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# CALORIMETRIC STUDY OF THE MISCIBILITY OF POLY(STYRENE-CO-ACRYLONITRILE) / POLY(METHYL METHACRYLATE) / POLY(ETHYL METHACRYLATE) TERNARY BLENDS

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## ABSTRACT

The miscibility of poly(styrene-co-acrylonitrile) (SAN)/poly(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) (PEMA) ternary blends was studied by DSC. The assessment of miscibility is based on the glass transition temperature of the blend. The addition of SAN helps compatibilize the immiscible PMMA/PEMA blends.

## INTRODUCTION

The miscibility of poly(styrene-co-acrylonitrile) (SAN) with various polymethacrylates has been studied [1–6]. SAN is miscible with poly(methyl methacrylate) (PMMA) and with poly(ethyl methacrylate) (PEMA), but is immiscible with higher homologues of the polymethacrylate.

Blends containing two polymethacrylates are usually immiscible [7]. For example, PMMA/PEMA, PMMA/poly(*n*-propyl methacrylate) and PMMA/poly(*n*-butyl methacrylate) blends are immiscible. The addition of a suitable third polymer can help compatibilize an immiscible binary blend. A notable example is the use of poly(vinylidene fluoride) (PVDF) to compatibilize PMMA/PEMA blends since PVDF is miscible with PMMA and with PEMA [8]. We have reported the miscibility of poly($\alpha$-methyl styrene-co-acrylonitrile) (MSAN)/PMMA/PEMA ternary blends [9]. A miscible ternary blend can be formed if there is a high MSAN and/or PMMA content. We are now reporting a similar study on the miscibility of SAN/PMMA/PEMA ternary blends. The assessment of the miscibility is based on the glass transition temperature ($T_g$) of the blend. A single $T_g$ value indicates the one-phase nature of a miscible blend while an appearance of two $T_g$ values indicates the two-phase nature of an immiscible blend.

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## EXPERIMENTAL

### *Materials*

SAN containing 30% by weight of acrylonitrile was obtained from Scientific Polymer Products, Inc. The intrinsic viscosity of SAN was found to be 0.61 dl $g^{-1}$ in 2-butanone at 303 K.

PMMA (Elvacite 2010) and PEMA (Elvacite 2042) were obtained from Du Pont. The weight-average molecular weights of PMMA and PEMA are 120,000 and 310,000, respectively, as determined by intrinsic viscosity measurements.

### *Preparation of blends*

The blends were prepared by solution casting using tetrahydrofuran (THF) as solvent. 0.5 g of polymer mixture was dissolved in 25 $cm^3$ of THF. The solution was poured into an aluminium dish and solvent was allowed to evaporate slowly at room temperature. The blend was then dried in a vacuum oven at 383 K for 48 h.

### *Calorimetric measurements*

$T_g$ values of the blends were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter using a heating rate of 20 K $min^{-1}$. The $T_g$ value was taken to be the initial onset of the slope in the DSC curve. Each sample was scanned between 303 and 413 K for at least three times to check the consistency of the $T_g$ values.

### *Detection of lower critical solution temperature (LCST)*

All the blends were examined for the existence of LCST using the method described previously [9].

## RESULTS AND DISCUSSION

The DSC curves of some SAN/PMMA/PEMA ternary blends are shown in Fig. 1. The $T_g$ values of all the blends are given in Table 1. Depending on the composition of the blend, some blends show one $T_g$ while some other show two $T_g$ values. The lower $T_g$ of an immiscible blend is 5–19 K higher than the $T_g$ of PEMA. This phase is predominantly PEMA with some SAN and PMMA. The higher $T_g$ values of an immiscible blend ranges between 367 and 377 K. This phase is predominantly PMMA with some SAN and PEMA. The presence of PEMA in this phase is apparent as some of the $T_g$ values are lower than that of PMMA (samples 2 and 5).

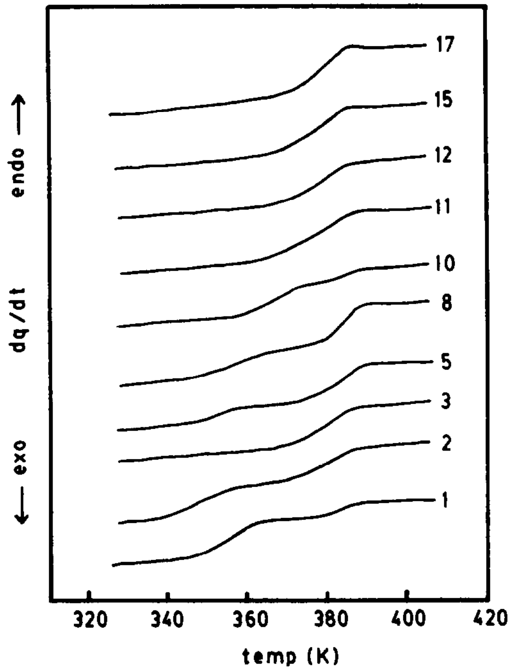


Fig. 1. DSC curves of some SAN/PMMA/PEMA ternary blends. Number refers to sample number in Table 1.

TABLE 1

$T_g$ values and cloud points of ternary blends

| Sample | Composition [a] SAN/PMMA/PEMA | $T_g$ (K) | Cloud point (K) |
|---|---|---|---|
| 1 | 10/20/70 | 345, 378 | 468 |
| 2 | 10/45/45 | 338, 367 | 458 |
| 3 | 10/70/20 | 369 | 470 |
| 4 | 20/20/60 | 347, 377 | 448 |
| 5 | 20/40/40 | 344, 373 | 451 |
| 6 | 20/60/20 | 372 | 451 |
| 7 | 30/20/50 | 352,377 | 458 |
| 8 | 30/35/35 | 348, 376 | 448 |
| 9 | 30/50/20 | 365 | 448 |
| 10 | 40/15/45 | 358, 378 | 453 |
| 11 | 40/30/30 | 358 | 453 |
| 12 | 40/45/15 | 366 | 453 |
| 13 | 50/10/40 | 359 | 438 |
| 14 | 50/25/25 | 363 | 442 |
| 15 | 60/20/20 | 363 | 437 |
| 16 | 70/15/15 | 365 | 453 |
| 17 | 80/10/10 | 371 | 463 |

[a] Composition in weight %. $T_g$ of SAN = 379 K, PMMA = 373 K and PEMA = 333 K.

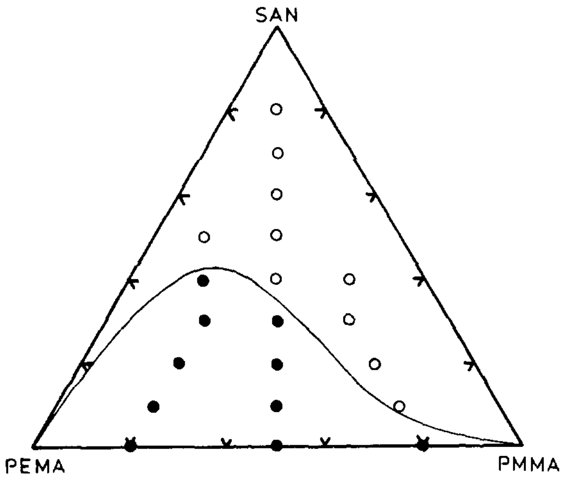


Fig. 2. Phase diagram of SAN/PMMA/PEMA ternary blends.

A phase diagram for the SAN/PMMA/PEMA ternary system is shown in Fig. 2. Open circles denote blends showing one $T_g$ and closed circles denote blends showing two $T_g$ values. It is apparent that the formation of a miscible ternary blend is favored when there is a high content of SAN and/or PMMA in the blend. The phase diagram resembles that of the MSAN/PMMA/PEMA system [9]. This is not surprising as the miscibility behavior of SAN with polymethacrylates is similar to that of MSAN. Both SAN and MSAN are miscible with PMMA and with PEMA but not with the higher homologues of the polymethacrylate; and they are immiscible with poly(methyl acrylate) and with poly(ethyl acrylate) [6,10].

Phase separation of miscible binary blends of SAN/PMMA and SAN/PEMA can be induced by heating, showing LCST behavior [6]. Similarly, a transparent miscible ternary blend of SAN/PMMA/PEMA becomes cloudy when heated above its LCST. The cloud points of the blends are given in Table 1. Some of the immiscible ternary blends also have good optical clarity in spite of their two-phase nature. An immiscible blend can be transparent if the difference between the refractive indices of the two phases in the blend is smaller than 0.01 or the domain size is smaller than the wavelength of the incident light [11]. The refractive indices of PMMA and SAN (containing 25% acrylonitrile) are 1.492 and 1.570, respectively [12], and that of PEMA is estimated by the Vogel method to be 1.493 [13]. The refractive indices of PMMA and PEMA are closely matched. Thus if SAN is equally distributed in both the PMMA-rich and the PEMA-rich phases, the refractive indices of the two phases will also be closely matched and the immiscible blend will have good clarity. Similar to the MSAN/PMMA/PEMA system [9], all the immiscible SAN/PMMA/PEMA ternary blends develop cloudiness on heating caused by the phase separation of each of the two phases in the blends.

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REFERENCES

1 D.J. Stein. R.H. Jung, K.H. Illers and H. Hendus, Angew. Makromol. Chem., 36 (1974) 89.
2 L.P. McMaster, Adv. Chem. Ser., 142 (1975) 43.
3 W.A. Kruse, R.G., Kirste, J. Hass, B.J. Schmitt and D.J. Stein, Makromol. Chem., 177 (1976) 1145.
4 K. Naito, G.E. Johnson, D.L. Allara and T.K. Kwei, Macromolecules, 11 (1978) 1260.
5 V.J. McBrierty, D.C. Douglas and T.K. Kwei, Macromolecules, 11 (1978) 1265.
6 J.S. Chiou, D.R. Paul and J.W. Barlow, Polymer, 23 (1982) 1543.
7 C. Tremblay and R.E. Prud'homme, J. Polym. Sci., Polym. Phys. Ed., 22 (1984) 1857.
8 T.K. Kwei, H.L. Frisch, W. Radigan and S. Vogel, Macromolecules, 10 (1977) 157.
9 S.H. Goh, K.S. Siow and K.S. Yap, Thermochim. Acta, 102 (1986) 281.
10 S.H. Goh, D.R. Paul and J.W. Barlow, Polym. Eng. Sci., 22 (1982) 34.
11 W.J. MacKnight, F.E. Karasz and J.R. Fried, in D.R. Paul and S. Newman (Eds.), Polymer Blends, Vol. 1, Academic Press, New York, 1978, Chap. 5.
12 J. Brandrup and E.H. Immergut (Eds.), Polymer Handbook, 2nd edn., Wiley-Interscience, New York, 1975.
13 D.W. Van Krevelen (Ed.), Properties of Polymers, 2nd edn., Elsevier, Amsterdam, 1976, Chap. 10.