

Ultrasonic Investigation on Compatibility of PVC-Modified Liquid Natural Rubber Blends

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Received 26 December 1996; accepted 11 September 1997

ABSTRACT: The extent of compatibility of the blend solutions poly(vinyl chloride)–liquid natural blends (PVC–LNR), PVC–expodized LNR-20 (PVC–ELNR-20), and PVC–ELNR-50 has been studied using an ultrasonic technique. The variation of ultrasonic velocity with composition is nonlinear in the case of blends of PVC–LNR and PVC–ELNR-20, showing incompatibility. The ultrasonic velocity versus composition plot for PVC–ELNR-50 showed linear behavior showing compatibility. The above behavior was confirmed by heat of mixing calculations as well as ultrasonic attenuation measurements. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 785–790, 1998

Key words: liquid natural rubber; poly(vinyl chloride); ultrasonic measurements

INTRODUCTION

Blending as a route to enhance specific material properties has been widely accepted and exploited in a variety of commercial products. For a blend system to show optimum properties, compatibility of the components to a desired extent is essential. Many experimental and theoretical methods have been used to study polymer compatibility.¹ The viscometric measurements, glass transition measurements by differential scanning calorimetry (DSC) and dynamic mechanical response, electron microscopy, and infrared (IR) spectroscopy are some of the experimental methods adopted for the purpose.

Several reports have appeared in literature^{2–9} regarding the use of ultrasonic velocity measurements in the study of extent of compatibility in highly viscous or solid forms of polymer blends. Detailed ultrasonic velocity measurements showed that in compatible blends the ultrasonic velocity varies linearly with composition while it deviates from linearity in incompatible blends. The ultra-

sonic attenuation increases with phase separation between the constituent polymers.¹⁰ Also, it was observed that inadequate adhesion between the matrix and dispersed phase leads to high values of attenuation coefficient.¹¹

Among theoretical methods, measurement of heat of mixing provides an indication regarding the extent of compatibility. Mixing of polymers with each other is usually an endothermic process. Systems that separate into phases are characterized by positive values for heat of mixing while compatible blends are characterized by negative values.¹²

Schneier¹³ suggested an equation for heat of mixing of two-component blend systems, either compatible or incompatible, which is given in the following form:

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

where \bar{x} , ρ , and M are the weight fractions of polymers, density, and monomer unit molecular

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Journal of Applied Polymer Science, Vol. 69, 785–790 (1998)
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weight, respectively, and δ is the solubility parameter of the polymer. Results obtained by applying this equation gave an approximate measure of polymer compatibility. Singh and Singh⁵ calculated the heat of mixing of some compatible blends using Schneier equation. They reported that the heat of mixing with values below 10×10^{-3} cal/mol, which is considered to be the upper limit of compatibility, indicates compatibility.

In the present article, we report the experimental ultrasonic study of the compatibility of polyblends of poly(vinyl chloride–liquid natural rubber (PVC–LNR), poly(vinyl chloride–epoxidized liquid natural rubber of different mol % of epoxidation (PVC–ELNR-*X*), where *X* represents the mol % of epoxidation) with a view to establish the effect of oxirane content of these diene polymers on the compatibility with PVC. The study also covers the theoretical calculation of heat of mixing values of these blends based on Schneier's equation.

EXPERIMENTAL

Materials

PVC (*K*-value 65, \bar{M}_n 55,000, density 1.37) was obtained from M/s Chemicals and Plastics Ltd., Madras. Liquid natural rubber (\bar{M}_v 5,000) was made by the depolymerization of NR.¹⁴ Epoxidized LNR of 20 mol % epoxidation (ELNR-20) and 50 mol % epoxidation (ELNR-50) have been prepared by the epoxidation of LNR in our laboratory.¹⁵ Hydrogen peroxide, acetic acid, methanol, and 2-butanone were of reagent grade and supplied by BDH, Mumbai.

Procedure

*Preparation of Liquid Natural Rubber*¹⁴

A 7% solution of natural rubber (100 g) in toluene were prepared in a 2-L flask made up of borosil glass, and it was mixed with 100 mL of hydrogen peroxide. This was partly homogenized with the addition of 50 mL of methanol. The solution was then placed in sunlight and irradiated with stirring for 50 h. After the irradiation, the organic layer was separated, and the solvent was removed by distillation. The LNR was then precipitated by the addition of methanol and dried in vacuum.

Preparation of Epoxidized Liquid Natural Rubber

ELNR-50. LNR (25 g) dissolved in 166 mL of toluene to obtain a 15% solution was stirred at 50°C for 10 h with 1.1 mol of H₂O₂ and 0.35 mol of glacial acetic acid. At the end of the reaction, the product was isolated by precipitating from methanol and dried in vacuum. It was then characterized by titrimetric, IR, nuclear magnetic resonance (NMR), and DSC techniques.

ELNR-20. LNR (25 g) dissolved in 166 mL of toluene to obtain a 15% solution was stirred at 50°C for 3 h with 0.55 mol of H₂O₂ and 0.35 mol of glacial acetic acid. Isolation and characterization were done as above.

Preparation of Blends

Three series of blends have been prepared by blending PVC with (1) LNR, (2) ELNR-20, and (3) ELNR-50. Each series of blend has been reported in the composition ratios, as shown in Table I. Blending has been done in solution. The components were first dissolved in 2-butanone. The two solutions were then thoroughly mixed to get a homogeneous solution.

Measurements

Compressional Ultrasonic Velocity

The compressional ultrasonic velocity measurements were performed on solution by ultrasonic pulse echo overlap technique using Matec Model 7700 pulse modulator and receiver Model 110 high-resolution frequency source and Model 122B decade divider and dual delay generator. The measurements were carried out at 6 MHz.

Longitudinal Ultrasonic Absorption (α)

The solution was placed in a double-walled glass cell, where the transducer formed its base. Thermostated water was circulated from an ultrathermostat with thermal stability of $\pm 0.5^\circ\text{C}$. The height of the blend solution in the cell (*d*) was measured accurately. Also, the heights (amplitude) of two echoes, which resulted from applying an ultrasonic pulse to the solution under study, were measured. The absorption of longitudinal ultrasonic waves was then calculated using the following equation:

Table I Composition of Blends

PVC (%)	0	20	30	40	50	60	70	80	100
LNR or ELNR-20 or ELNR-50 (%)	100	80	70	60	50	40	30	20	0

$$\alpha = \frac{20 \log h_1/h_2}{2d}$$

where h_1 and h_2 are the heights or amplitudes of the successive echoes. All the measurements were performed at 6 MHz at a constant temperature of $28 \pm 0.5^\circ\text{C}$.

Heat of Mixing

The heat of mixing was calculated using the equation suggested by Schneier.¹³

The Adiabatic Compressibility (β)

The adiabatic compressibility of the blend system was calculated by applying the equation of Newton and Laplace, which is given as $\beta = 1/C^2\rho$, where C is the longitudinal ultrasonic velocity, and ρ is the density of the solution.

RESULTS AND DISCUSSION

LNR and the epoxidized products of 20 and 50 mol % epoxy groups have been mixed in solution separately with PVC in different compositions. These blends were subjected to detailed ultrasonic analysis, and the results were presented below.

PVC-LNR Blends

The ultrasonic velocity has been measured for PVC-LNR systems of varying compositions at 2 and 5% concentrations. Figure 1 shows the plot of ultrasonic velocity versus composition for these blends. It is observed that the plots deviate from linearity. This type of behavior is characteristic of an incompatible blend. The variation of ultrasonic attenuation with composition is shown in Figure 2. Two maxima at 20 and 70% and two minima at 30 and 60 are clearly seen. This, again indicates that the blends are incompatible and they still have different phases. The incompatibility is also predicted by the adiabatic compressibility-composition plot, which shows a nonlinear behavior (Fig. 3).

The above results are in accordance with the theoretical prediction of compatibility based on heat of mixing values. The variation of calculated heat of mixing value with composition (Fig. 4) showed that the ΔH_m values are all above the upper limit of compatibility (that is, 10×10^{-3} cal/mol), showing incompatibility. The incompatibility of the blend systems is explained on the basis of lack of interaction between PVC and the LNR.

PVC-ELNR-20 Blends

Epoxidation is a simple technique of modification of diene polymers. LNR has been subjected to epoxidation, thereby increasing its polarity. Thus, ELNR of 20 mol % epoxidation (ELNR-20) has been prepared using acetic acid and hydrogen peroxide, and this material was then blended with PVC in different compositions. The compatibility behavior of these blends in solution has been followed by ultrasonic technique.

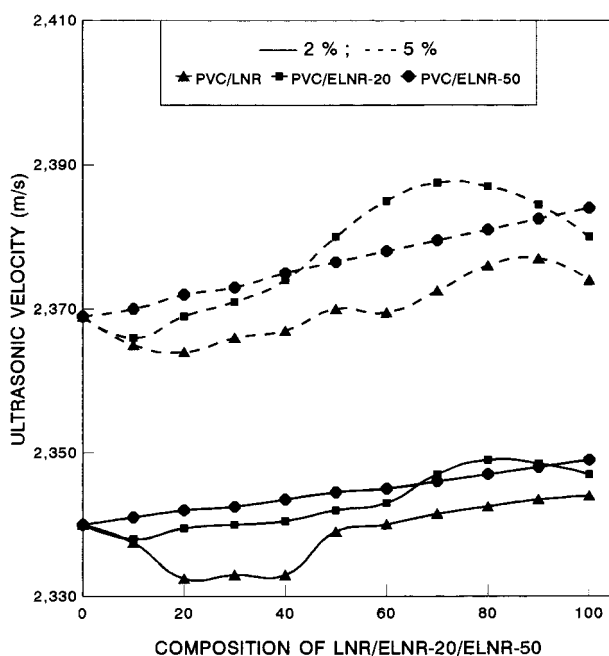


Figure 1 Ultrasonic velocity versus composition of LNR-ELNR-20-ELNR-50.

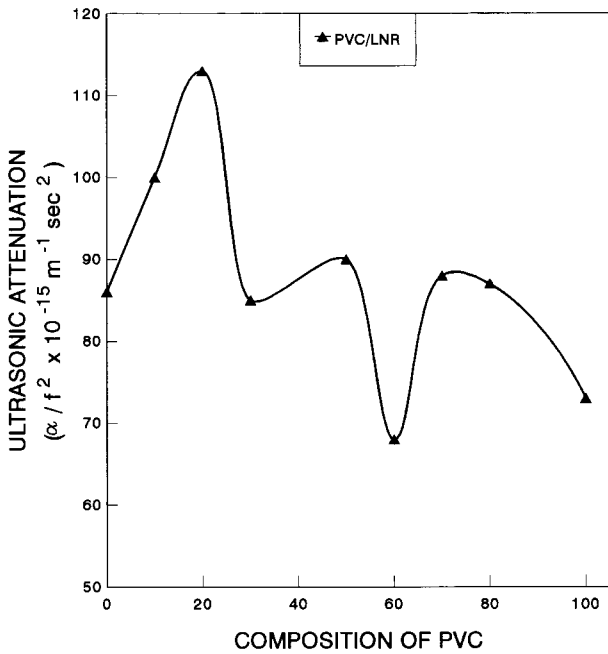


Figure 2 Ultrasonic attenuation versus composition of PVC for PVC-LNR blends.

The plot of ultrasonic velocity versus composition for PVC-ELNR-20 blends is shown in Figure 1. It is found that the plot deviates from linearity. The deviation is more pronounced at higher ELNR-20 content. The S-type behavior of the

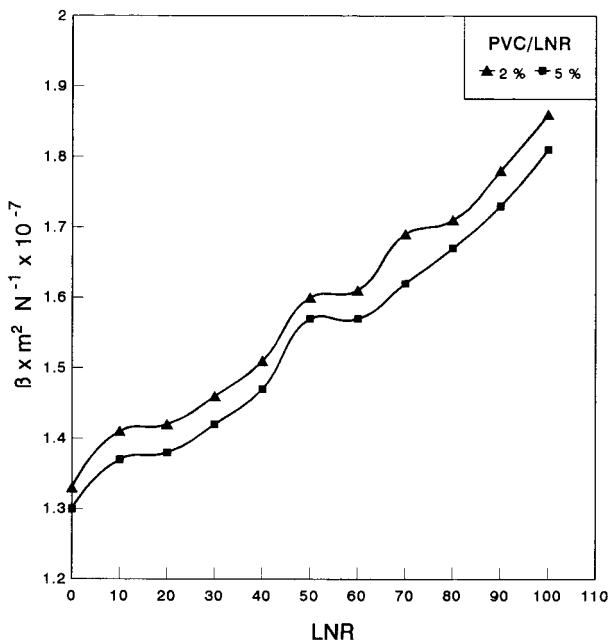


Figure 3 Adiabatic compressibility versus composition of LNR for PVC-LNR blends.

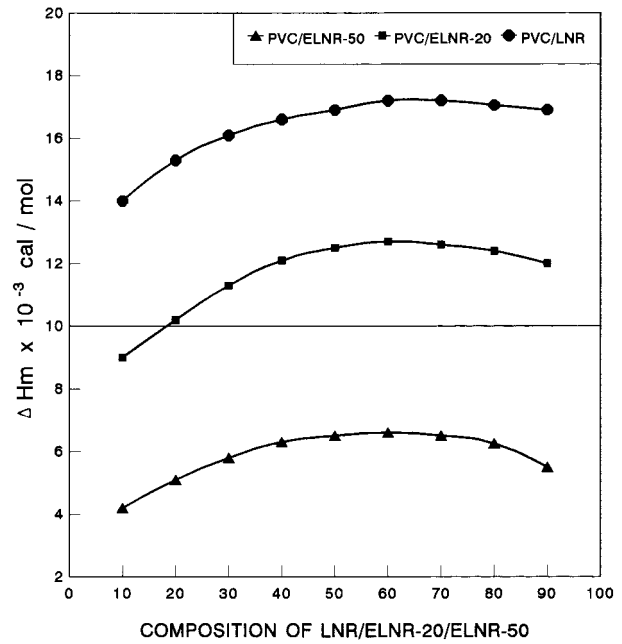


Figure 4 ΔH_m versus composition of PVC for PVC-LNR, PVC-ELNR-20, and PVC-ELNR-50 blends.

curve indicates two-phase formation with reversal of phases at intermediate compositions, and, hence, the system is incompatible.

The variation of ultrasonic attenuation with composition (Fig. 5) shows two maxima at 50 and

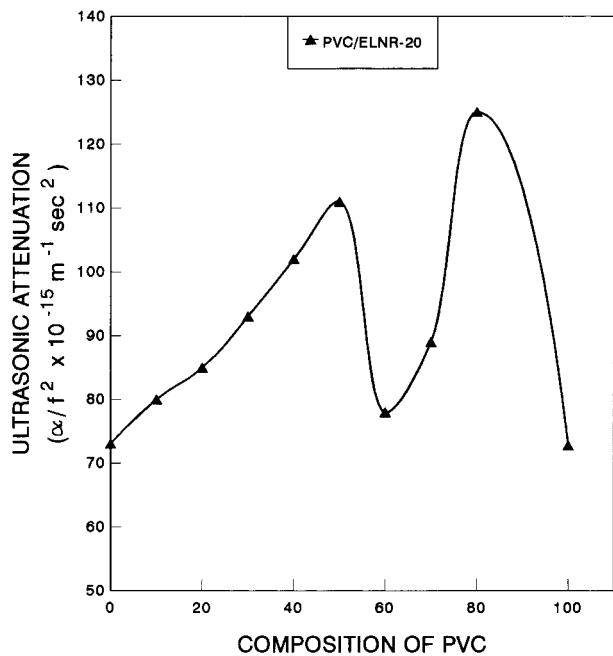


Figure 5 Ultrasonic attenuation versus composition of PVC for PVC-ELNR-20 blends.

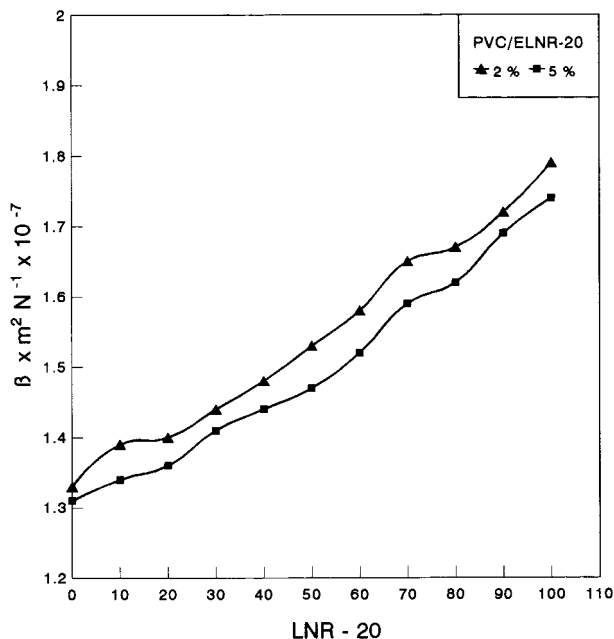


Figure 6 Adiabatic compressibility versus composition of ELNR-20 for PVC-ELNR-20 blends.

80% PVC. The presence of more than one maximum indicates phase inversion with composition, and, hence, the blend is incompatible.

The plot of adiabatic compressibility versus composition (Fig. 6) shows a nonlinear behavior, suggesting phase separation. The immiscibility is due to insufficient interaction between the component polymers. The calculated heat of mixing values versus composition (Fig. 4) showed that the ΔH_m value of 90% of PVC lie below the upper range of compatibility, and the rest of the values lie above this limit, showing incompatibility of the two components.

PVC-ELNR-50

With a view to increase the compatibility of the diene polymer with PVC, polar oxirane groups have been introduced into the diene backbone to a greater extent, and, consequently, ELNR-50 has been prepared, and compatibility is followed by the ultrasonic technique. The plots of ultrasonic velocity versus composition for PVC-ELNR-50 blends (Fig. 1) showed a linear relationship characteristic of a compatible blend.

The relation between ultrasonic attenuation and composition (Fig. 7) showed only one maximum at about (40%) and one minimum at about 60% of PVC. The presence of one maximum and one minimum reflects the compatibility of the two

components. The molecular origin of compatibility is attributed to polar and/or donor-acceptor interaction among the acidic hydrogen atom of PVC and the oxirane group.

The heat of mixing values of PVC-ELNR-50 blend system has been calculated over the entire range of composition by applying the equations given by Schneier; the variation of calculated heat of mixing values versus composition (Fig. 4) showed that the ΔH_m values lie well below the upper limit of compatibility (that is, 10×10^{-3} cal/mol), showing compatibility. The variation of adiabatic compressibility with composition of PVC-ELNR-50 blends (Fig. 8) showed a linear relationship. This behavior also supports that the diene polymer carrying a sufficient number of oxirane groups is compatible with PVC.

All the above results are fully supported by our previous studies on compatibility based on a viscometric technique.¹⁶

CONCLUSION

The present investigation shows that ultrasonic measurements are highly useful in assessing the compatibility of the blend systems comprising of PVC and LNR or modified LNR. The basically incompatible blends of PVC with LNR are made compatible by incorporating oxirane groups into

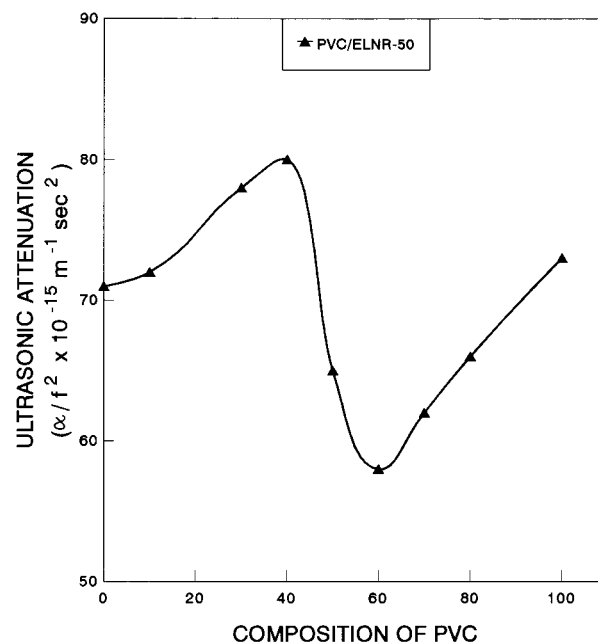


Figure 7 Ultrasonic attenuation versus composition of PVC for PVC-ELNR-50 blends.

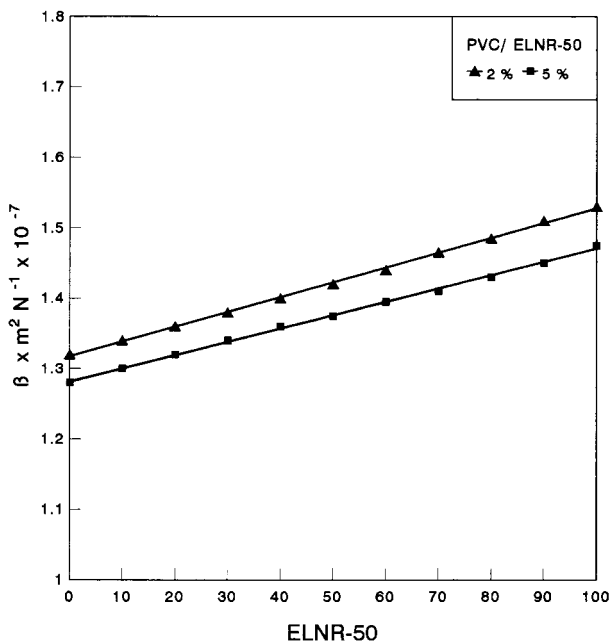


Figure 8 Adiabatic compressibility versus composition of ELNR-50 for PVC-ELNR-50 blends.

the NR chain backbone. It is observed that as the oxirane content increases, the miscibility also increases due to enhanced interaction between the two kinds of molecules. This is corroborated by the calculated heat of mixing values of the various blend systems.

The authors thank Dr. M.A. Ittyachen, Head, School of Pure and Applied Physics, Mahatma Gandhi University, for extending the ultrasonic facility.

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