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Ultrasonic properties of ENR-EPDM rubber blends

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Summary

The velocities of propagation of longitudinal and transverse ultrasonic waves in epoxidized natural rubber-ethylene propylene diene monomer (**ENR-EPDM**) blends with **EPDM** content of 0,25,50,75 and 100 weight percent were measured at a frequency of 2 MHz using pulse echo method. Density of the rubber blend was also measured. Longitudinal modulus, shear modulus, Young's modulus, bulk modulus, Poisson's ratio, crosslink density, and microhardness, of the rubber blends were then calculated. The variations of these parameters with the content of **EPDM** have been discussed, based on the structural changes of the network.

Introduction

Polymer blends represent the most rapidly growing area of polymer technology [1]. Interest in blends arises from the potential for achieving properties that are not possible with a single homopolymer or copolymer. For example, blends find applications as toughened plastics, barrier films, membranes, engineering thermoplastics and even self-reinforcing composites [2]. Moreover the current pressure towards recycling of plastics waste means that mixtures of polymers not hitherto in use must be considered and evaluated.

Many authors have studied a lot of techniques to evaluate the physical properties of polymers, especially the ones dealing with blends. Implementation of near-infrared (NIR) spectroscopy in on-line applications was based on spectral differences reflecting the changes in composition of polymer blend [3,4]. Problems related with this technique concern the probe design that would withstand adverse conditions inherent to polymer processing.

Ultrasonic technique has found numerous uses in widely different fields of application, in particular to characterize polymers, in both the solid and molten states. Recently, attention turned to multiphase systems where attempts have been made to relate the ultrasonic velocity with the concentration and the degree of dispersion of two-phase systems. Some ultrasonic measurements were performed [5-10] on polymer blends with various compositions. The ultrasonic velocity and ultrasonic attenuation were used to study the compatibility and elastic properties of the studied blends.

Ultrasonic velocity, attenuation coefficient and compatibility were studied for natural rubber-ethylene propylene diene monomer (**NR-EPDM**) rubber blends using pulse echo method [11]. The relation between ultrasonic velocity and composition showed a curvilinear type of S shape and a region of phase inversion was shown. This S type curve interpreted as a formation of two phases and consequently incompatible blend system. Therefore, in the first part of this study [12] we proved that the epoxidization of natural rubber improves the degree of compatibility between **NR** and **EPDM** rubber blends. So, this epoxidation enhances the compatibility and can be used in oil sealing application especially contains both plastic and rubber parts. The ultrasonic absorption, glasses transition temperature, moony-viscosity, compressibility and heat of mixing have also been evaluated.

The aim of this work is to continue the first part of this study to evaluate the physical properties of **ENR-EPDM** using ultrasonic pulse echo method. The ultrasonic velocity of longitudinal waves and that of shear waves were measured. Longitudinal modulus, shear modulus, Young's modulus, bulk modulus, Poisson's ratio, crosslink density and microhardness of the rubber blend system have been calculated and tabulated. The blend compositions covered the whole concentration range of **EPDM**.

Experimental

Materials

In the first part of this study [12] we mentioned about the preparation method of **ENR-EPDM** rubber blend and the density as well.

Pulse-Echo Technique

Ultrasonic techniques have been widely used for a number of types of investigation [13]. Recently the most commonly used method is the pulse echo technique in which a short sinusoidal electrical wave activates the ultrasonic transducer. The transducer then produces sound wave train into the sample that is cemented with the transducer. Some advantages of this method are that the sound velocity can be measured at the same time with the attenuation.

Using an oscilloscope, such as 60 MHz time base oscilloscope, direct measurement of the time required for the pulses to travel twice the length of the specimen is possible, which allows immediate calculation of the ultrasonic wave velocity as given in the following equation

$$V = 2X/\Delta t \qquad (1)$$

Where X is the sample thickness and Δt is the time interval.

All velocity measurements in this study were carried out at nominal frequency of 2 MHz (central frequency of 0.64 MHz and band width of 1.27 MHz) at room temperature (300K). The measurements were repeated three times to check the reproducibility of the data. The estimated accuracy of our velocity measurement is about 0.04 %.

Result and discussion

The experimental data of the ultrasonic velocity of longitudinal wave (v_l) and that of shear wave (v_s) as well as the density (ρ) of the **ENR-EPDM** blend samples for different compositions are tabulated in Table 1. Analyzing the experimental and their derived ultrasonical parameters one can obtain more interesting observation on the addition of **EPDM** in **EPDM-ENR** blend system. The densities of the produced samples are increased with the increase in weight percent of **EPDM** from 0 to 100. Moreover, both longitudinal and shear ultrasonic velocities, as shown in Figure 1, first increased with **EPDM** content and then showed some curvature at 75 wt%. After that the ultrasonic velocity decreased with the addition of **EPDM** up to 100 wt%.

The increase in ultrasonic velocity suggests the occurrence of strong specific intermolecular interaction within the components of the **EPDM-ENR** system up to 75 wt% of **EPDM**. This behavior confirms the good miscibility of the two component rubbers forming one single phase. Such trend indicates that **ENR** and **EPDM** macromolecules are more orderly and hence **ENR-EBDM** rubber blends are compatible in the range from 0 to 75 wt% of **EPDM**. It has been reported that [14, 15] linear behavior between ultrasonic velocity and composition could be interpreted as a sign of the presence of single –phase morphology. It should be mentioned however that this observation was made and confirmed [16,17] for blends in solution or in solid state, at room temperature.

Table 1. Measured density (ρ) longitudinal ultrasonic velocity (v_l) and shear ultrasonic velocity (vs) of rubber blends.

Sample Nod	Composition in weight percent		ρ (gm / cm^3)	v_l (m / sec)	v_s (m / sec)
	EPDM	**ENR**			
1	0	100	1.1646	3123±0.04	1240±0.04
2	25	75	1.1844	3351±0.03	1403±0.04
3	50	50	1.1986	3387±0.03	1406±0.05
4	75	25	1.1930	3501±0.04	1439±0.05
5	100	0	1.2004	3291±0.04	1372±0.04

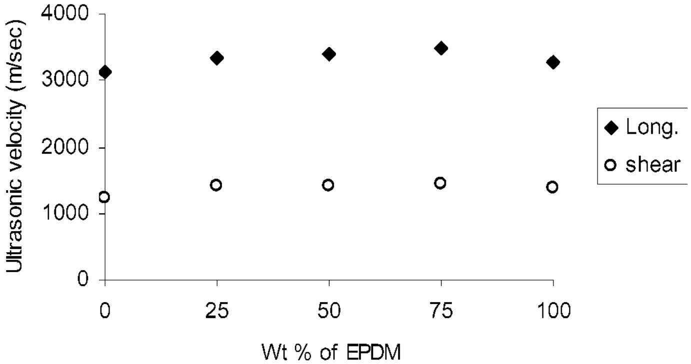

Figure 1. Variation of ultrasonic velocity (long. & shear) with weight percent of **EPDM** in **ENR-EPDM** rubber blend

Longitudinal modulus (L), shear modulus (G), Young's modulus (E), bulk modulus (K) and Poisson's ratio, σ, are calculated from ultrasonic velocities and the density of the isotropic materials as given in Equations 2 [18].

$$\begin{aligned} L &= \rho\, v_l^2 \\ G &= \rho\, v_s^2 \\ K &= L - (4/3)\, G \\ E &= 2\,G\,(1+\sigma) \\ \sigma &= (L-2G)/2(L-G) \\ H &= (1-2\sigma)\,E/[6\,(1+\sigma)] \end{aligned} \qquad (2)$$

Figures (2-5) illustrate the calculated values of elastic constants (longitudinal modulus, shear modulus, Young's modulus, and bulk modulus) as a function of the weight percent of **EPDM**.

All curves showed nearly linear relation between the elastic constants and the composition of **EPDM**, especially in the rang 25-75 wt % of **ENR-EPDM** system. However, a maxima was obtained at 75 wt % of **EBDM** content as a result of the rigidity of the rubber blend. After that the elastic constants get lower, as given in Table 2. On the other hand the region above 75 wt% is an **EPDM** domain-domainated region showing a decrease in elastic constants, which reveals weak two-phase interaction of the blend in this region. This could be explained on the basis that, **EPDM** being a copolymer of ethylene propylene (**EP**) units has a higher degree of crystallinty, due to the long-range ordering in **EP** segments. This higher degree of crystallinty may be responsible for the higher strength properties of **EPDM** and of those blends containing higher proportions of it. Furthermore, the presence of epoxy or **OH** groups on the chain of **ENR** may hinder the ability of the chain for orientation. This means that the use of small percents of **ENR** would be recommended to obtain high values of

elastic constants. This conclusion is in agreement with the results reported earlier [19].

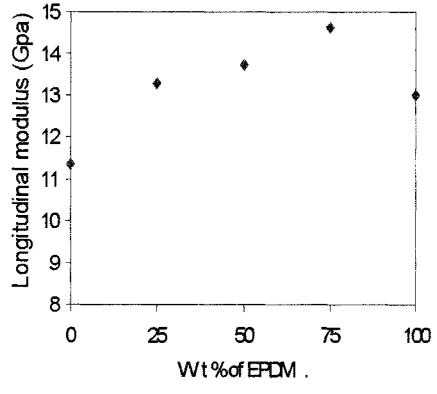

Figure 2. Variation of longitudinal modulus with weight percent of **EPDM** in **ENR- EPDM** rubber blend.

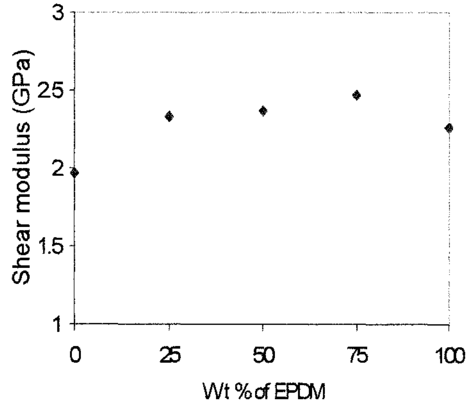

Figure 3. Variation of shear modulus with weight percent of **EPDM** in **ENR - EPDM** rubber blend.

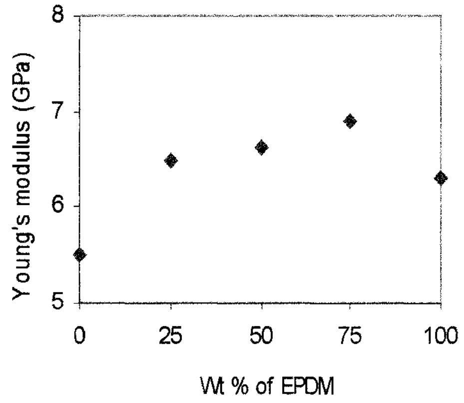

Figure 4. Variation of Young's modulus with weight percent of **EPDM** in **ENR-EPDM** rubber blend.

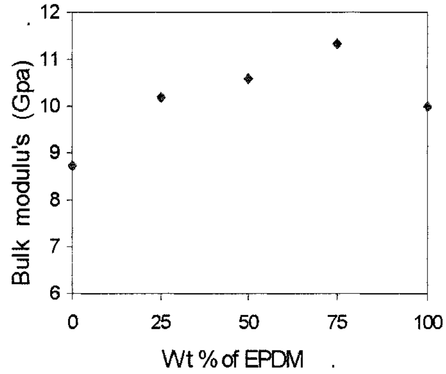

Figure 5. Variation of bulk modulus with weight percent of **EPDM** in **ENR-EPDM** rubber blend.

Table 2. Longitudinal modulus (L), shear modulus (G), Young's modulus (E), bulk modulus (K), Poisson's ratio (σ) and microhardness (H) of rubber blend system.

No	L (GPa)	G (GPa)	E (GPa)	K (GPa)	σ	H (GPa)
1	11.36±0.04	1.97±0.03	5.50±0.07	8.73±0.06	0.395±0.06	0.138±0.09
2	13.30±0.04	2.33±0.04	6.50±0.07	10.19±0.06	0.394±0.06	0.165±0.09
3	13.75±0.03	2.37±0.03	6.62±0.06	10.59±0.05	0.396±0.05	0.164±0.08
4	14.62±0.03	2.47±0.03	6.91±0.06	11.33±0.05	0.398±0.05	0.168±0.08
5	13.00±0.04	2.26±0.04	6.31±0.07	9.99±0.06	0.395±0.06	0.158±0.09

Figure 6 shows the changes in Poisson's ratio for **ENR-EPDM** blend with varying **EPDM** weight percent. From the figure, it can be seen that the Poisson's ratio increases with increasing the percentage of **EPDM** from 25 to 75 wt% and then decreases when **EPDM** reaches to 100 wt%. Poisson's ratio is formally defined, for any structure, as the ratio of lateral to longitudinal strain, produced when tensile forces are applied. For tensile stresses applied parallel to the chains, the longitudinal strain produced will be the same for all three networks. However, the lateral strain (strain perpendicular to the chain) is clearly greatest for the pure chain network. The lateral strain is greatly decreased with increasing crosslink density (defined as the number of lateral or transverse chemical bonds per atom). The behavior of Poisson's ratio with composition ought to be nearly the reverse of the crosslink density of the network. For that reason, it can be assumed that the increase in Poisson's ratio with the **EPDM** content up to 75 wt% is attributable to the decrease in crosslink density as it can be seen in Figure 7. As a result, an ordering of the chain would be obtained. On the opposition of that above 75 wt% the Poisson's ratio decreases with increasing the crosslink density.

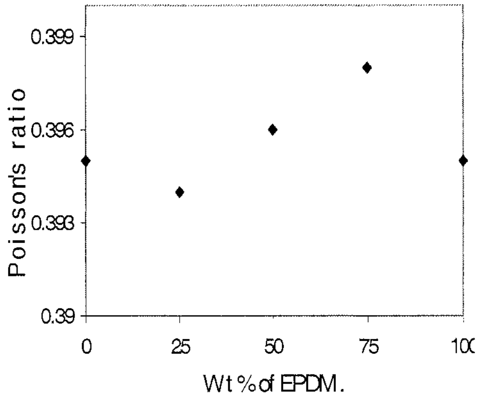

Figure 6. Variation of Poisson's ratio with weight percent of **EPDM** in **ENR-EPDM** rubber blend.

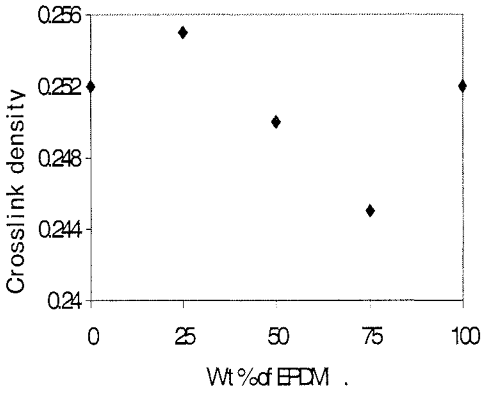

Figure 7. Variation of crosslink density with weight percent of **EPDM** in **ENR-EPDM** rubber blend.

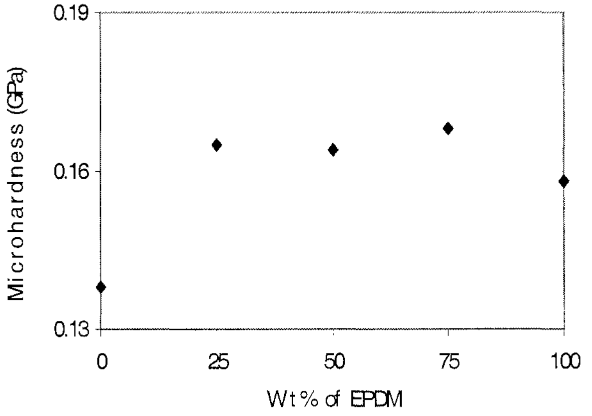

Figure 8. Variation of microhardness with weight percent of **EPDM** in **ENR - EPDM** rubber blend.

The measurements of microhardness of the blend shown in Figure 8 show a similar trend to that showed by the elastic constants upto 75 wt% **EPDM**. The increase in hardness of the blends may also be interpreted as being due to strong intermolecular interaction in the blend. In the region above 75 wt% of **EPDM** this property showed some decrease in the hardness due to the weak interaction between the two polymers, as explained earlier.

Conclusions

Ultrasonic measurements were performed on **ENR-EPDM** rubber blends of different weight percent of **EPDM** by use of pulse echo method with 2MHz frequency. The ultrasonic velocity data of longitudinal waves and that of shear waves were used together with the data of density to estimate the elastic moduli, Poisson's ratio and microhardness of the rubber blends. It was found that the **ENR-EPDM** blend system exhibits good mechanical properties in the range of 0-75 wt% **EPDM**. This behavior is attributed to the fact that the addition of **EPDM** improved the mechanical properties of the studied rubber blend. Whereas the use of 100% **EPDM** resulted in a decrease of the mechanical properties. Hardness of the blends showed behavior similar to those elastic moduli. This work is in good agreement with our previous work that the measurements of glass transition temperature, ultrasonic absorption and moony viscosity of **ENR-EPDM** blend system provide a clue to the compatibility of rubber blend within the same range we used.

Finally, it can be concluded that the pulse echo method has the ability to evaluate the mechanical properties of polymer blends. It is a useful tool to determine whether or not there is a phase separation in the blend system being studied.

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