

Compatibility Studies on Some Solutions of Rubber Blends by Ultrasonic Techniques

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SYNOPSIS

The degree of compatibility of the blend solutions, SBR–NR, SBR–BR, and SBR–NBR, dissolved in toluene was studied using ultrasonic methods. The variation of longitudinal ultrasonic velocity with composition is linear with SBR–NR and SBR–BR blends indicating compatible systems. For SBR–NBR the plots of ultrasonic velocity versus composition deviates from linearity according to the degree of compatibility of this blend system. The behavior was confirmed by heat of mixing calculations as well as ultrasonic attenuation measurements.

INTRODUCTION

The chemical or physical blending of two or more polymers is the simplest means to obtain a variety of physical and chemical properties from the constituent polymers. However, the gain in newer properties depends on the degree of compatibility of the polymers at a molecular level. Therefore, the compatibility is the most fundamental property in polymer blends. Many experimental and theoretical studies reported in the literature¹ include methods of determining the degree of compatibility. Among these methods are viscometric measurements, dynamic mechanical response, electron microscopy, glass transition temperatures, and infrared spectroscopy.¹ More recently, many workers^{2–9} report that the ultrasonic velocity measurements may reveal the extent of compatibility in highly viscous or solid forms of polymer blends. Detailed ultrasonic velocity studies indicated that, in compatible polymer blends, the ultrasonic velocity varies linearly with composition while it deviates from linearity in the incompatible blends. New approach to the study of compatibility of polymer blends using ultrasonic attenuation was offered by Arman et al.,¹⁰ Belaribi¹¹ and his co-workers, and Schneider.¹² Arman reported that bad adhesion between the matrix and

dispersed phase leads to high values of attenuation coefficients. Belaribi showed that the attenuation increases as a result to phase separation between the polymers. Schneider reported that compatible polymer blends exhibit specific glass transition composition behavior. Measurements of mixing enthalpies in polymer–polymer pairs is also of interest in arriving at criteria for compatibility.

Slonimskii and Struminskii¹³ determined heat of mixing of polymers with each other and found that mixing of polymers with each other is usually an endothermic process. Moreover, they found that systems that separate into phases (incompatible blends) are characterized by positive values for heat of mixing ($\Delta H > 0$) while systems that do not separate into phases (compatible blends) are characterized by negative values for heat of mixing ($\Delta H < 0$). Schneider¹⁴ suggested an equation for heat of mixing for two-component blend systems, either compatible or incompatible, given in the form

$$\Delta H = \left[\bar{x}_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \times \left(\frac{\bar{x}_2}{(1 - \bar{x}_2) M_2 \rho_2 + (1 - \bar{x}_1) M_1 \rho_1} \right)^2 \right]^{1/2}$$

where \bar{x} , ρ , and M are the weight fraction of polymer, density, and monomer unit molecular weight, respectively; δ is the solubility parameter of the polymer. Results obtained by applying this equation gave an approximate measure of polymer–polymer com-

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patibility. Singh and Singh⁶ calculated the heat of mixing of some polymer blends using the Schneier equation and reported that heat of mixing with values below a limiting value of 4.185×10^{-2} J/mol indicate compatible blends while values for heat of mixing for incompatible blends are mostly above this limiting value.

EXPERIMENTAL

The investigated rubber blends are: SBR (styrene-butadiene rubber) + NR (natural rubber Rss1), SBR + BR (polybutadiene rubber), and SBR + NBR (acrylonitrile butadiene rubber). These blends were prepared by masticating on two roller mill the two-component rubbers separately for 20 min.

Requisite proportions of the two rubbers were then dissolved in toluene and mixed thoroughly. Two blend concentrations were prepared (2 and 10%) and different compositions were then prepared. The measurement techniques were described in details

in a previous article.¹⁵ All measurements were carried out at room temperature (295 K) using one ultrasonic frequency of 6 MHz.

The heat of mixing was calculated by applying the equation suggested by Schneier. The adiabatic compressibility β of the blend systems was calculated by applying the equation of Newton and Laplace¹⁶ gives as

$$\beta = \frac{1}{C^2 \rho}$$

where C is the longitudinal ultrasonic velocity and ρ is the density of the blend solution.

RESULTS AND DISCUSSION

Blends of SBR-NR

The variation of longitudinal ultrasonic velocity with composition in SBR-NR blend is shown in Figure 1(a). The ultrasonic velocity shows linear variation

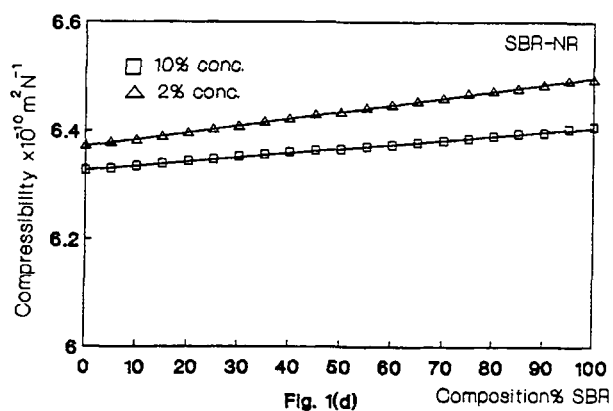
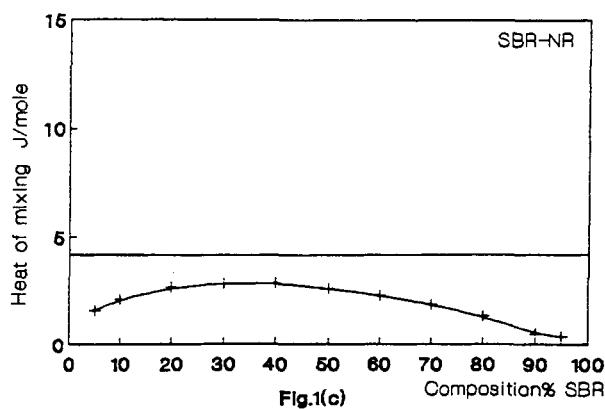
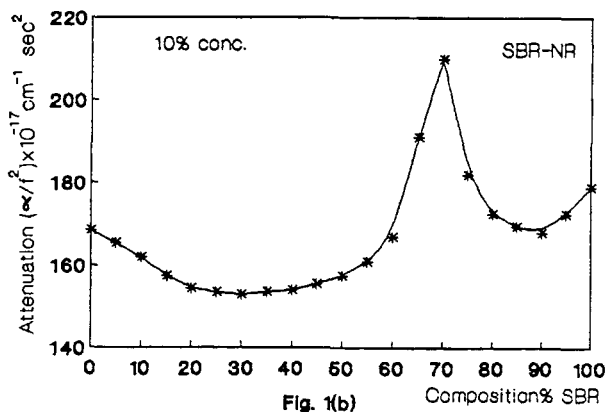
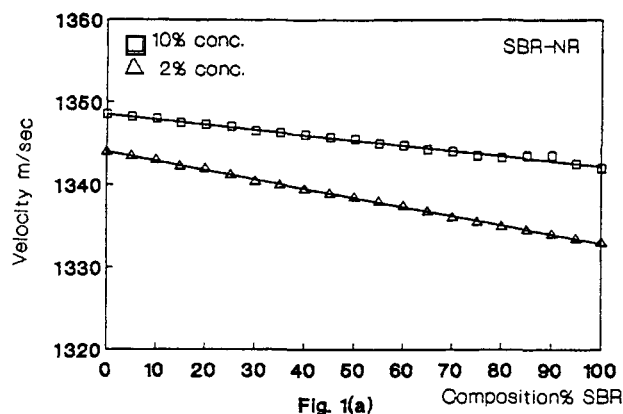


Figure 1 The variation of (a) longitudinal ultrasonic velocity, (b) ultrasonic attenuation, (c) heat of mixing, and (d) adiabatic compressibility with composition of SBR-NR blend solutions.

with composition in the two concentrations indicating clearly the compatible miscibility in all compositions. This is mainly due to the strong interaction between the two rubbers leading to the formation of one single phase.

The variation of ultrasonic attenuation with composition is represented in Figure 1(b). One can observe only one well-defined sharp maximum for attenuation near 70% SBR concentration. The presence of only one maximum reflects the mutual solubility of component rubbers and the formation of a true solution out of them.¹⁵ This behavior indicates that SBR and NR macromolecules in the mixture are packed more orderly than in individual components.

The heat of mixing of SBR-NR blend solutions has been calculated over the entire range of compositions and are shown in Figure 1(c). Values of the heat of mixing of these blends are found to lie between 0.358×10^{-2} and 2.876×10^{-2} J/mol, i.e., well below 4.185×10^{-2} J/mol, the figure considered to be the upper limit of compatibility.

Variation of adiabatic compressibility β with composition is shown in Figure 1(d). The relation is linear and is represented by a straight lines characterizing compatible behavior.

Blends of SBR-BR

Figure 2(a) shows a plot of longitudinal ultrasonic velocity versus composition for SBR-BR blend solutions. The plot is linear, represented by straight lines characterizing a compatible rubber blends. The linearity of this relation confirms the complete solubility of these two components in each other in all proportions.

Figure 2(b) describes the variation of ultrasonic attenuation and composition of this blend system. The figure shows only one maximum at about 50% SBR composition. The presence of only one maximum indicates the formation of a single phase system.¹⁵

Figure 2(c) gives the calculated heat of mixing of the rubber blend over the entire range of compositions.

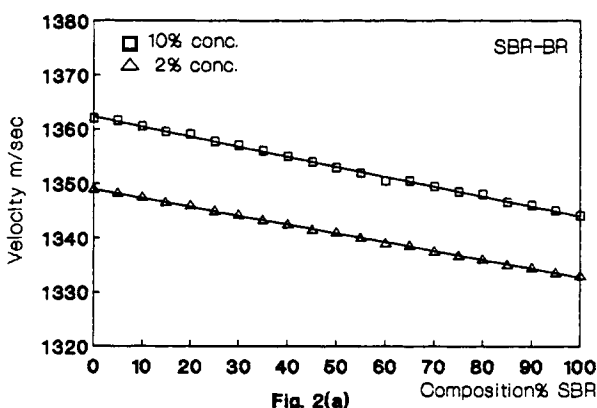


Fig. 2(a)

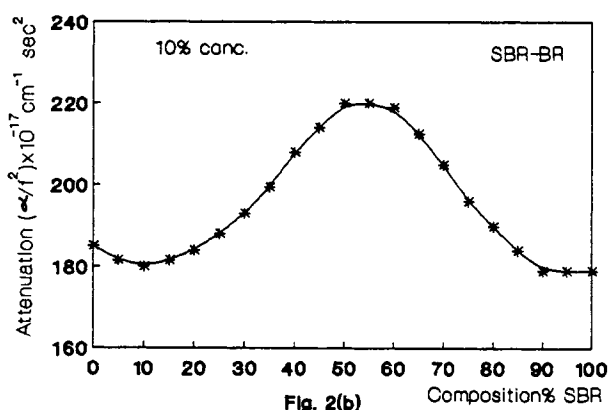


Fig. 2(b)

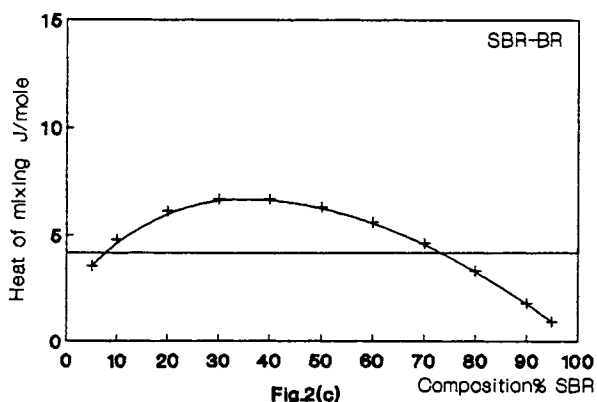


Fig. 2(c)

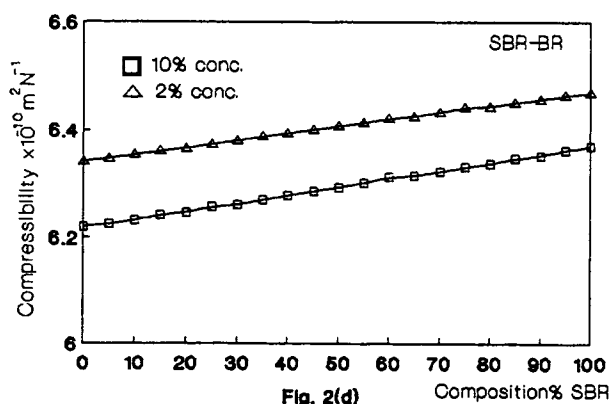


Fig. 2(d)

Figure 2 The variation of (a) longitudinal ultrasonic velocity, (b) ultrasonic attenuation, (c) heat of mixing, and (d) adiabatic compressibility with composition of SBR-BR blend solutions.

Although some of the values for heat of mixing lie above the upper limit of compatibility, we can presume that the blends are compatible since many values for heat of mixing are less than limiting values.

Figure 2(d) shows the relation between adiabatic compressibility versus composition of SBR-NBR blend solutions at two concentrations (2 and 10%). It is clear that the relation is linear, which predicts the compatibility manner of this blend system.

Blends of SBR-NBR

The variation of longitudinal ultrasonic velocity with compositions of SBR-NBR blend solutions is plotted and shown in Figure 3(a). The curves show deviation from linear behavior. The ultrasonic velocity curve may be divided into two distinct regions; viz. 0-40% and 40-100% SBR composition. The first region depicts S-type behavior, showing a region of

phase inversion. The second region also shows the same behavior emphasizing the incompatibility of the blends. Again, this S-type behavior indicates two-phase formation with reversal of phases at intermediate compositions. The sudden increase or decrease in the ultrasonic velocity in the phase inversion region may be attributed to the association of macromolecules indicating aggregation of rubber domains in rubber-rubber-solvent system.¹⁷

The relation between ultrasonic attenuation and composition of the blend solutions is given in Figure 3(b). Two maxima are clearly observed at 20 and 60% SBR composition. The presence of more than one maximum indicates phase inversion and consequently incompatible blend system.

Figure 3(c) gives the relation between the calculated heat of mixing of SBR-NBR blends and composition. Values in the range 1.368×10^{-2} and 11.007 J/mol , above the limiting value of compatibility, are obtained. This implies that macromole-

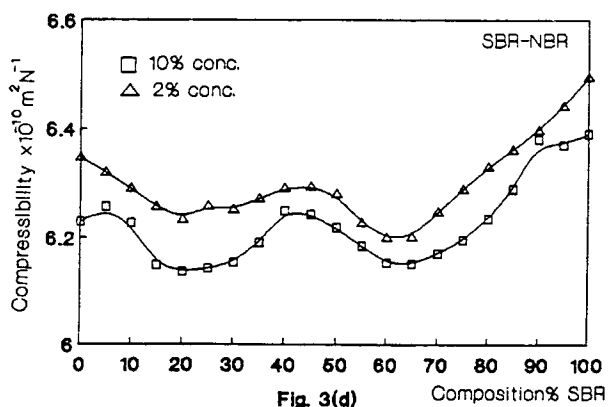
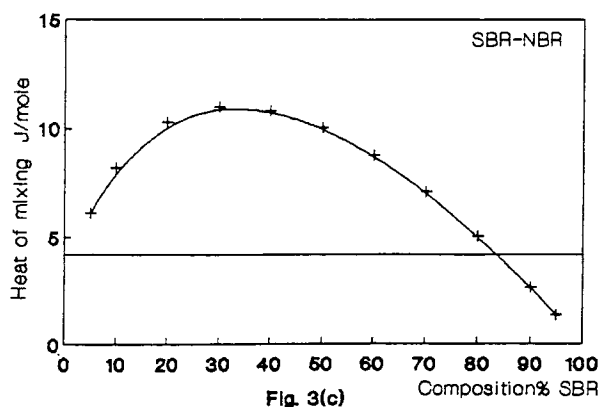
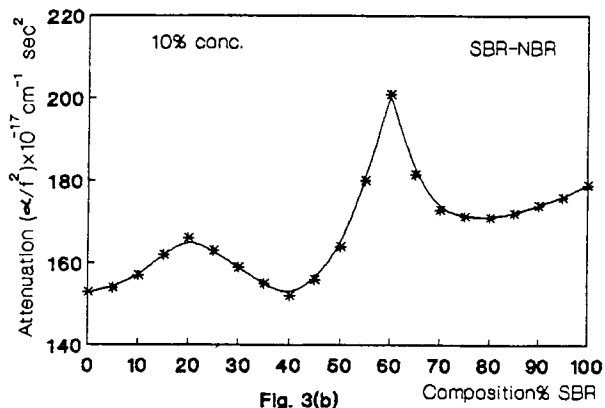
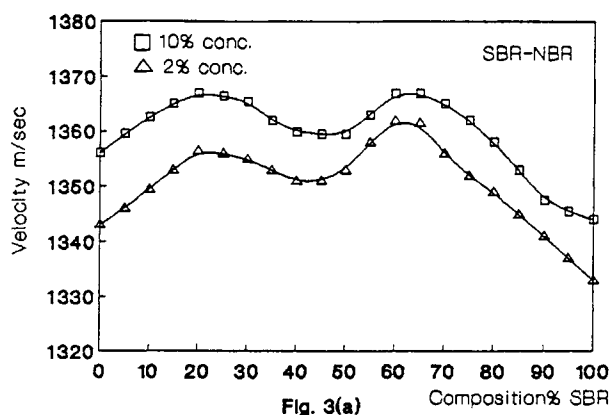


Figure 3 The variation of (a) longitudinal ultrasonic velocity, (b) ultrasonic attenuation, (c) heat of mixing, and (d) adiabatic compressibility with composition of SBR-NBR blend solutions.

cules in the mixture are in disordered state and the incompatibility of this blend system may be due to the differences in their nature.

Figure 3(d) describes the relation between the calculated adiabatic compressibility of SBR-NBR blend solutions versus compositions. The shape of the curves at the two concentrations has two minima at 20 and 60% SBR composition.

On the basis of values of heat of mixing, linearity of ultrasonic velocity versus composition, the existence of one single maximum in attenuation-composition plot and linearity of adiabatic compressibility versus composition SBR-NR, and SBR-BR blends are predicted to be compatible over the entire range of composition while blends of SBR-NBR are predicted to be incompatible.

For compatible and incompatible systems, the present ultrasonic results agree with the observations made by Yahia¹⁸ and his co-workers who reported viscometric results for compatible and incompatible systems.

The present investigation indicates clearly that the compatibility of rubber blends may be studied by ultrasonic techniques. It may be concluded that the simplest measurements of ultrasonic velocity and ultrasonic attenuation presents clues to the compatibility of blends, which is in general obtained by sophisticated techniques.

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