_{g,\text{PS}} \quad (1)$$

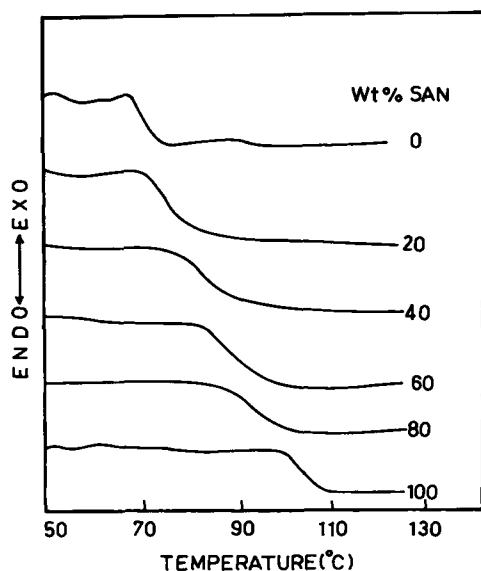
the weight fraction of VYHH in either the VYHH or PS phase can be computed:

$$W_{\text{VYHH}} = T_{g,\text{VYHH}}(T_{g,\text{PS}} - T_g) / T_g(T_{g,\text{PS}} - T_{g,\text{VYHH}}) \quad (2)$$

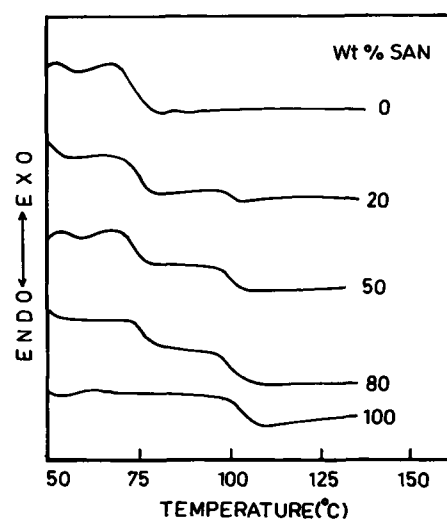
by inserting the  $T_g$  observed for the phase of interest. The results of these calculations are given in Figure 2. Based on this analysis, it appears that VYHH is more soluble in PS than PS is in VYHH.

### VYHH/SAN Blends

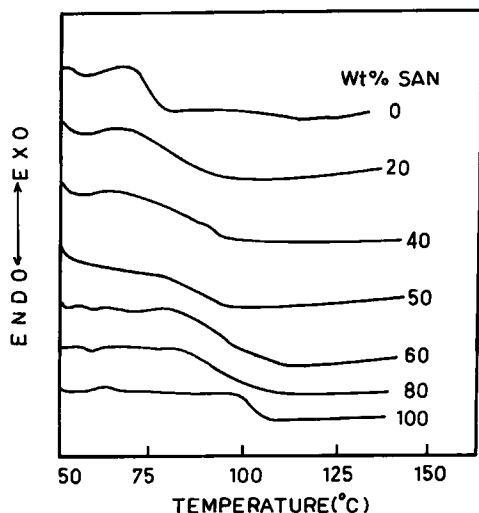
The blends films cast from THF and MEK were completely transparent and showed a compositionally dependent glass transition temperature (Fig. 3), indicating the compatible nature of the blends over the whole composition range. But the blend films cast from chloroform and dichloromethane were opaque in contrast to the transparency of the pure VYHH and SAN films and showed dual  $T_g$ 's corresponding to the respective  $T_g$ 's of the component polymers (Fig. 4), indicating the incompatible nature of the blends. The influence of the solvents on blend compatibility was observed in the other blend systems also<sup>18-20</sup> and was explained by Robard and Patterson<sup>19</sup> in that the miscibility of two polymers in a common solvent is influenced by the difference between the individual polymer-solvent interaction parameters  $\chi_{ij}$ , i.e.,  $|\Delta\chi| = |\chi_{12} - \chi_{13}|$ , where com-



**Figure 3** DSC thermograms of compatible blends of VYHH/SAN cast from THF at ambient temperature.



**Figure 4** DSC thermograms of incompatible blends of VYHH/SAN cast from chloroform solution at ambient temperature.

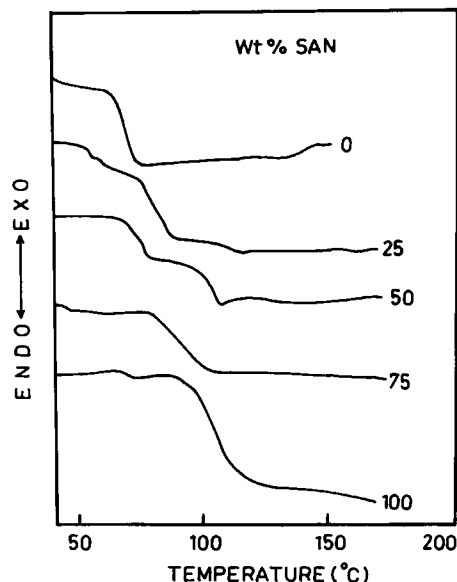


**Figure 5** DSC thermograms for VYHH/SAN blends films cast from chloroform solution at elevated temperature.

ponent 1 is the solvent and 2 and 3 represent the polymers.

An alternative method of casting was employed, i.e., elevated temperature-casting from the chloroform solution where the blends gave single compositionally dependent  $T_g$ 's, but the transition breadth is broader (as shown in Fig. 5). It has been suggested<sup>21</sup> that broadening of  $T_g$  arises mainly from compositional fluctuation in the blend. The magnitude of the fluctuation increases as the interaction between the components in the blend decreases and the fluctuation becomes macroscopic at the extreme limit of phase instability. The compatibility of the two components in this case may be due to the fact that the solvent evaporated so rapidly that an intermediate two-phase structure did not have time to develop.

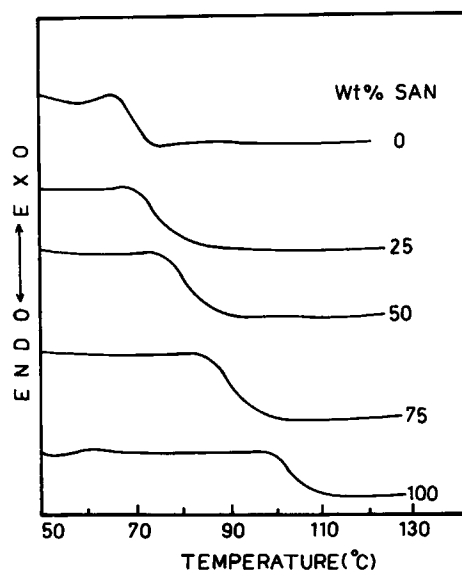
The blends prepared by the coprecipitation method using methanol as a nonsolvent gave a single compositionally dependent  $T_g$  as shown in Figure 6, indicating the compatible nature of the blend over the whole composition range. In the case of melt-blending, dual  $T_g$ 's were found in the composition range  $W_{SAN} = 0.24-0.74$ , indicating that these blends are incompatible, with only limited miscibility at either end of the composition range;  $W_{SAN}$  is the weight fraction of SAN in the blends. In the case of melt-mixing consisting of equal weight fractions of the each component, the  $T_g$ 's of the higher  $T_g$  component was lowered, whereas the  $T_g$ 's of the lowered  $T_g$  component was enhanced because some molecular mixing took place. The results are shown in Figure 7.



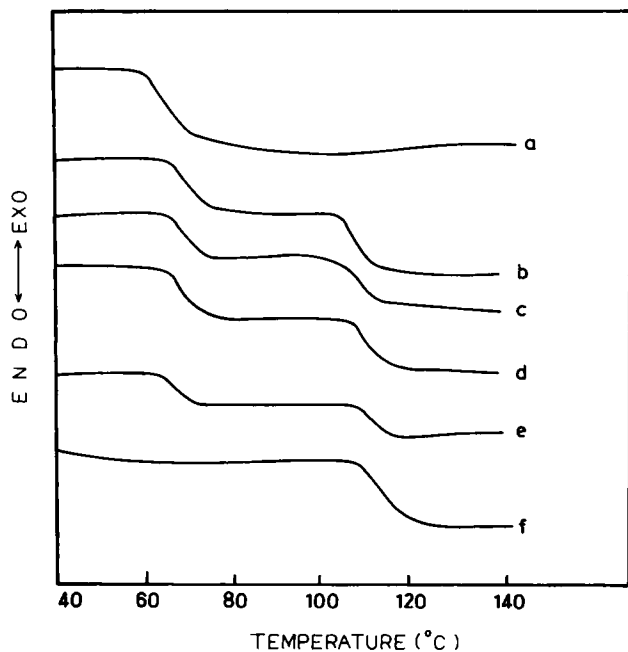
**Figure 6** DSC thermograms for melt-mixed VYHH/SAN blends.

#### VYHH/PMMA Blends

The blend films cast from THF, MEK, dichloromethane, and chloroform are opaque and showed two  $T_g$  values corresponding to the pure polymers, indicating the incompatible nature of the blends (Fig. 8). High-temperature casting of the blends showed a single  $T_g$  (Fig. 9), but the transition breadth was broader, indicating the semicompatible nature of the blend. Melt-mixed blends showed the dual



**Figure 7** DSC thermograms of compatible VYHH/SAN blends coprecipitated from chloroform solution by methanol.

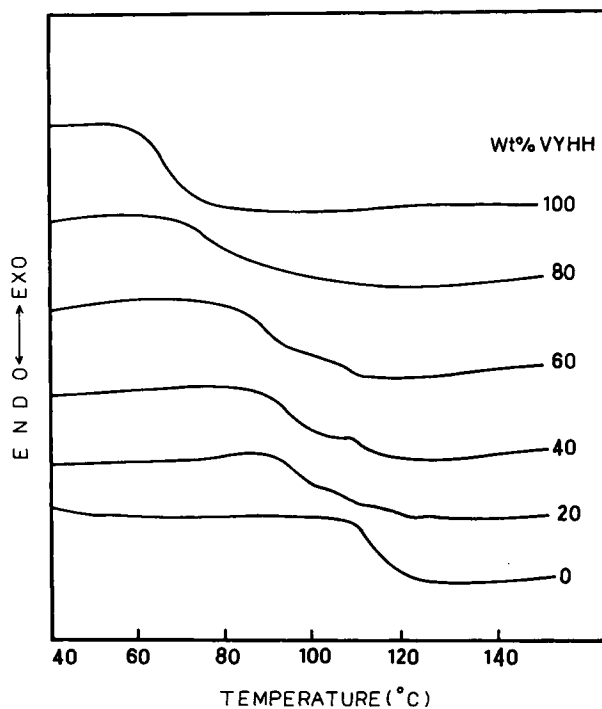


**Figure 8** DSC thermograms of incompatible blends of VYHH/PMMA: (a) pure VYHH; (b) blend (50 : 50) cast from THF at ambient temperature; (c) blend (50 : 50) cast from MEK solution at ambient temperature; (d) blend (50 : 50) cast from chloroform at ambient temperature; (e) melt-mixed blend (50 : 50); (f) pure PMMA.

$T_g$ 's over the whole composition range (Fig. 8). The blend powder prepared by the coprecipitation method gave a single compositionally dependent  $T_g$ , indicating the compatible nature of the blend over the whole composition range (Fig. 10).

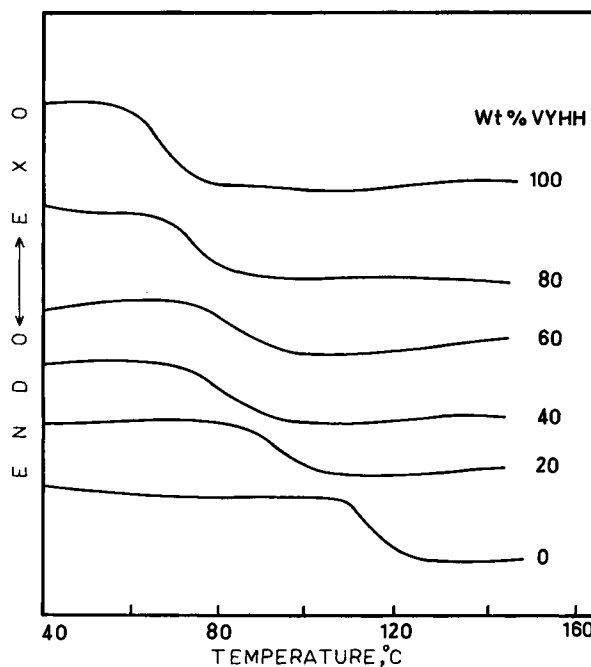
## CONCLUSION

From the study of the above-mentioned three types of blend systems, i.e., PS/VYHH, SAN/VYHH, and PMMA/VYHH, it can be concluded that the compatibility of the polymers may be dependent on the method of blending (i.e., methods of blend preparation) and compatibility also varies from one blend system to another. PS/VYHH systems show the incompatible nature of the blends regardless of the method of blending. The SAN/VYHH system is compatible in solution-casting from THF and MEK at ambient temperature and in the coprecipitated method of blending, but incompatible in solution-casting from chloroform and dichloromethane at ambient temperature, but elevated temperature-casting gave a semicompatible nature of the blend. Melt-mixed blends of VYHH/SAN give mixed results; blends are only compatible when the



**Figure 9** DSC thermograms of VYHH/PMMA blend films cast at elevated temperature from THF solution.

concentration of the one component is below 25 wt % in the blend. The VYHH/PMMA blend is compatible when prepared by the coprecipitation method of blending only.



**Figure 10** DSC thermograms of VYHH/PMMA blends coprecipitated from THF solution into methanol.

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