

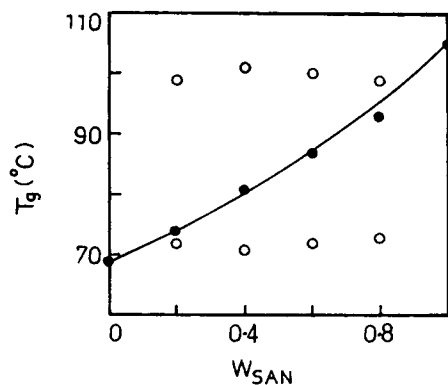
# Tensile Modulus–Structure Relationship of Poly(styrene-co-acrylonitrile) and Poly(vinyl chloride-co-vinyl acetate) Blends

## INTRODUCTION

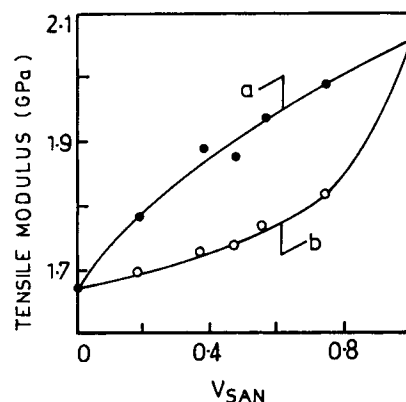
Polymer blends have attracted the increasing attention of polymer researchers in both academic and industrial communities.<sup>1,2</sup> Broadly classified, the two types of polymer blends are homogeneous (i.e., miscible or compatible) and heterogeneous (i.e., immiscible or incompatible) blends. From the literature survey it is found that very little work has been reported, if any, on relation of tensile moduli with the microstructure of the blend of poly(styrene-co-acrylonitrile) (SAN) and poly(vinyl chloride-co-vinyl acetate) (VYHH). This article presents tensile moduli of miscible and immiscible blends of SAN and VYHH films cast from different solvents and correlates tensile modulus with the structure. The parallel voids model<sup>3</sup> has been applied to the modulus-composition data in order to understand the microstructure of these blends.

## EXPERIMENTAL

SAN with an acrylonitrile content of 22% by weight from elemental analysis, was obtained from Polychem Limited



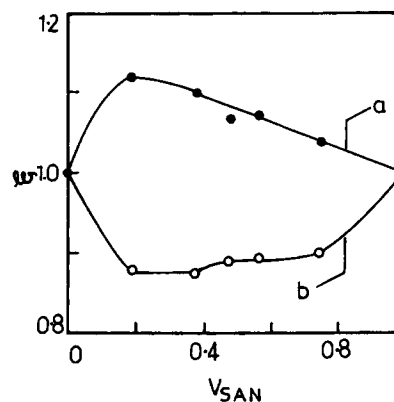
**Figure 1** Glass transition temperature,  $T_g$ , of VYHH and SAN blends as a function of weight fraction of SAN: (●) films cast from THF and (○) films cast from chloroform. The solid line is drawn according to the eq. (1).



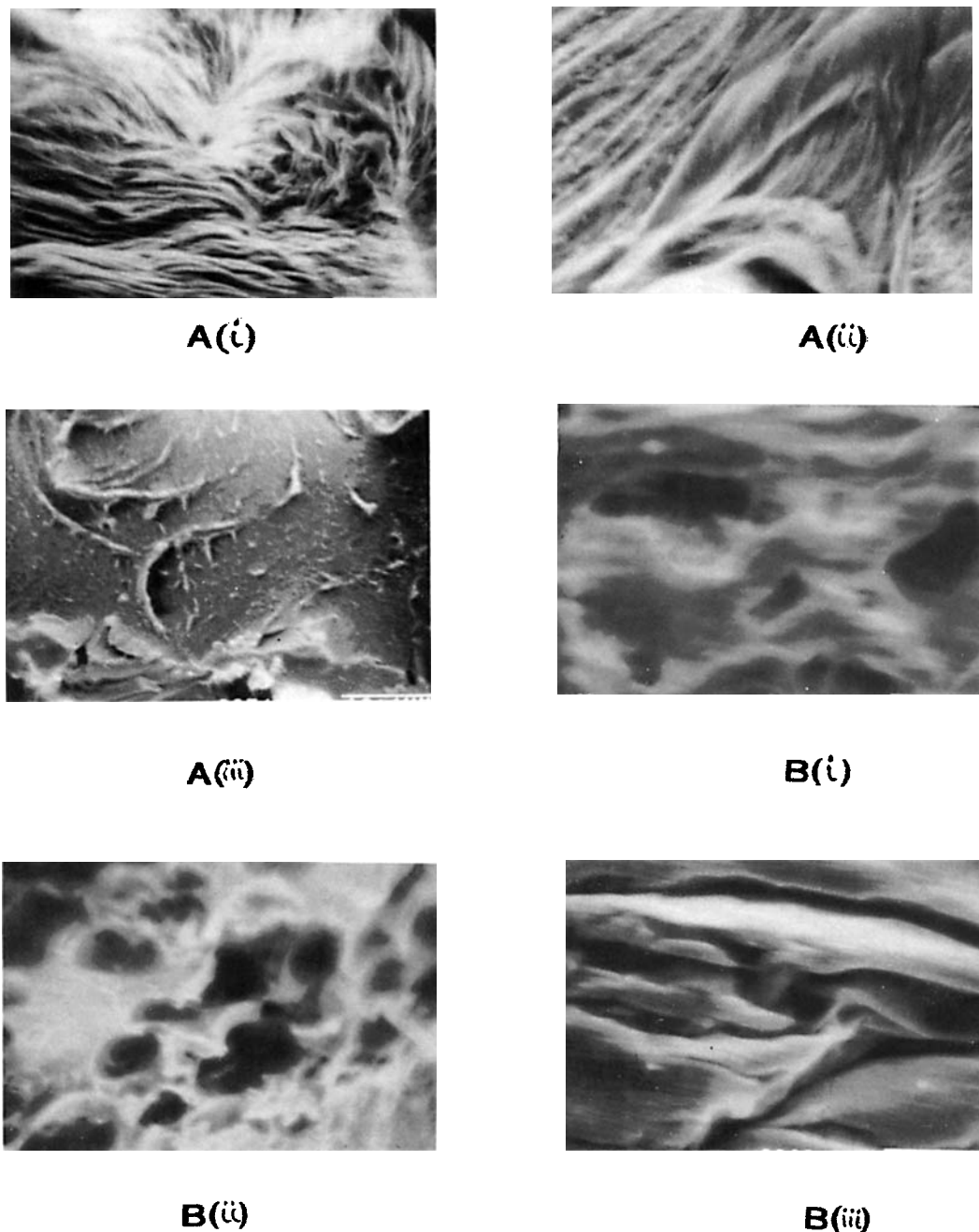
**Figure 2** Tensile modulus as a function of volume fraction of SAN content: (a) miscible and (b) immiscible blend.

(India, Polylan 1000 IM-1). VYHH, supplied by the Union Carbide Company, contained 87 wt % vinyl chloride, 13 wt % vinyl acetate, and had an intrinsic viscosity value (cyclohexanone at 20°C) of 0.53. All solvents mentioned were reagent grade.

Films of SAN, VYHH, and their blends were cast from 4% solutions in different solvents (such as tetrahydrofuran, THF, and chloroform) on a mercury surface at ambient temperature to achieve uniform film thickness.



**Figure 3** Reinforcing factor as a function of volume fraction of SAN content: (a) miscible blend and (b) immiscible blend.



**Figure 4** Scanning electron micrographs of the fracture surface of VYHH/SAN blends: (A) miscible, (B) immiscible blend, (i) 75 : 25 blend, (ii) 50 : 50 blend, (iii) 25 : 75 blend. Magnification 250 $\times$ .

Evaporation of solvents was done slowly under reduced pressure at 100 $^{\circ}$ C until the films reached constant weight.

Glass transition temperatures ( $T_g$ ) of blends were determined with a DSC 20 Mettler TA 3000 system with a TC 10A microprocessor using a heating rate of 10 $^{\circ}$ C/min. Each sample was first heated from room temperature to 130 $^{\circ}$ C. The reported  $T_g$  values were the average values based on the second and subsequent runs.

Tensile modulus measurements of cast films of samples were carried out at ambient temperature using a dumbbell-shaped test specimen in an Instron Universal Testing machine (Model 4301). The specification of the dumbbell was as follows: gauge length 25.4 mm, width 3.65 mm, and average thickness 0.55 mm. A strain rate of 20 mm/min was used throughout the investigation. Fracture surfaces were gold sputtered within 24 h of testing and were ex-

amined in a Hitachi 415 S scanning electron microscope (SEM).

## RESULTS AND DISCUSSION

The blend films cast from THF were transparent and gave compositionally dependent glass transition temperatures (Fig. 1), indicating the compatible nature of the blends over the whole composition range. These results are represented by the Fox equation,<sup>4</sup>

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (1)$$

where  $T_g$ ,  $T_{g1}$ , and  $T_{g2}$  are the glass transition temperatures of the blend, VYHH, and SAN, respectively, and  $W_1$  and  $W_2$  are the corresponding weight fractions. The blend films cast from chloroform were opaque in contrast to the transparency of pure VYHH and SAN films and showed dual  $T_g$ s (Fig. 1) corresponding to the respective  $T_g$ s of the component polymer. This suggests that the system results in phase separation.

Tensile moduli of the miscible and immiscible blends are plotted in Figure 2 as a function of the SAN content. It is well known that the mechanical properties of polymer blends depend on the degree of compatibility, i.e., interaction between the components. These observations (Fig. 2) suggest that there may exist either chemical or physical interaction or a combination of both between these two polymers. Interaction would entail the interlocking of the chain of the composites. Even in the case of the immiscible blend system, a slight gradual increase of the modulus of the lower modulus component by the addition of the higher modulus component was observed, and probably in addition to the interlocking of the chains of the composites, may be due to the same scale of partial miscibility of the two polymers as depicted from the differential scanning calorimetry study.

A recent model proposed by Dobkowski<sup>3</sup> (parallel void model) suggested that the fraction of the reinforcing material in the filler space,  $\xi$ , is given by,

$$\xi = 1/r + 1/r \cdot e/V \quad (2)$$

where  $r$  is the ratio of the tensile moduli of the pure polymers,  $V$  is the volume fraction of the reinforcing material, and  $e$  is the reinforcing factor.

$$e = (E/E_2) - 1 \quad (3)$$

where  $E$  is the modulus of the blend and  $E_2$  that of the polymer matrix.

If  $\xi = 1$ , voids are not present and there is a perfect adhesion between the matrix and the filler. If  $\xi < 1$ , there are voids in the filler space and the filler does not adhere to the surface of the matrix. On the other hand if  $\xi > 1$ ,

the reinforcing material occupies more space than its original volume.

In the case of the miscible blend films of SAN/VYHH cast from THF, all the compositions show values of  $\xi > 1$  (Fig. 3). This behavior is possible for blends where the chains of the compatible polymers are penetrating the neighboring material at the phase boundary.<sup>3</sup> This interphase gives rise to an additional zone of the reinforcing materials that increases the properties of the blends with respect to those of the filler. However, in the case of immiscible blend films of VYHH/SAN cast from chloroform, the  $\xi < 1$  is observed for all blend compositions, indicating that there are voids in the two polymers and there is no perfect adhesion between the components (Fig. 3).

SEM photomicrographs (Fig. 4) of the blends show that in the case of immiscible systems, large number of holes or voids are present; in the case of the miscible system, voids or holes are practically absent, the continuous or discontinuous striations and/or almost uniform smooth failure are observed. The presence of voids or holes in the case of immiscible blends is due to poor interphase adhesion between the components.<sup>5</sup>

The CSIR grant to Gaurab Das (SRF) is acknowledged.

## REFERENCES

1. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic Press, New York, 1979.
2. L. A. Utracki, *Polymer Alloys and Blends*, Hanser Publishers, Munich, 1990.
3. Z. Dobkowski, *Polymer Blends, Processing, Morphology and Properties*, E. Martuscelli, R. Palumbo, and M. Krysewski, Eds., Plenum Press, New York, 1980, p. 86.
4. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).
5. A. K. Kulshreshtha, G. C. Pandey, S. F. Xavier, and J. S. Anand, *Eur. Polym. J.*, **25**, 925 (1989).

Gaurab Das  
A. N. Banerjee\*

Department of Plastics and Rubber Technology  
University College of Science and Technology  
University of Calcutta  
92 A.P.C. Road  
Calcutta 700 009, India

Received April 26, 1995

Accepted May 17, 1995

\* To whom correspondence should be addressed.