

Rheological Studies of the Poly(styrene-*co*-acrylonitrile) and Poly(vinyl chloride-*co*-vinyl acetate) Blends

GAURAB DAS, A. N. BANERJEE

Department of Polymer Science and Technology, University Colleges of Science and Technology, Calcutta University, 92 A.P.C. Road, Calcutta 700009, India

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ABSTRACT: The rheological studies of the poly(vinyl chloride-*co*-vinyl acetate) and poly(styrene-*co*-acrylonitrile) blends were performed by a Brabender Rheotron at three different temperatures and also at different shear rates. Flow curves of the blends at different temperatures were drawn. The flow behavior index and, also, zero-shear viscosity of the blends at different temperatures were determined. From the flow curves, it has been found that as shear stress increases, melt viscosity decreases at all temperatures, indicating that pseudoplastic behavior and experimental values lies above the line of the log-additivity value and below the line of the additivity rule of mixture. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2577–2583, 1998

Key words: rheology; polymer blends; viscosity; pseudoplastic behavior

INTRODUCTION

Rheology is the science of deformation and flow and of the interrelation between the force and its effect. Polymer rheology is a well-investigated subject in its fundamental and experimental aspects. However, the rheology of polymer blends is still in an early stage of development.^{1–5}

The determination of polymer–polymer miscibility by rheological measurements on binary systems is rare and, indeed, may be difficult to justify.⁶ But because the morphology of a two-phase system can change with shearing rate, whereas the structure of a soluble system cannot, it is expected that the shear viscosity function of soluble system will change monotonically with composition and deviation from monotony can be taken as positive evidence of two phases.

Three significantly different behavior patterns may be found in blends.⁷ First are the rare of cases of compatible blends, as found in poly(phen-

ylene oxide) (PPO) and polystyrene (PS), in which the rheology is a true marriage of the two components.⁸ Second are blends of high-viscosity, incompatible polymers, in which the blend may have significantly lower viscosity than either parent⁷ (for example, blends of polycarbonate and poly(4-methyl pentene-1), an effect which is presumably associated with the weakness of shear planes at the interfaces between the phases. Han⁹ has made an extensive study of such systems. A completely different response may be observed in blends of low-viscosity melts, in which the blends may have a higher viscosity than either parent and appear remarkably elastic (for example, blends of nylon 66 and polypropylene).⁷

This article reports the rheological studies of the blends of [poly(vinyl chloride-*co*-vinyl acetate)–poly(styrene-*co*-acrylonitrile)] (VYHH–SAN) cast from tetrahydrofuran.

EXPERIMENTAL

Poly(styrene-*co*-acrylonitrile) (SAN) (Polylan 1000 IM-1) was supplied by Polychem Limited

Correspondence to: A. N. Banerjee.

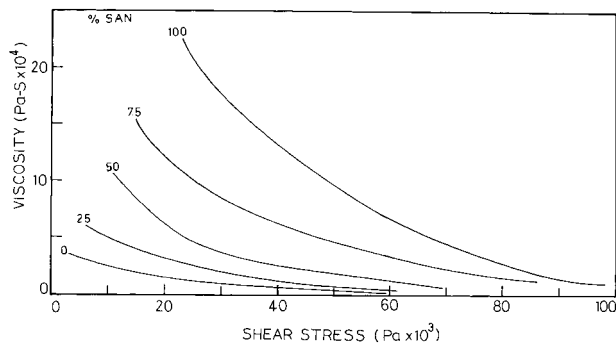


Figure 1 Viscosity as a function of shear stress of the VYHH-SAN blends at 150°C.

(India). It had an acrylonitrile content of 22% by weight from elemental analysis. It was a random copolymer, with an average molecular weight of 95,000 to 105,000. Poly(vinyl chloride-co-vinyl acetate) (VYHH) was supplied by Union Carbide International Company, USA, contained 87% vinyl chloride, 13 wt % vinyl acetate, and had an intrinsic viscosity value (cyclohexanone at 20°C) of 0.53. Octyl tin mercaptide supplied by M/S ALA Chemicals, India, was used as a stabilizer for VYHH. Tetrahydrofuran (THF) was purchased from EMerk Ltd. (India).

The individual polymer solutions were prepared by dissolving the individual polymers in THF, followed by stirring for approximately 24 h. The concentration of the solutions was 4% on a weight basis. The solutions were subsequently blended in the proper proportions and stirred for approximately 24 h, then the blend solutions were settled for 7 days. The resulting blend solutions were then cast on to the mercury surface at ambient temperature in order to get uniform film thickness; in all cases, the same volume of the aliquots of the blend were poured on the same diameter of the mercury surface. The evaporation of the

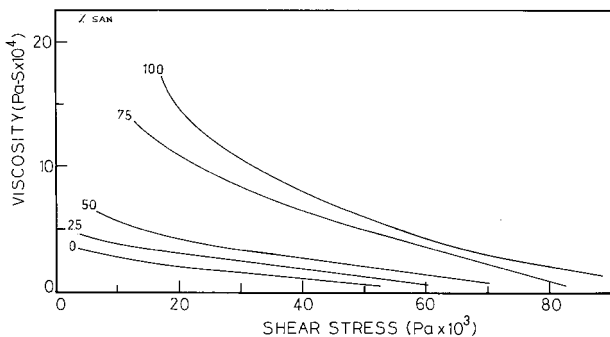


Figure 2 Viscosity as a function of shear stress of the VYHH-SAN blends at 160°C.

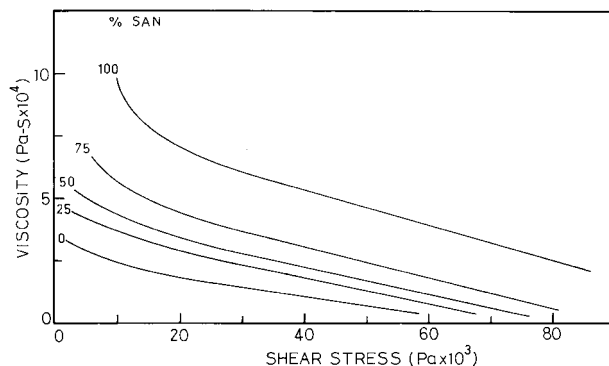


Figure 3 Viscosity as a function of shear stress of the VYHH-SAN blends at 170°C.

solvents was done slowly under reduced pressure at 100°C until the films reached constant weight.

The Brabender rheotron consists of a low angle (3°) cone and plate. The experimental material is kept between the cone and the plate. The electronic drive, which consists of a motor, operates the plate; thus, the plate rotates at different rate per minute (rpm), and a torque is generated within the material. The torque is applied to the measuring shaft, which carried the cone, through a transducer. This torque is displayed in the electric control unit. There is a temperature control vessel that controls the temperature of the plate.

The threaded spindle of the cone is connected to the measuring shaft. At first, a zero point has been set. For zero point setting, the cylinder plate was inserted in the open bottom of the temperature control vessel without the test material. The pressing device was fastened. The cone contact switch at the electronic control unit was on. This turned the contact signal on.

The signal light for cone contact was lit up, and the range selector was set to 10. The plate cylinder was allowed to rotate at 5 min^{-1} . The zero point was then set by the setter. This compensates for the friction between the plate and cone. After the zero point adjustment, the plate cylinder was removed, and the test material was placed on the plate. The required quantity was between 0.3 to 0.5 g. The plate cylinder was then inserted, and the force pressing device was screwed onto the temperature control chamber until it was moderately hand tight. Then the scale drum was raised so that the spring pushed the plate upwards until cone contact is made.

The test method results are always based on rpm values of the plate and on measuring the resulting torque values at the cone. The rheologi-

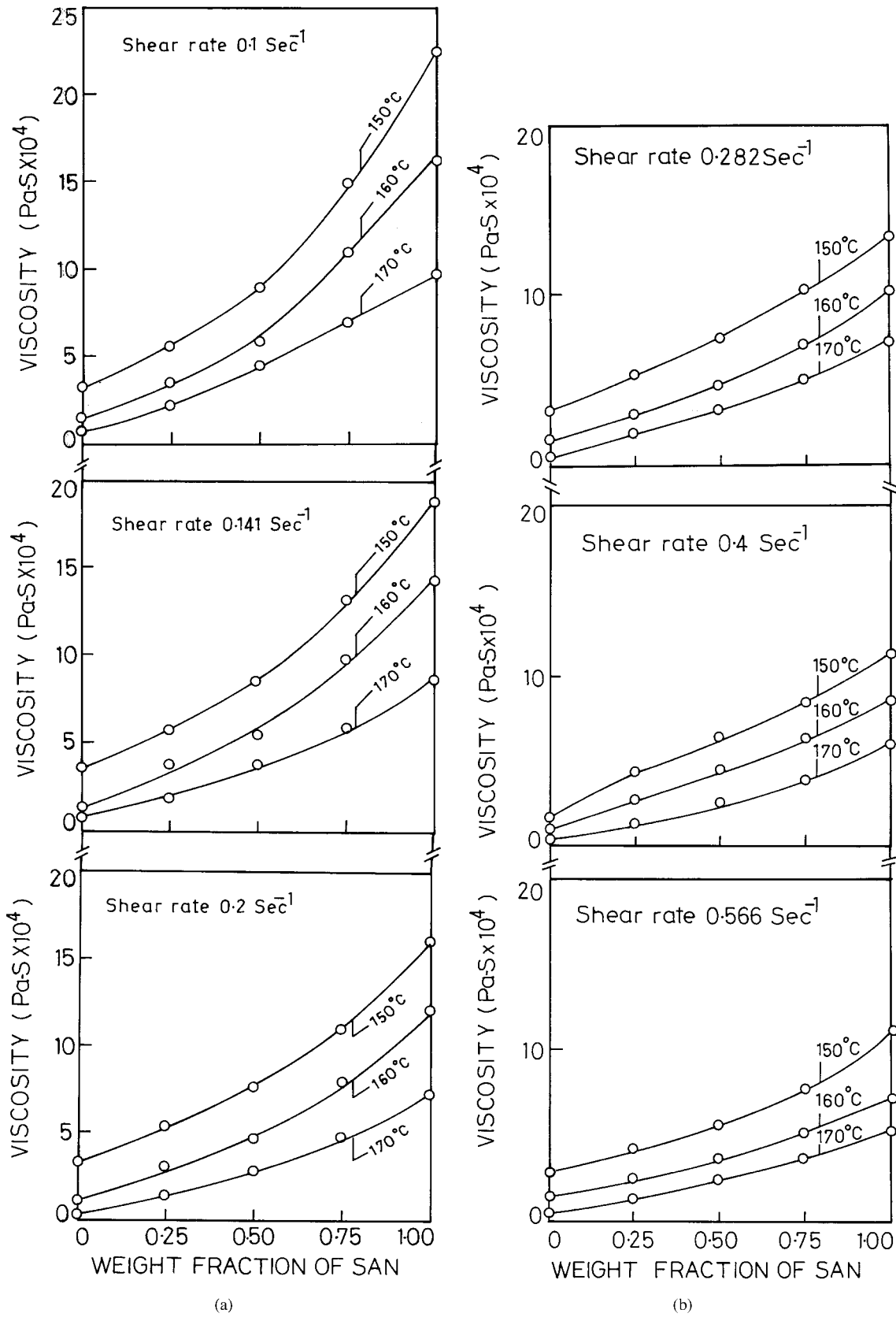


Figure 4 (a, b) Viscosity as a function of composition of VYHH-SAN blends at different temperatures at different shear rates.

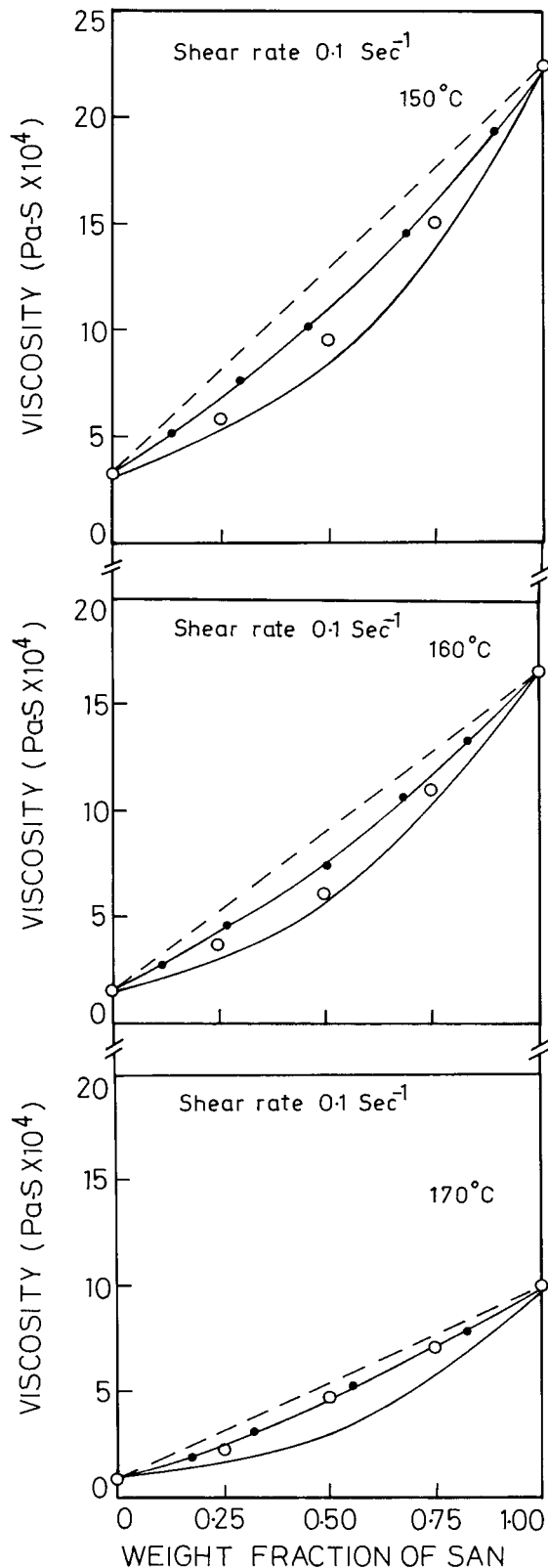


Figure 5 Viscosity as a function of composition of the VYHH-SAN blends: (· · · · ·) line drawn according to the additivity rule of mixture; (- · - · -) line drawn ac-

cal values are calculated as follows (which are given in the Rheotron Manual for data calculations): Shear rates, $D = nX$ in s^{-1} ; shear stress = BSY in Pa; viscosity, $\eta = BSK \cdot \frac{1}{n}$ in mPa s, where n is the rpm of the outer cylinder (min^{-1}), B is the range factor (10, 3, 1), S is the digital display, X is the shear rate factor (an instrument constant), Y is the shear stress factor (an instrument constant), and K is the calibration constant.

RESULTS AND DISCUSSION

Flow Curves of the Blends

Flow curves of every composition of VYHH-SAN blends for the temperature range of 150–170°C are shown in Figures 1–3, respectively. As shear stress increases, the melt viscosity in all cases decreases, indicating their pseudoplastic flow behavior. The concentration dependence of viscosity of the blends at various shear rates for 3 different temperatures (that is, 150, 160, and 170°C) are shown in Figure 4.

Numerous attempts have been made to predict the compositional dependence of the viscosity of polymer blends, notwithstanding a noteworthy absence of success. For miscible blends, a number of empirical and semiempirical equations predicting the viscosity of polymer blends have been proposed with varying degrees of success. They are the additivity rule of mixture, as follows:

$$\eta_b = W_1 \eta_1 + W_2 \eta_2 \quad (1)$$

the log additivity rule, as follows:

$$\log \eta_b = W_1 \log \eta_1 + W_2 \log \eta_2 \quad (2)$$

and the free-volume additivity rule, as follows:

$$1/\log \eta = W_1 \frac{1}{\log \eta_1} + W_2 \frac{1}{\log \eta_2} \quad (3)$$

where η_b is the viscosity of the blend, η_1 and η_2 are the viscosities of the two components, and W_1

according to the log additivity rule of mixture; (- ○ -) line drawn according to the free volume additivity rule of mixture at shear rate of $0.1 s^{-1}$.

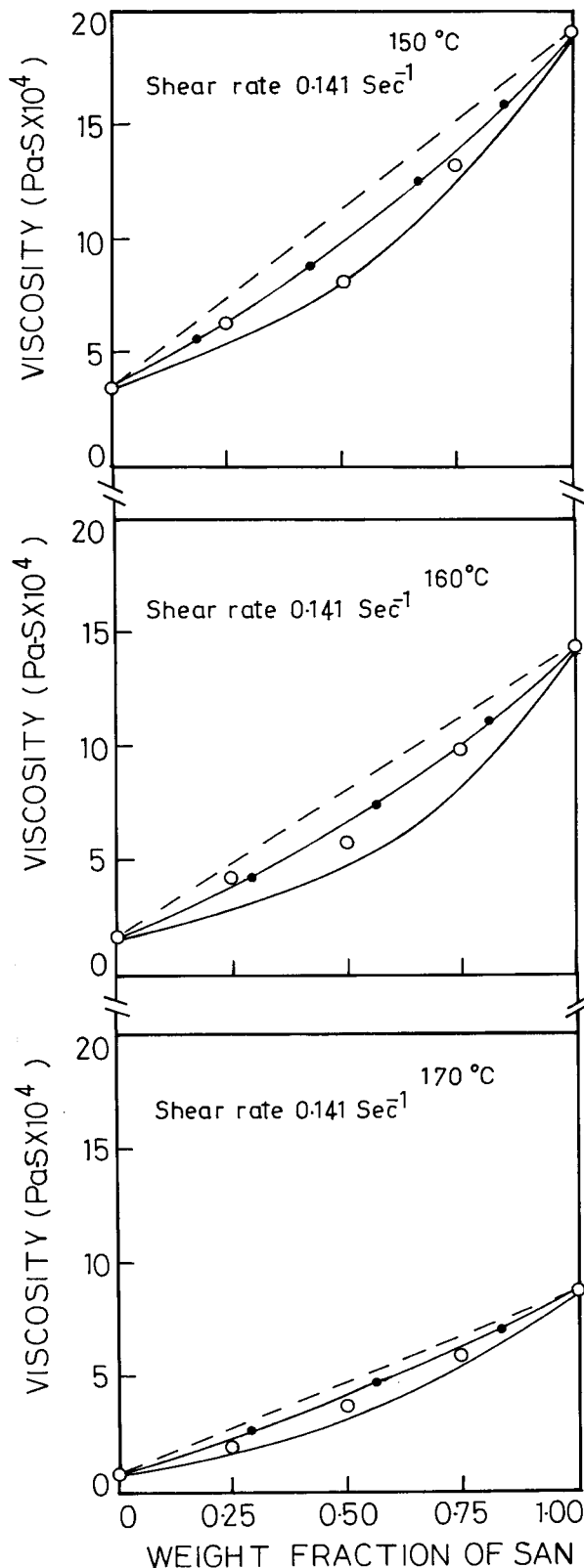


Figure 6 Viscosity as a function of composition of the VYHH-SAN blends: (· · · · ·) line drawn according to the additivity rule of mixture; (-----) line drawn ac-

and W_2 are the weight fraction of the two components.

Figures 5 and 6 show the comparison of the experimental values of the viscosity versus the composition of the blends with the value calculated from the additivity rule of mixture [eq. (1)] from the log-additivity rule [eq. (2)] and from the free volume additivity rule of mixture [eq. (3)]. From Figures 5 and 6, it has been observed that experimental points lie above the line of the log-additivity rule but below the line of additivity rule of mixture.

In the case of completely miscible blends, that is, 100% miscible blends, experimental values will be similar to the values calculated from the additivity rule of mixture, which is practically rare in the polymer blend systems. When the blend is less than 100% miscible, or partially miscible, the values predicted from the log-additivity rule of mixture will be close to the experimental value. The blend systems that show the large negative deviation from the rule of mixture of log-additivity value will be considered as an immiscible blend system. So from the above discussion, it is observed that the studied blends system (that is, VYHH-SAN blends) is not completely miscible blend; that is, it shows the behavior of partial miscible systems.

The complexity of the viscosity-composition behavior of polymer blends is best described by Utracki and Kamal.¹¹ Using rheological data from a large number of systems, they divided the blends into three categories, depending on the deviations of the viscosity from the log-additivity rule. Blends that exhibited viscosities higher than that predicted by the log-additivity rule were labelled as positively deviating, and those with lower viscosities were labeled as negatively deviating; finally, those showing both behaviors were labelled as positively-negatively deviating. The variability of viscosity-composition behavior with the nature of the blend indicates that, presently, no generalization or prediction is possible.

There are several reports in which, indeed, a positive deviation from the log-additivity rule has been observed for miscible polymer blends, for example, polyisoprene-poly(vinyl ethylene)¹⁰ and poly(methyl methacrylate) (PMMA)-poly(styrene-co-acrylonitrile) (SAN).¹² It also has been observed for immiscible polymer blends, for exam-

plified according to the log additivity rule of mixture at shear rate 0.141 s^{-1} .

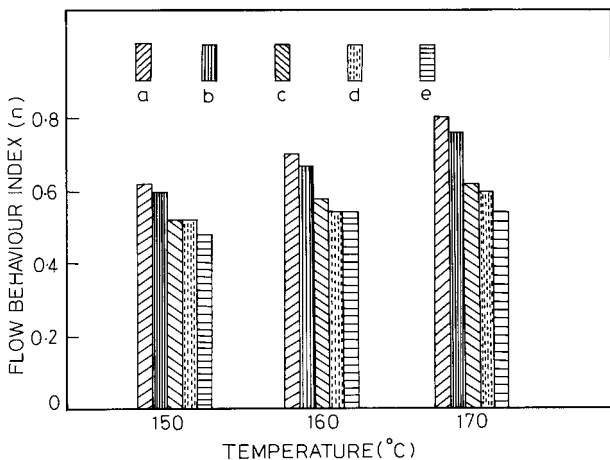


Figure 7 Flow behavior index as a function of temperature of the VYHH-SAN blends: (a) pure VYHH; (b) 75 : 25 (VYHH-SAN); (c) 50 : 50 (VYHH-SAN); (d) 25 : 75 (VYHH-SAN); (e) pure SAN.

ple, high-density polyethylene (HDPE)-poly(ethylene-co-vinyl acetate) (EVA),¹³ HDPE-low-density polyethylene (LDPE),¹⁴ polystyrene (PS)-polyethylene,¹⁵ and polycarbonate (PC)-tetramethylene polycarbonate (TMPC).¹⁶

The number of miscible blends with negative deviations from the log-additivity rule is increasing steadily. This behavior was reported for PS/TMPC,¹⁷ poly(styrene-co-maleic anhydride) (SMA)-(SAN),¹⁸ polyethylene oxide (PEO)-PMMA,¹⁹ PMMA-poly(vinylidene fluoride) (PVDF),²⁰ and others. In PEO-poly(vinyl acetate) (PVAc)¹² blends, mixed positive and negative deviations were observed. The examples of the negative deviations of the log-additivity rule in the case of the immiscible blends reported are HDPE-polyamide-6 blends²¹ and PS-PC blends.²²

Flow Behavior Index (n)

The power law, $\tau = K\dot{\gamma}^n$, is widely used as a model for non-Newtonian fluids,²³ where τ is shear stress, $\dot{\gamma}$ is shear rate, and K and n are constant. For Newtonian fluids, $n = 1$; and for dilatant fluids, $n > 1$; for pseudoplastic fluids, $n < 1$, n is known as the flow behavior index. The effect of the temperature and blend ratio on the flow behavior index is presented in Figure 7. From Figure 7, it is observed that the value of n is less than 1 for all the temperatures under investigation, indicating the pseudoplastic nature of the polymer blends in the melting condition. The pseudoplasticity of every VYHH-SAN melt decreases with temperature.

Zero-Shear Viscosity

The zero-shear viscosity is usually the Newtonian viscosity in the case of polymer melts because, in practice, Newtonian behavior is confined to low-molecular-weight liquids, but polymer melts obey Newtonian law only at shear rates close to zero and polymer solutions only at concentrations close to zero.²⁴ Figure 8 shows the plot of zero shear viscosity versus composition of the blends at different temperatures. The zero shear viscosity versus the blend composition show negative deviations from the additivity rule for all the temperatures under investigation. Yang et al.²⁵ have shown that the miscible blends of PMMA-SAN showed positive deviation of zero-shear viscosity versus the blend composition from linearity, but miscible blends of PMMA-PVDF showed negative deviation from linearity of the zero-shear viscosity versus the blend composition plot.

CONCLUSION

Miscible blends of VYHH-SAN melts are pseudoplastic in nature and show the positive devia-

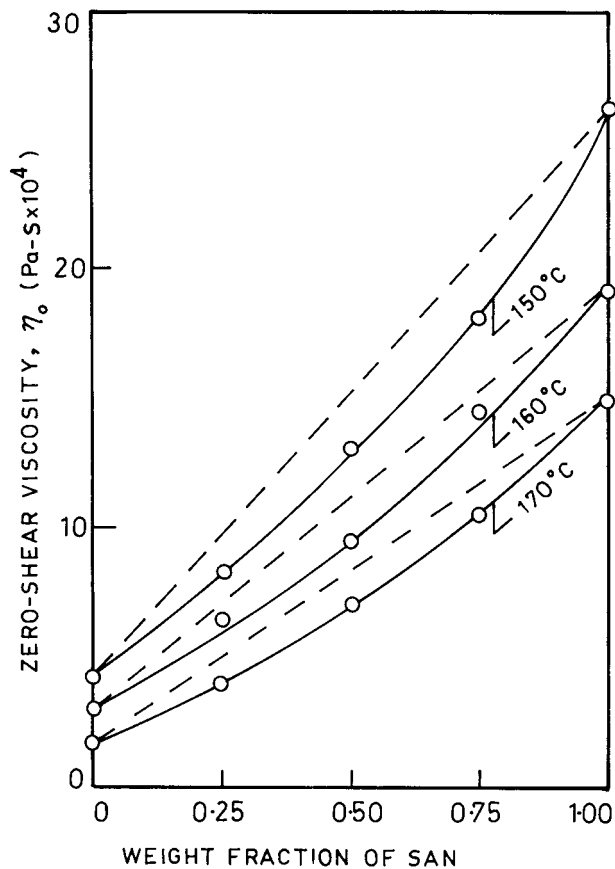


Figure 8 Compositional dependence of the zero-shear viscosity at different temperatures.

tion from log-additivity rule but follow the negative deviation from additivity rule of mixture.

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