

Improvement of the Compatibility of Natural Rubber/Ethylene–Propylene Diene Monomer Rubber Blends via Natural Rubber Epoxidation

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Received 6 December 2001; accepted 26 March 2002

ABSTRACT: The longitudinal ultrasonic velocity, longitudinal ultrasonic absorption (attenuation coefficient), glass-transition temperature, and Mooney viscosity for epoxidized natural rubber/ethylene–propylene diene monomer blends were measured. The variation of the longitudinal ultrasonic velocity with the blend ratios was linear, indicat-

ing a compatible system in comparison with the same system without epoxidation (natural rubber/ethylene–propylene diene monomer), which was incompatible. Also, the behavior was confirmed by heat of mixing calculations as well as Mooney viscosity measurements. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2816–2819, 2002

INTRODUCTION

The ever increasing demand for polymer blends spells the need for monitoring the blend properties, such as compatibility and morphology, that dictate most of the physical properties of the end product. The chemical or physical blending of two or more polymers is the simplest means of obtaining a variety of physical and chemical properties from the constituent polymers.

The concept of physically blending two or more polymers to obtain a new product has not been developed as fully as the chemical approach to blending. The physical approach is now attracting widespread interest. Methods of determining the degree of compatibility have been reported, both theoretically and experimentally.^{1–3} Among these methods are the glass-transition temperature (T_g), IR, and electron microscopy.¹

Many researchers^{4–11} have reported that ultrasonic velocity measurements might show the extent of compatibility in highly viscous or solid forms of polymer blends. A new approach to the study of polymer blend compatibility with ultrasonic attenuation was investigated by Arman and coworkers.^{12–14} They reported that poor adhesion between two polymers led to high values of the attenuation coefficient. Singh and coworkers^{5–8} studied the ultrasonic velocity for compatible, semicompatible, and incompatible polymeric blends, and they found that in compatible blends, the ultrasonic velocity varied linearly with composition.

In contrast, the ultrasonic velocity deviated from linearity, depending on the degree of compatibilization.

It is known that the miscibility of any mixture is governed by the free energy of mixing (ΔG_m):¹⁵

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (1)$$

where ΔH_m is the enthalpy change on mixing, ΔS_m is the entropy change on mixing, and T is the temperature. A criterion for polymer miscibility (compatibility) based on fundamental thermodynamics states that ΔG_m should be negative. Schneier¹⁶ calculated the heat of mixing (ΔH) for a number of compatible and incompatible blends and suggested an equation based on the formulation of Gee.¹⁷

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

where \bar{X} , ρ , and M are the weight fraction of the polymer, the density of the monomer unit, and the molecular weight, respectively. δ is the solubility parameter of the polymer. However, Singh and Singh⁶ calculated ΔH for some compatible blends with the Schneier equation.¹⁶ They reported values of ΔH below a figure considered to be the upper limit of compatibility: 4.185×10^{-2} J/mol.

Because ultrasonic and Mooney viscometry studies on the compatibility of epoxidized natural rubber (ENR)/ethylene–propylene diene monomer (EPDM) rubber blends have not received enough attention and clear investigation, we decided to use both ultrasonic

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velocity and Mooney viscometry techniques to investigate the degree of compatibility between ENR and EPDM rubber. Also, we aimed to improve the degree of compatibility between natural rubber (NR) and EPDM rubber through NR epoxidation.

EXPERIMENTAL

Materials

NR (SMR-100) was a product of Guthrie Corp., Biang City, Malaysia. EPDM rubber (Vistalon 6505) was a product of Esso Chimie, Germany. The epoxidation of NR latex was carried out to 30 mol % according to ref. 18. Glacial acetic acid was added to the dough of the NR in benzene in a 1:10 ratio in a three-necked, conical flask under a heating temperature of 353 K. Then, hydrogen peroxide was added dropwise within 2 h, as described in ref. 18, and the epoxide content was determined by IR according to a published method.¹⁹

NR/EPDM rubber blends

NR/EPDM rubber blends were prepared on a two-roll mill. Different blend ratios were prepared according to the following percentages: 0, 25, 50, 75, and 100 ENR and 100, 75, 50, 25, and 0 EPDM.

Ultrasonic techniques

Longitudinal ultrasonic velocity

The ultrasonic wave velocity (ν) as a function of the time interval Δt between two echos on the screen of a double-beam oscilloscope (Phillips PM 3055, Enschede, The Netherlands) was obtained from the following relation:

$$\nu = 2l / \Delta t \quad (3)$$

where l is the thickness of the rubber blend specimen. All velocity measurements were carried out at 2-MHz frequencies at room temperature. The measurements were repeated several times to check the reproducibility of the data. The percentage of error for the velocity measurements of each sample was 0.01%.

Longitudinal ultrasonic absorption (attenuation)

Measurements of the change in the ultrasonic absorption with the blend composition were made by the measurement of the change in the height of a particular echo as observed on the screen of the flaw detector. The general equation for obtaining the ultrasonic attenuation (α) is as follows:

$$\alpha = (20/2l) \log A_0/A_1 \quad (4)$$

where A_0 and A_1 are the heights of two successive echos.

Compressibility

The adiabatic compressibility of the rubber blends (β) was calculated with the following equation:²⁰

$$\beta = 1 / \nu^2 \rho \quad (5)$$

where ρ is the density of the rubber blend. The densities of the rubber blend material were measured at room temperature (308 K) by the standard displacement method, with toluene as an immersion liquid. The following formula was used:

$$\rho = \rho_0 \frac{(W - W_t)}{(W - W_t) - (W_1 - W_{1t})}$$

where ρ_0 is the density of toluene at 398 K; W and W_1 are the weights of the samples in air and toluene, respectively; and W_t and W_{1t} are the weights of the suspended thread (0.01 mm in diameter) in air and toluene, respectively. A Mettler H72 (Zurich, Switzerland) sensitive balance was used in these measurements. The accuracy of the measurements was found to be less than 0.001%.

Mooney viscometry

The Mooney viscosities of different blend ratios were measured with a Mooney viscometer (Alpha Technologies MV 2000, Akron, OH) at 373 K.

Differential scanning calorimetry (DSC)

The bulk T_g 's of different blend compositions were measured with DSC (Shimadzu 50, Kyoto, Japan) under a nitrogen atmosphere at a heating rate of 10 K min⁻¹.

RESULTS AND DISCUSSION

It is very interesting to investigate the behavior of the ultrasonic velocity and ultrasonic absorption in ENR/EPDM rubber blends to establish the shapes of the curves. Also, the compatibility or affinity of ENR to be mixed with EPDM can be determined by the linearity behavior of these curves.

Figure 1 shows the variation of the ultrasonic velocity of ENR/EPDM versus the blend ratios, that is, the weight percentage of EPDM. The figure shows a linear relation below 75% EPDM in the blend. The region above 75% is an EPDM domain-dominated region showing a slight decrease in the ultrasonic velocity, thereby revealing a weak interaction between the two

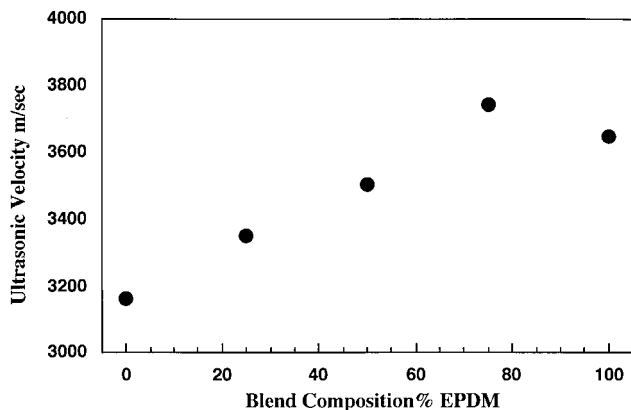


Figure 1 Variation of the longitudinal ultrasonic velocity with the composition of EPDM in the ENR/EPDM rubber blend.

phases of the blend in this region. The linear relation may be attributed to the strong association of the two-rubber blend due to the presence of a high percentage of epoxide groups in NR. These epoxide groups may improve the degree of compatibility between NR and EPDM in this region. In contrast, Sideky et al.²¹ reported that NR/EPDM without NR epoxidation was an incompatible system over the entire range studied.

Figure 2 shows the relation between the longitudinal ultrasonic absorption (attenuation) and the composition of this blend system. One maximum and one minimum indicate that the mutual solubility and the blend behave as one phase. This behavior indicates that ENR and EPDM are packed more orderly than in individual components.

Figure 3 shows the influence of the blend composition on the adiabatic compressibility in the ENR/EPDM system. The shape of the curve is almost linear, which confirms the compatibility of this system over a certain range of blend compositions.

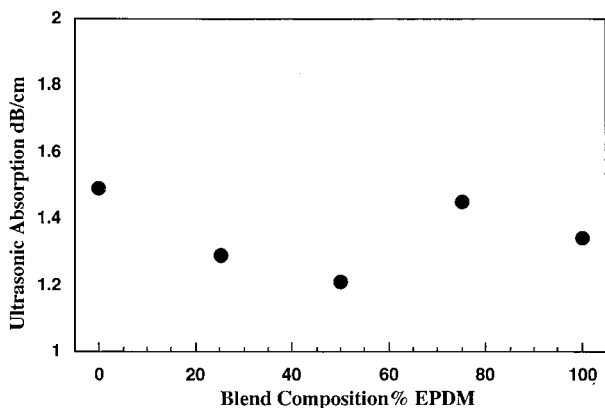


Figure 2 Variation of the ultrasonic absorption with the composition of EPDM in the ENR/EPDM rubber blend.

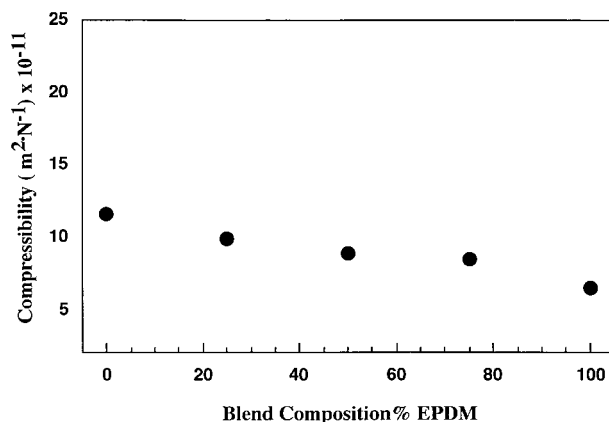


Figure 3 Variation of the adiabatic compressibility with the composition of EPDM in the ENR/EPDM rubber blend.

Figure 4 shows the variation of the Mooney viscosity (ML_{1+4}) with the ENR/EPDM blend composition. It seems that the curve is composed of two discrete curves: an arc type in EPDM-rich blends and linear variation in ENR rich blends. This means that ENR has stronger interparticle interactions than EPDM because of the presence of epoxide groups in NR.²² This may increase the compatibility of ENR with EPDM in the blend. When the percentage of EPDM increases above a certain range, the degree of compatibility between ENR and EPDM decreases because of the existence of ethylene-propylene units in EPDM. These units increase the viscosity of EPDM and accordingly decrease the dispersion of EPDM in the blend.

Figure 5 shows the variation of the heat of mixing with the blend composition. ENR/EPDM is supposed to be a compatible blend because the heat of mixing is less than 4.185×10^{-2} J/mol, the figure considered to be the upper limit of compatibility.⁶ Although some of the values lie above the upper limit of compatibility, we can presume that the blends are compatible because many values of the heat of mixing are less than

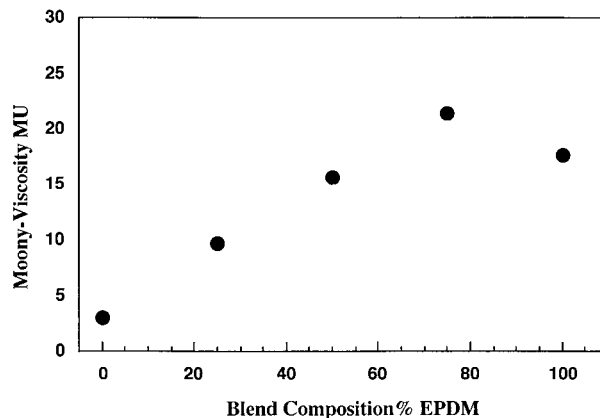


Figure 4 Variation of the Mooney viscosity with the composition of EPDM in the ENR/EPDM rubber blend.

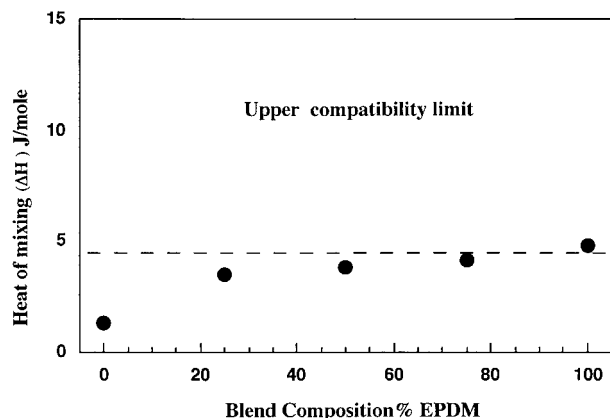


Figure 5 Heat of mixing as a function of the composition of EPDM in the ENR/EPDM rubber blend.

the limiting values. From a thermodynamic point of view, it can be concluded that the ENR/EPDM rubber blend is compatible in comparison with the NR/EPDM blend without epoxidation.²¹ One can see from these results that the epoxidation of NR forms epoxy groups. As a result, the ring opening of the epoxy groups²³ suggests the formation of hydroxyl and possibly carbonyl groups that create more active sites. These active sites²⁴ are able to improve the degree of compatibility in the ENR/EPDM blend system with respect to the unmodified system. Also, it can be concluded that epoxidation may decrease the viscosity of NR and accordingly enhance the dispersion of ENR in the blend.

Table I shows the T_g values of this blend system. The temperature at the midpoint of the baseline shift was defined as T_g in this study. The presence of a single glass transition indicates that the ENR/EPDM blend system is compatible, and only one phase is

TABLE I
 T_g 's Different ENR/EPDM Blend Compositions

Rubber blend composition	T_g^a (K)
100% ENR	220
100% EPDM	247, 249
75% EPDM	227
50% ENR	235
25% ENR	241

^a Measured by DSC.

formed. The glass-transition results agree with those results shown in Figures 1, 2, 4, and 5; this means that the compatibility of this blend system was improved after the NR was transformed into ENR.

The measurements of the ultrasonic absorption, ultrasonic velocity, heat of mixing, T_g , and Mooney viscosity of the ENR/EPDM blend system provide clues to the compatibility of rubber blends. These clues are generally obtained by sophisticated and expensive techniques involving thermal dynamics, electron microscopy, and so forth. Also, they may improve the degree of compatibility in this blend system through the epoxidation of NR and increase its dispersion in the blend.

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