

Ultrasonic Investigation of Some Rubber Blends

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SYNOPSIS

Compression ultrasonic velocity, longitudinal ultrasonic absorption, and heat of mixing for NR-BR, NR, NBR, and NR-IIR rubber blends were measured. Results show the applicability of examining the compatibility degree by using longitudinal ultrasonic absorption techniques. Results showed that NR-BR blends are compatible, whereas NR-NBR and NR-IIR blends are semicompatible and incompatible, respectively.

INTRODUCTION

The concept of physically blending two or more existing polymers to obtain a new product has not been developed as fully as the chemical approach to blending, but the physical approach is now attracting widespread interest and is being used commercially.

Polymer blends are physical mixtures of structurally different polymers, which interact through secondary forces with no covalent bonding.¹ The manifestation of superior properties depends upon compatibility or miscibility of homopolymers at molecular levels. Depending upon the degree of molecular mixing, the blends may be categorized thus; totally miscible (compatible blends), semimiscible (semicompatible), and immiscible (incompatible blends). The word compatibility, therefore, refers to miscibility of homopolymers on a molecular scale, and of random copolymers blending with each other in various combinations.

Compatibility of polymer blends can be examined by sophisticated experimental and theoretical techniques.² Such techniques include studies on viscosities, heat of mixing, mechanical properties, glass transition temperature, and morphology by electron microscopy. Recently, Hourston et al.³ has indicated the use of ultrasonic measurements for compatibility determination. Singh et al.⁴ and Singh⁵⁻⁷ have measured viscosity and ultrasonic velocity for compatible, semicompatible, and incompatible polymeric

blends. They found that in compatible blends, the ultrasonic velocity varies linearly with composition, while the velocity deviates from linearity in incompatible polymer blends.

Kuleznev et al.⁸ have carried out viscometric and sonic investigations to reveal various aspects of the compatibility of polymer blends in highly viscous and solid form. More recently, Bagchi et al.⁹ measured ultrasonic velocity, density, and absolute viscosity for solutions of ISRO polyol in various solvents. The salvation number was found to be higher in highly hydrogen-bonded solvents. The theoretical and experimental values of Roa constants are found to be identical within experimental errors.

Slonimskii and Struminskii,¹⁰ determined the heat of mixing of many polymer pairs with the same ratio as that of the components. They found that, in most cases, systems which do not separate into phases (compatible) are characterized by negative values for heat of mixing (i.e., $\Delta H < 0$), while systems that separate into phases (incompatible) are characterized by positive values for heat of mixing, (i.e., $\Delta H > 0$). Slonimskii¹¹ calculated the heat of mixing of polymers with each other; the behavior of the mixture of solutions of various polymers was also investigated. He found that the mixing of polymers with each other is usually an endothermic process and leads to the formation of macroscopically homogeneous, but actually microheterogeneous, systems with extremely high degrees of dispersion.

Bohn¹² prepared a list of compatible and incompatible pairs of polymer blends. He found that the heat of mixing is an approximate measure of free energy of mixing and thus may indicate the degree of compatibility. Schneier¹³ calculated the heat of

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mixing for a number of compatible and incompatible polymer blends. He suggested an equation based upon the formulation of Gee,¹⁴ which is given as;

$$\Delta H = [\bar{X}_1 M_1 \varphi_1 (\delta_1 - \delta_2) \{ \bar{X}_2 / (1 - \bar{X}_2) M_2 \varphi_2 + (1 - \bar{X}_1) M_1 \varphi_1 \}^2]^{1/2} \quad (1)$$

Where \bar{X} , φ , and M are the weight fraction of polymer, density, and monomer unit molecular weight, respectively. The δ is the solubility parameter of the polymer. Singh and Singh⁵ calculated the heat of mixing of some compatible blends using the Schneier equation. They reported that the heat of mixing, with values below a figure that is considered to be the upper limit of compatibility (10×10^{-3} cal/Mol), indicate compatible and semicompatible blends. On the other hand, values for the heat of mixing for incompatible blends are mostly above this upper-limit value. The present study describes an experimental investigation of compatibility in solutions of the rubber blends: NR-BR, NR-NBR, and NR-IIR, by ultrasonic techniques. The study also covers theoretical calculations of the heat of mixing in these rubber blends.

EXPERIMENTAL

Materials

The following blends have been prepared:

1. NR (Natural rubber RSSI) + BR (Cis I,4 polybutadiene rubber),
2. NR (Natural rubber RSSI) + NBR (Acrylonitrile butadiene rubber),
3. NR (Natural rubber RSSI) + IIR (Isobutylene Isoprene rubber).

The rubber blends were prepared by masticating, on two roller mills, the two component rubbers separately for 20 min. Requisite proportions of the two rubbers were then dissolved in toluene and were mixed thoroughly. Two blend concentrations were prepared (2% and 10%). Different composition ratios were then prepared according to the following percentages:

Natural Rubber	0	10	20	30	40	50	60	70	80	90	100
Synthetic Rubber	100	90	80	70	60	50	40	30	20	10	0

Measurements

1. Density (φ): The densities of dilute solutions (2%) were measured by pycnometer, and

those of concentrated solutions (10%) by specific gravity bottle. All density measurements were measured accurately to four decimal places.

2. Compressional ultrasonic velocity (C): The compressional velocity measurements were performed on solutions using an echo pulse technique. The time elapsed between two successive echoes was accurately measured using a double beam oscilloscope (Phillips PM 3055). Measurements were carried out at 6 MHz; velocity measurements were accurate to $\pm 0.5\%$.
3. Longitudinal ultrasonic absorption (α): An Ultrasonic Flow Detector USM2 (Krautkramer, W. Germany) was used in these measurements. This apparatus is capable of producing high-frequency oscillations in the frequency range of 0.5–12 MHz, and the apparatus usually operates with the same transducer as transmitter and receiver. The solution was contained in a double-walled glass cell where the transducer formed its base. Thermostated water was circulated from an ultrathermostat with thermal stability of $\pm 0.25^\circ\text{C}$. The height of the blend solution in the cell (d) was measured accurately. Also, the heights (amplitude) of two or three echoes, which resulted from applying an ultrasonic pulse to the solution under investigation, were measured. The absorption of longitudinal ultrasonic waves was then calculated from the equation, $\alpha = 10 \left(\log \left(\frac{A_0}{A_1} \right) / 2d \right)$, A_0 is the amplitude of the pulse at $d = 0$, and A_1 is the amplitude of the reflected echo. All measurements were performed at 6 MHz and at a constant temperature of $25^\circ \pm 0.5$.
4. Compressibility (β): The adiabatic compressibility β of the rubber blend solution was calculated by the equation of Newton and Laplace,¹⁵ $\beta = 1/C^2\varphi$, where C is the compression ultrasonic velocity, and φ is the density of the blend solution.

RESULTS AND DISCUSSION

It is of great interest to investigate the behavior of the compressional ultrasonic velocity and longitudinal ultrasonic absorption in a number of rubber blend solutions in order to establish the general

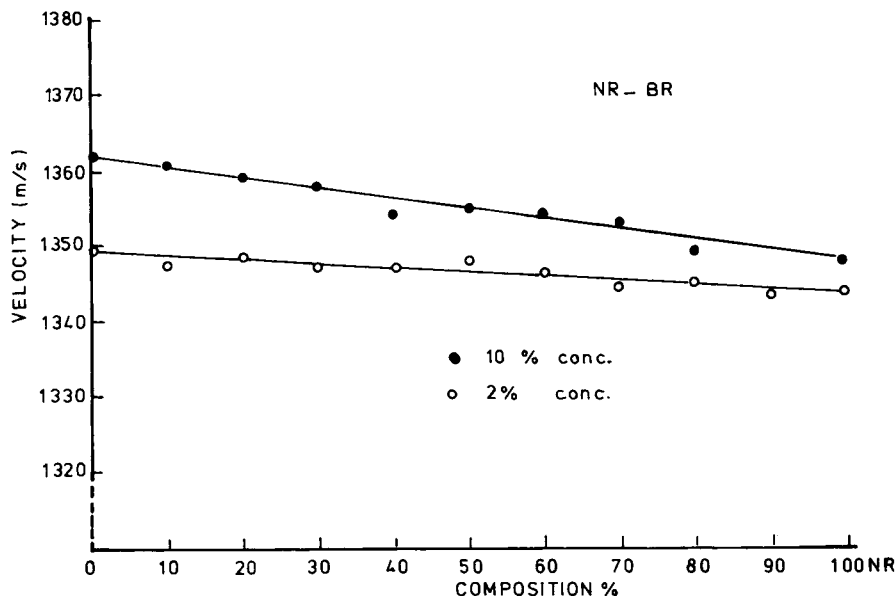


Figure 1 Ultrasonic velocity vs. NR composition in NR-BR blend solution.

shape of the curves. The compatibility, or the affinity of natural rubber, to be mixed with different types of rubber is determined according to the linearity behavior of these curves.

NR-BR Blend System

Figure 1 describes the compressional ultrasonic velocity measurements in the NR-BR blend solutions

vs. the composition of blend, that is, the weight percentage of NR. The figure shows a linear relation that is represented by straight lines characterizing a compatible rubber blend. The linearity of this relation confirms the complete solubility of these two rubbers in each other in all proportions.

The relation between longitudinal ultrasonic absorption and composition of this blend system is shown in Figure 2. The figure shows only one max-

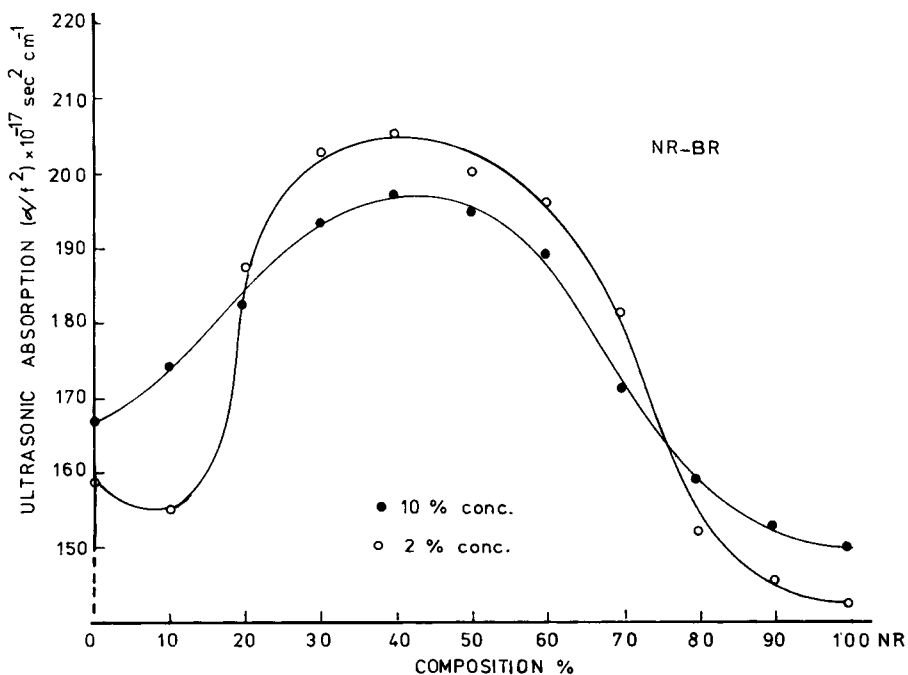


Figure 2 Ultrasonic absorption vs. NR composition in NR-BR blend solution.

imum and one minimum at about 40% and 80%, respectively. The presence of one maximum and one minimum reflects the mutual solubility of component rubbers and the formation of a true solution from them. This behavior indicates that NR and BR macromolecules in the mixture are packed in a more orderly fashion than they are in individual components.

The heat of mixing of the NR-BR blend has been calculated by applying the equation, given by Schneier,¹³ over the entire range of compositions; the variation of the calculated heat of mixing with composition is shown in Figure 3. The NR-BR blend is supposed to be a compatible blend since the calculated heats of mixing at all compositions are found to be in the range of 5.43×10^{-3} – 1.45×10^{-3} cal/mol. This range is well below 10×10^{-3} cal/mol, the figure considered to be the upper limit of compatibility. These thermodynamic calculations indicate a significant degree of miscibility in the NR and BR blend.

Figure 4 depicts the variation of the adiabatic compressibility with the composition of the NR-BR blend system. A linear relationship is shown. This linear behavior suggests a compatible NR-BR blend.

NR-NBR Blend System

The variation of compressional ultrasonic velocity with NR-NBR solution blend composition is plotted and is shown in Figure 5. The curves are nonlinear and of an *S* type, which clearly indicates a region of

phase inversion. The nonlinearity is more pronounced in the high concentration blend (10%). Departure from linearity has been indicated in the sonic velocity measurements in semicompatible blends by Hourston and Hughes.³ There may be an interaction between NR-NBR macromolecules on the mill during mastication through the free radicals interaction.

The relation between longitudinal ultrasonic absorption and blend composition is shown in Figure 6. Two maxima and two minima are observed in the curve. The appearance of these maxima and minima suggests a region of distinct phase reversal at intermediate composition. A shape of relation such as this can, therefore, characterize a semicompatible blend.

The above stated semicompatible nature of NR-NBR blend is further confirmed by calculations of the heat of mixing. Figure 7 shows the calculated heat of mixing against the blend composition. The values of heat of mixing lie in a range between 19.4×10^{-3} and 5.2×10^{-3} cal/mol, which is higher than the upper limit value of compatibility.

Figure 8 shows the influence of blend composition on the adiabatic compressibility. The shape of the curve is curvilinear, which is characteristic of semicompatible rubber blends.

NR-IIR Blend System

Figure 9 shows the variation of ultrasonic velocity with composition of NR-IIR blends. The figure de-

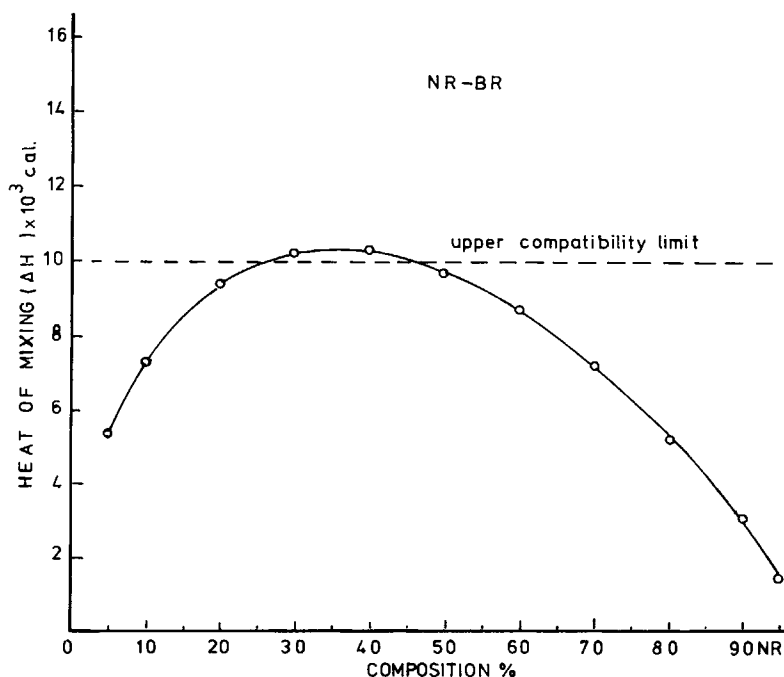


Figure 3 Heat of mixing as a function of NR composition in NR-BR blend solution.

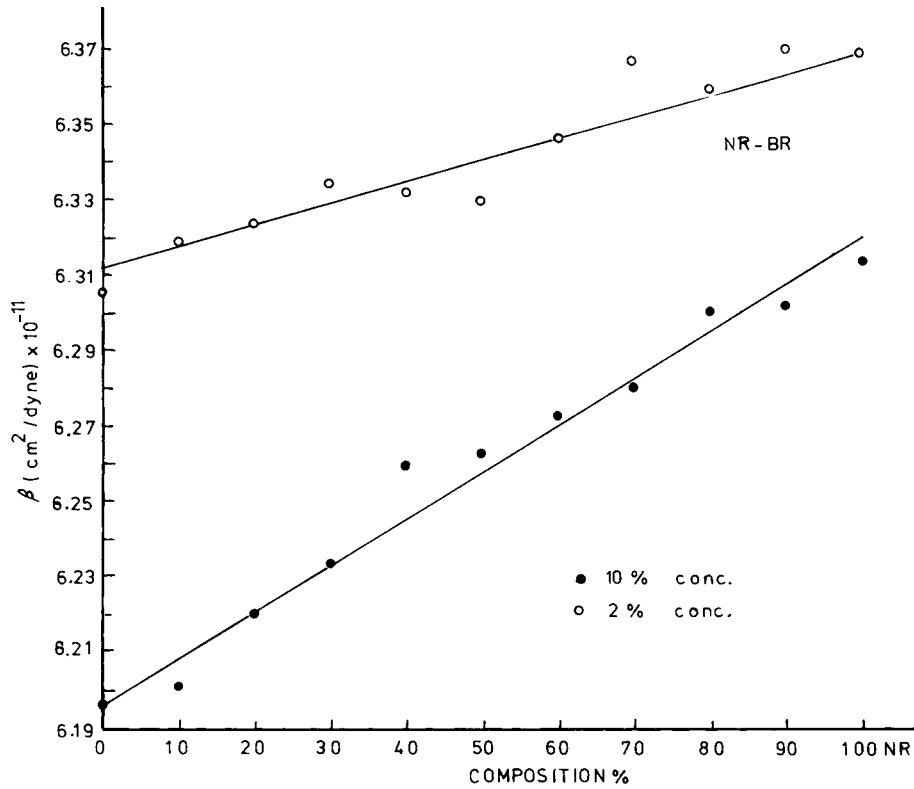


Figure 4 Variation of adiabatic compressibility with the composition of NR-BR blend solution.

picts a curvilinear behavior, showing the multiphase nature of this system, and clearly indicating the region of phase separation. On the basis of the linear and nonlinear portions of the curve, the whole curve may be divided into three distinct regions of IIR composition; 0-30, 30-70, and 70-100%. The middle

region shows almost no change in ultrasonic velocity. The region between 0-30%, by weight of IIR, is an NR domain-dominated region, showing a decrease in ultrasonic velocity. In the third region, above 70% of IIR, there exists an increase in ultrasonic velocity with curvature, which reveals the weak two phase

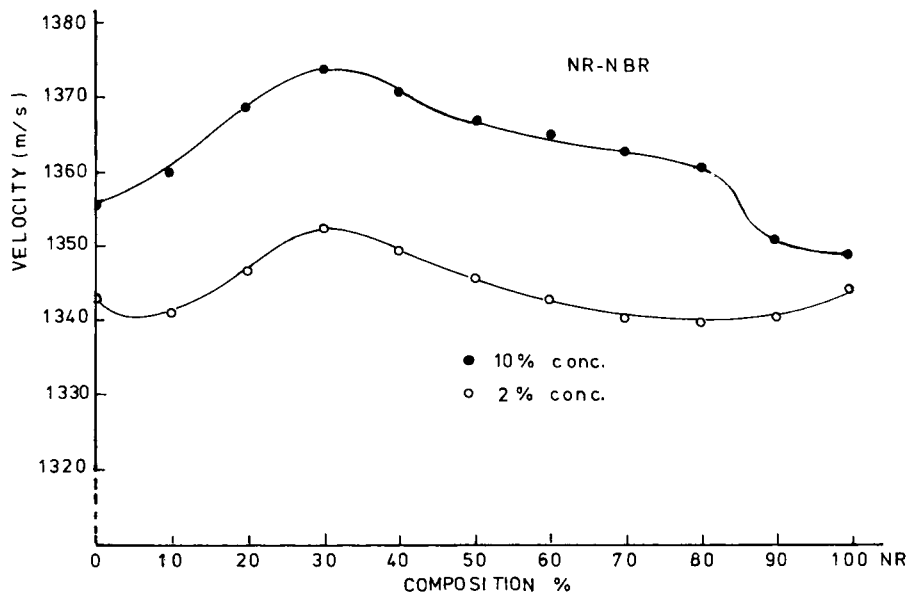


Figure 5 Ultrasonic velocity vs. NR composition in NR-BR blend solution.

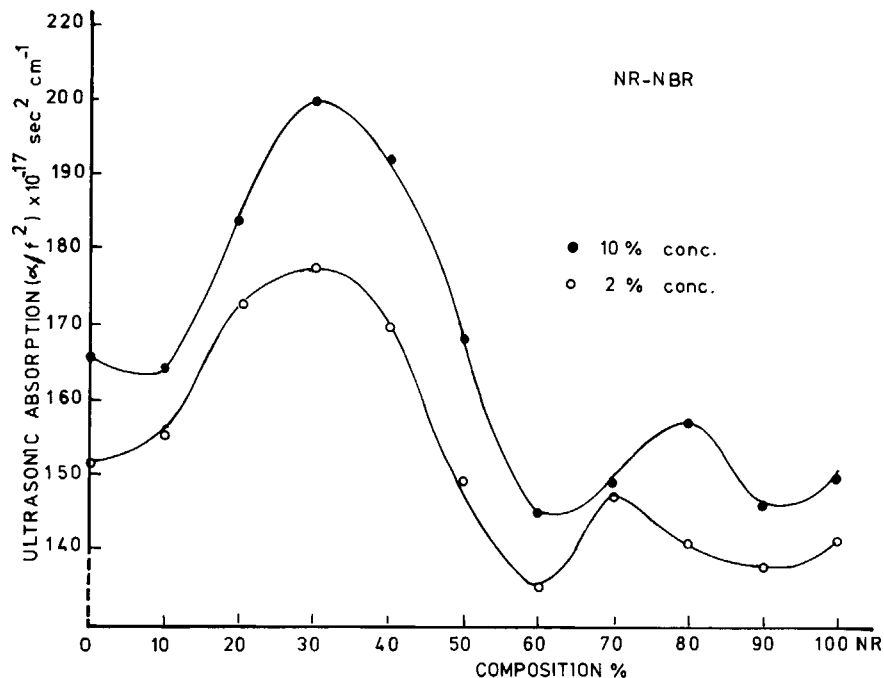


Figure 6 Ultrasonic absorption vs. NR composition in NR-NBR blend solution.

interaction of the blend in this region. This phase inversion may be attributed to the association of macromolecules, which indicates the aggregation of rubber domains in rubber-rubber solvent system.¹⁶

Figure 10 shows the relation between longitudinal

ultrasonic absorption and weight percentage composition of the NR-IIR blend. Two maxima and two minima are clearly seen, indicating that the blend of natural rubber on butyl rubber behaves as two phases.

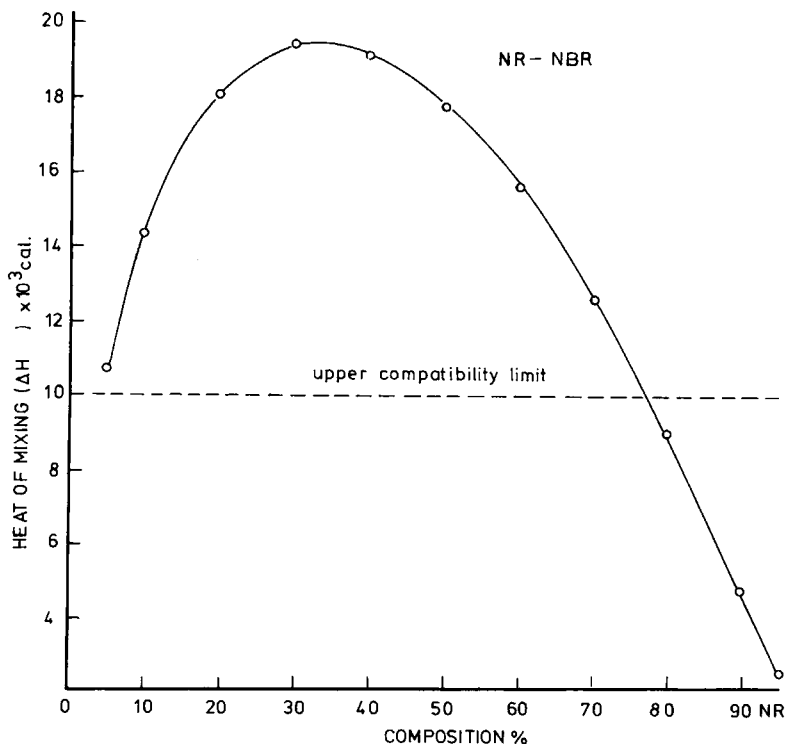


Figure 7 Heat of mixing as a function of NR composition in NR-NBR blend solution.

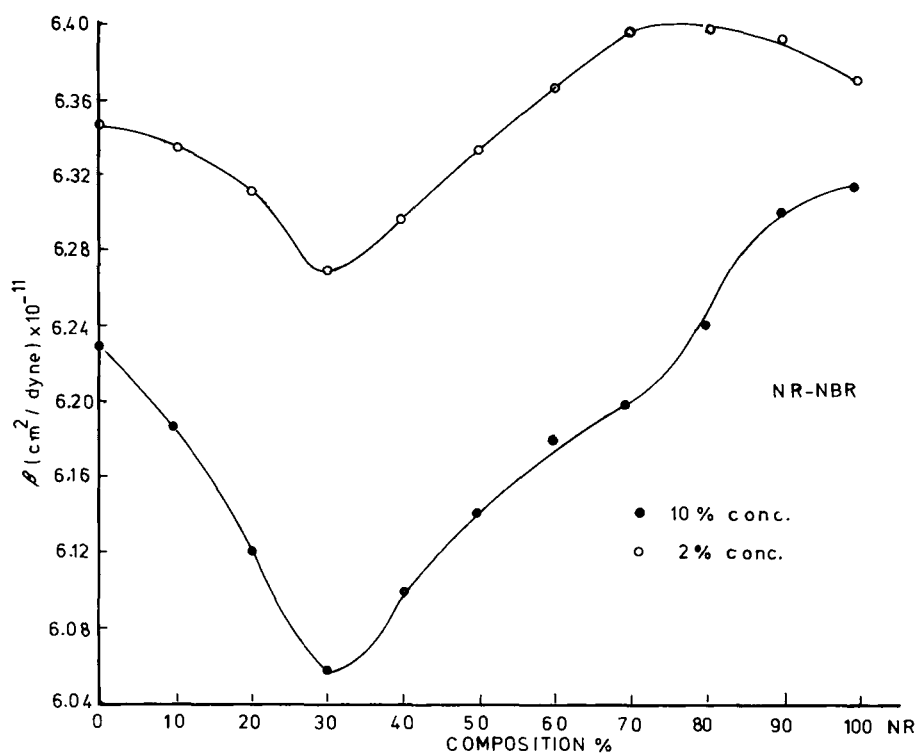


Figure 8 Variation of adiabatic compressibility with the composition of NR-NBR blend solution.

Figure 11 gives the relation between the calculated heat of mixing of NR-IIR blend and the composition of the blend. Values of ΔH range between 17.0×10^{-3} cal/mol and 8.9×10^{-3} cal/mol. These positive values imply that macromolecules in the mixture are in a more disordered state than they

are in a pure unstable mixture. The incompatibility of this blend may be a result of the difference in the nature of the macromolecules.

Figure 12 gives the relation between calculated adiabatic compressibility and composition of the blend. The shape of the curve is similar to that of

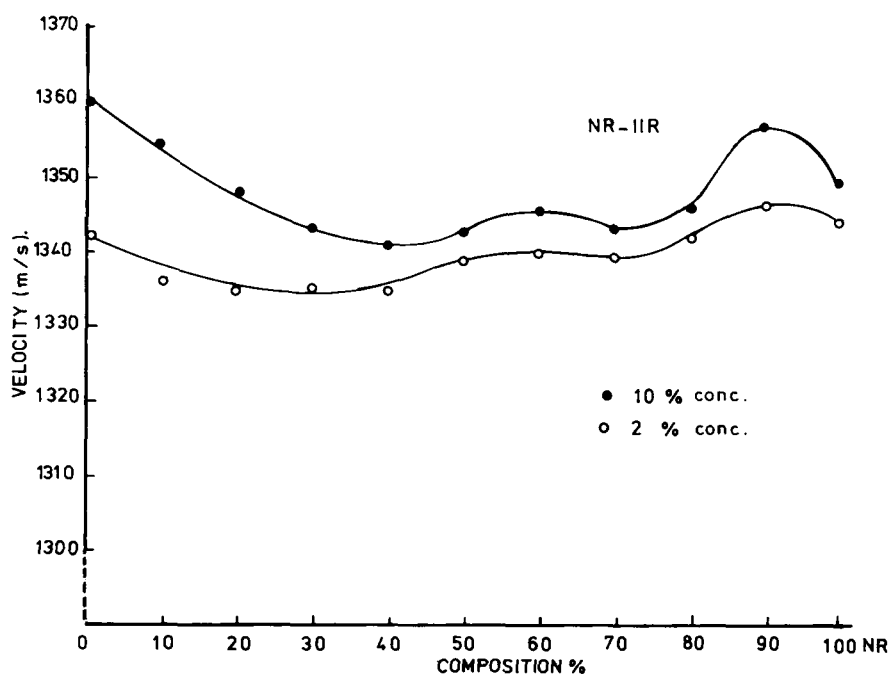


Figure 9 Ultrasonic velocity vs. NR composition with NR-IIR blend solution.

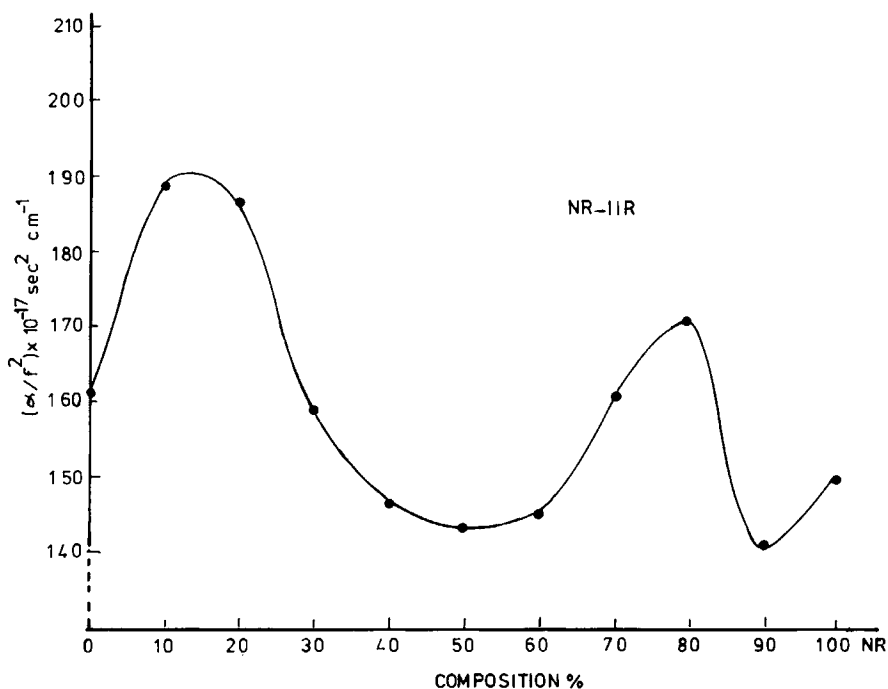


Figure 10 Ultrasonic absorption vs. NR composition with NR-IIR blend solution.

the NR-NBR blend, which characterizes a noncompatible blend.

The present investigation indicates clearly that the compatibility of rubber blends may be studied

in solutions by the ultrasonic absorption technique. It may be, therefore, concluded that the simple measurements of longitudinal ultrasonic absorption and compressional ultrasonic velocity provide a clue to

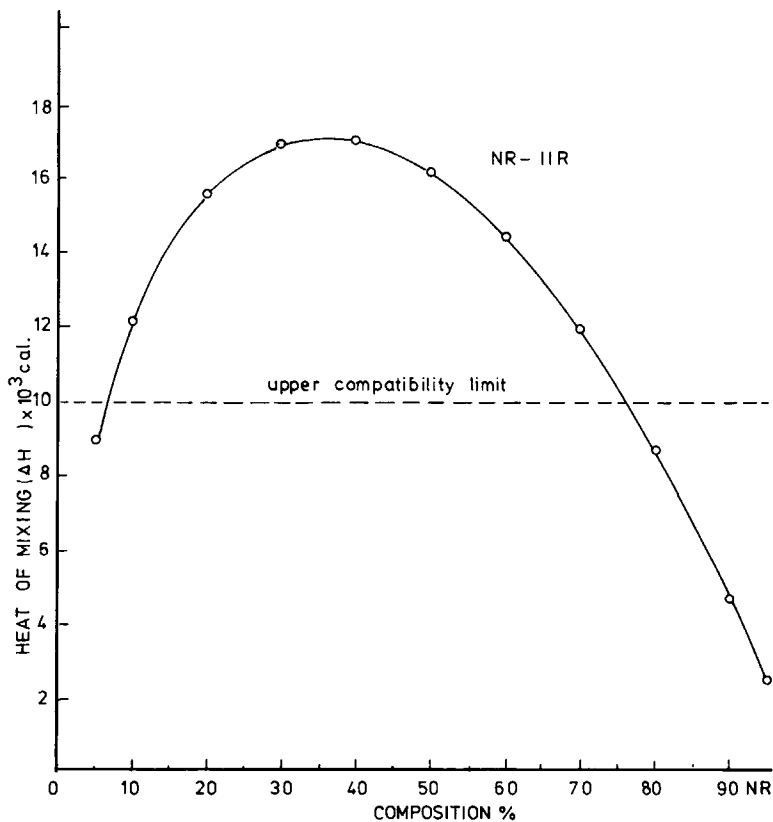


Figure 11 Heat of mixing as a function of NR composition in NR-IIR blend solution.

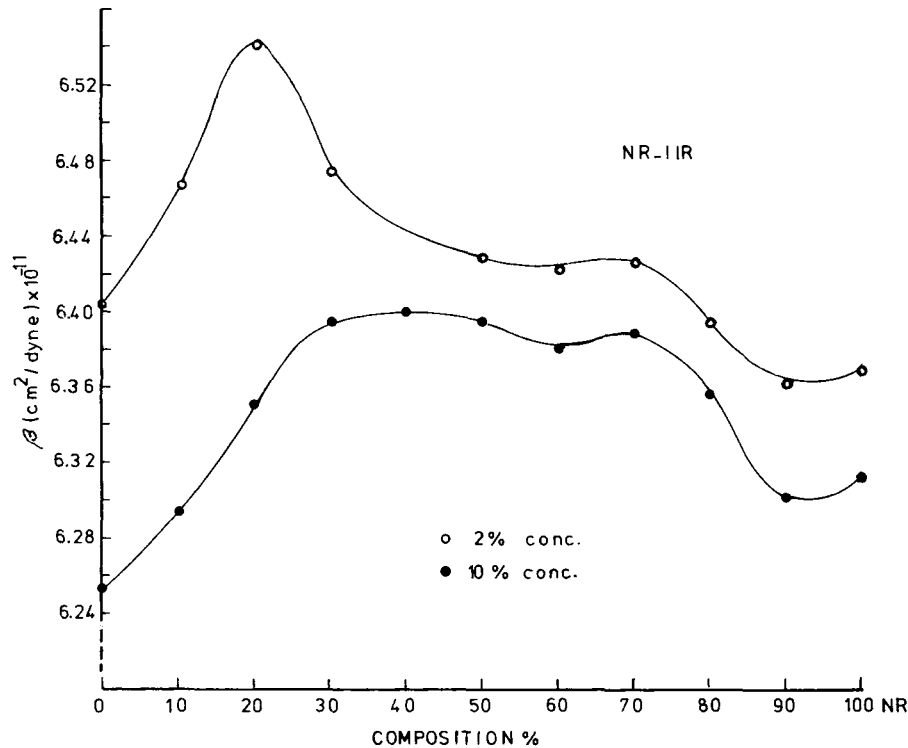


Figure 12 Variation of adiabatic compressibility with the composition of NR-IIR blend solution.

the compatibility of rubber blends, which clues are generally obtained by the sophisticated, rigorous, and expensive techniques of thermal, dynamic, and electron microscopic analysis.

The compatibility of NR-BR blends, the semi-compatibility of NR-NBR blends, and the incompatibility of NR-IIR blends are in agreement with the findings published by Yehia et al.^{17,18} which were based upon viscometric and dynamic modulus measurements.

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