Thermochimica Acta, 102 (1986) 281–285
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

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

S.H. GOH and K.S. SIOW

Department of Chemistry, National University of Singapore, Singapore 0511 (Republic of Singapore)

K.S. YAP

Chemical Process Technology Department, Singapore Polytechnic, Singapore 0513 (Republic of Singapore)

(Received 26 November 1985)

ABSTRACT

The miscibility of poly(α-methyl styrene-co-acrylonitrile) (MSAN)/poly(methyl methacrylate) (PMMA)/poly(ethyl methacrylate) (PEMA) ternary blends was studied by DSC. PMMA is immiscible with PEMA, but the addition of MSAN helps make PMMA and PEMA more compatible. The formation of a miscible ternary blend is favored when there is a high MSAN and/or PMMA content in the blend.

INTRODUCTION

The study of polymer blends has received considerable attention in recent years [1–5]. When two polymers are mixed, the resulting blend can be a homogeneous miscible blend or a phase-separated immiscible blend depending on the thermodynamics of polymer–polymer interaction. Measurement of the glass transition temperature (T_g) by DSC provides a simple means of ascertaining the miscibility of the blend. A miscible blend shows a composition-dependent value for T_g intermediate to the values of the T_g for the component polymers, while an immiscible blend shows two unperturbed T_g values for the component polymers. The application and practical limitations of thermal analysis in the study of polymer blends were reviewed by Fried [6].

The study of the miscibility of ternary polymer blends is scarce. Several ternary polymer blends which have been studied in recent years include poly(vinylidene fluoride)/poly(methyl methacrylate) (PMMA)/poly(ethyl

0040-6031/86/$03.50

methacrylate) (PEMA) blends [7], poly(vinyl chloride) (PVC)/poly(vinylidene chloride-co-vinyl chloride)/poly(acrylonitrile-co-butadiene) blends [8] and poly(α-methyl styrene-co-acrylonitrile) (MSAN)/PVC/styrene-acrylonitrile grafted butadiene rubber blends [9]. In this communication, we report the miscibility of MSAN/PMMA/PEMA ternary blends as studied by DSC. The miscibility of MSAN/PMMA and MSAN/PEMA binary blends has been reported earlier [10]. We have also reported the miscibility of MSAN with MMA/EMA copolymers [11] and with PMMA containing sterically hindered amine groups [12].

EXPERIMENTAL

Materials

The MSAN used was Luran KR 2556U manufactured by BASF. It contains 30% by weight of acrylonitrile and it has a molecular weight $\overline{M}_w$ of 160 000. PMMA (Elvacite 2010) and PEMA (Elvacite 2042) were obtained from Du Pont. The $\overline{M}_w$ values 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 the solvent; 0.5 g of polymer mixture was dissolved in 25 cm^3 of THF. The solution was then poured into an aluminium dish and the 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

The 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 was taken at 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. A polymer film was sandwiched between two microscopic cover glasses and heated in a Fisher–Johns melting apparatus with a heating rate of about 20 K min^{-1}. The optical appearance of the film was observed with a magnifying glass attached to the apparatus. A transparent sample which turned cloudy on

heating indicated the existence of LCST. The temperature at which the sample first showed cloudiness was recorded as the cloud point.

RESULTS AND DISCUSSION

The DSC curves of several MSAN/PMMA/PEMA blends are shown in Fig. 1. The values for the T_g of all the blends are given in Table 1. It has been shown that MSAN is miscible with PMMA and with PEMA [10], but PMMA is immiscible with PEMA [7,13]. The immiscibility of PMMA with PEMA is also confirmed in the present study as each PMMA/PEMA blend shows two T_g corresponding to the T_g values of PMMA and PEMA.

The addition of MSAN helps make PMMA and PEMA more compatible. As shown in Fig. 1, for ternary blends containing 10% by weight of MSAN, a blend with a high PMMA content (sample 3) shows only one T_g, indicating the single-phase nature of the blend while a blend with a low PMMA content (samples 1 and 2) shows two T_g, indicating the heterogeneous nature of the blend.

A three-component phase diagram for MSAN/PMMA/PEMA system is shown in Fig. 2. Open circles denote blends showing only one T_g and closed circles denote blends showing two T_g. A curve can be drawn on the diagram to separate two regions. Blends in the region under the curve are immiscible and blends in the region above the curve are miscible. It is apparent from the phase diagram that the formation of a miscible ternary blend is favored when there is a high content of MSAN and/or PMMA in the blend.

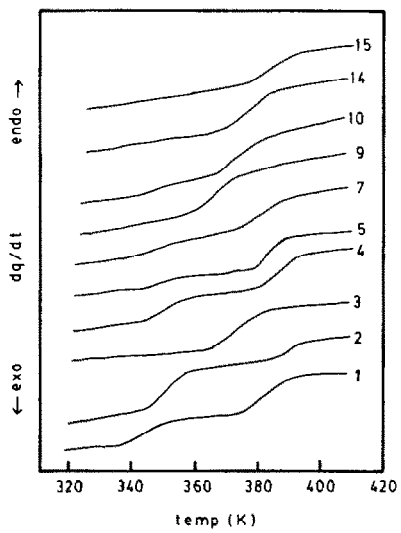

Fig. 1. DSC curves of several MSAN/PMMA/PEMA ternary blends; each number refers to the sample number in Table 1.

TABLE 1

T_g values and cloud points of ternary blends

Sample	Composition [a] (MSAN/PMMA/PEMA)	T_g (K) [b]	Cloud point (K)
1	10/45/45	337, 375	450
2	10/20/70	343, 383	463
3	10/70/20	364	463
4	20/40/40	343, 378	450
5	20/20/60	343, 378	463
6	20/60/20	369	458
7	30/35/35	341, 375	448
8	30/20/50	341, 371	465
9	30/50/20	358	453
10	40/30/30	343, 365	453
11	40/15/45	367	450
12	40/45/15	374	465
13	50/25/25	368	453
14	60/20/20	369	458
15	70/15/15	376	443
16	80/10/10	379	453

[a] Composition by weight %.

[b] T_g of MSAN = 388 K, PMMA = 373 K and PEMA = 333 K.

The lower T_g of an immiscible blend is 5–10 K higher than the T_g of PEMA, indicating this phase is predominantly PEMA containing some MSAN and a small amount of PMMA. The higher T_g of an immiscible blend ranges between 365 and 383 K. This phase is predominantly PMMA containing some MSAN and PEMA. The presence of PEMA in this phase is apparent as some of the T_g values are lower than the T_g of PMMA (samples 8 and 10).

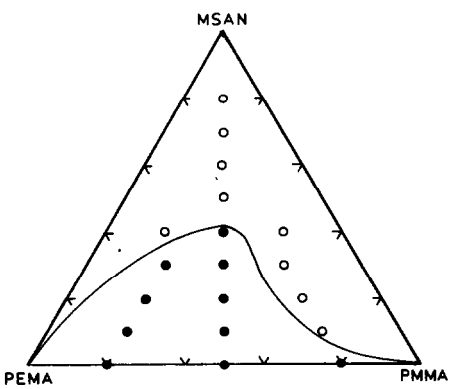

Fig. 2. Phase diagram of MSAN/PMMA/PEMA blends.

Many miscible binary blends undergo phase separation when heated to higher temperature, showing LCST behavior [14,15]. The phase separation can be observed visually since a transparent blend develops cloudiness when heated above the LCST. Both MSAN/PMMA and MSAN/PEMA binary blends show LCST behavior [10]. Depending on the molecular weights of the polymers and the composition of the blend, the cloud points of MSAN/PMMA blends range between 458 and 503 K and those of MSAN/PEMA blends range between 443 and 478 K [10].

All the miscible MSAN/PMMA/PEMA ternary blends are transparent and they develop cloudiness around 448–463 K. The cloud points of these miscible blends are given in Table 1. The immiscible blends are not as clear as those miscible blends. Nonetheless, the immiscible blends also develop cloudiness upon heating and the cloud points of these blends are also given in Table 1. The question arises of why an immiscible blend undergoes further phase separation. As mentioned earlier, in an immiscible blend, there is a PEMA-rich phase and a PMMA-rich phase. Each of these phases in the blend will also undergo phase separation at a higher temperature resulting in the appearance of cloudiness.

ACKNOWLEDGEMENT

Financial support of this work by the National University of Singapore is gratefully acknowledged.

REFERENCES

1 D.R. Paul and S. Newman (Eds.), Polymer Blends, Vols. 1 and 2, Academic Press, New York, 1978.
2 O. Olabisi, L.M. Robeson and M.T. Shaw, Polymer–Polymer Miscibility, Academic Press, New York, 1979.
3 D.R. Paul and J.W. Barlow, J. Macromol. Sci., Rev. Macromol. Chem., C18 (1980) 109.
4 A. Rudin, J. Macromol. Sci., Rev. Macromol. Chem., C19 (1980) 267.
5 L.M. Robeson, Polym. Eng. Sci., 24 (1984) 587.
6 J.R. Fried, in J.V. Dawkins (Ed.), Development in Polymer Characterisation–4, Applied Science Publishers, London, 1983, Ch. 2.
7 T.K. Kwei, H.L. Frisch, W. Radigan and S. Vogel, Macromolecules, 10 (1977) 157.
8 Y.Y. Wang and S.A. Chen, Polym. Eng. Sci., 21 (1981) 47.
9 M. Rink, L. Monfrini, P. Gasparini and A. Pavan, Plast. Rubber Process. Appl., 3 (1983) 145.
10 S.H. Goh, D.R. Paul and J.W. Barlow, Polym. Eng. Sci., 22 (1982) 34.
11 S.H. Goh, K.S. Siow and K.S. Yap, J. Appl. Polym. Sci., 29 (1984) 99.
12 S.H. Goh, S.Y. Lee and K.S. Siow, J. Appl. Polym. Sci., in press.
13 C.Tremblay and R.E. Prud'homme, J. Polym. Sci., Polym. Phys. Ed., 22 (1984) 1857.
14 R.E. Bernstein, C.A. Cruz, D.R. Paul and J.W. Barlow, Macromolecules, 10 (1977) 681.
15 T. Nishi, J. Macromol. Sci. Phys., B17 (1980) 517.