# **Characterization of Elastomer Blend and Compatibility**

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ABSTRACT: Binary blends of acrylonitrile-*co*-butadiene rubber and ethylene propylene diene monomer rubber are immiscible. However, they can be made compatible by addition of a third elastomer viz., chlorinated polyethylene or chlorosulphonated polyethylene in small concentrations. Various sophisticated analytical techniques, e.g., ultrasonic velocity measurements in solutions, infrared spectroscopy of solution cast films, thermo-mechanical analysis, processing characteristics through rubber process analyzer (RPA-2000), determination of the vulcanizate properties, and also phase morphology studies by atomic force microscopy have been made to elucidate compatibility and its effect on end-use properties of the evolved blends. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 480–489, 1999

**Key words:** elastomer blend; compatibilization; ultrasonic velocity measurement; infrared spectroscopy; thermo-mechanical analysis; atomic force microscopy; rubber process analyzer

# **INTRODUCTION**

With the advent of new technology and sophisticated analytical equipment, the characterization of rubber has become more perfect over the years. A flow visualization study on the influence of compatibilizing agents on rate of mixing in an internal mixer and scanning electron microscopy (SEM) study on phase morphology development in binary and ternary blends of nitrile (NBR), ethylene propylene (EPM), and polychloroprene (CR) rubbers have already been reported by Setua and White.<sup>1-4</sup> Rate of homogenization and scale of dispersed particles into continuous matrix were found to depend on the relative polarity and differences in the solubility parameter of the component phases in these blends. Lohmar<sup>5</sup> has reported the transmission electron microscopy (TEM) studies on compatibility of NBR and eth-

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ylene propylene diene monomer rubber (EPDM) added with poly-*trans*-octenylene rubber (TOR) as a compatibilizer. Coran and Patel<sup>6,7</sup> have discussed the utility of malic anhydride modified polypropylene (PP) combined with amine terminated low molecular weight liquid NBR as suitable compatibilizer for NBR and PP. Thermoplastic elastomers based on NBR and PP have been developed by the Monsanto Co. (Akron, OH) in the trade name of Geolast.

Several experimental and theoretical methods are commonly being used to characterize polymer compatibility.<sup>8,9</sup> Ultrasonics have been applied extensively to study the properties of polymer solutions.<sup>10–12</sup> Propagation of small amplitude ultrasonic waves through a specimen at a resonant frequency of transducer and measurement of corresponding frequency and wavelength provide an accurate method for the measurement of ultrasonic velocity in liquids. Ultrasonic studies of polymer solution and solid polymers have been the subject of extensive research activity for the last few decades.<sup>13,14</sup> The velocity of wave propagation and energy loss (attenuation) by the inter-

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	Content of Mix (Weight in Parts Per Hundred Parts of Rubber (phr))		
Parameter	Blend Without Compatibilizer	Blend with CPE	Blend with CSM
$NBR^{a}$	50	50	50
$EPDM^{b}$	50	50	50
CPE <sup>c</sup>	_	5	
$\mathrm{CSM}^{\mathrm{d}}$	_	_	5
$\operatorname{Zinc} \operatorname{oxide}^{\operatorname{e}}$	5	5	5
Stearic acid <sup>e</sup>	2	2	2
Dicumyl peroxide <sup>e</sup>	1.75	1.75	1.75

Table I Formulation of the Mixes

 $^{\rm a}$  NBR-JSR 220 (Japan Synthetic Rubber, acrylonitrile content 38 mol %).

<sup>b</sup> EPDM-Nordel 2722 (Du Pont, Wilmington, DE).

 $^{\rm c}$  CPE-Tyrin CM 0316 (Dow Chemical, Plaquemine, LA, chlorine content 36 mol %).

<sup>d</sup> CSM-Hypalon 20 (Du Pont, chlorine content 29 mol %).

<sup>e</sup> All other chemicals are of pure analytical grade.

action of polymeric microstructure are the key factors in determination of physical properties of polymers. Kuleznev et al.,<sup>15</sup> Hourston and Hughes,<sup>16</sup> Singh et al.,<sup>17,18</sup> and Sidkey et al.,<sup>19</sup> have reported their studies on viscometric and ultrasonic velocity measurements in solutions of various polymer blends including elastomers. Alex et al.<sup>20</sup> and Mukhopadhyay and De<sup>21</sup> have studied characteristic peak shifts and formation of new peaks in the infrared spectroscopy (FTIR) due to formation of chemical crosslinking in elas-

Table IIProcessing Characteristics ofthe Mixes<sup>a</sup>

	Blend Type		
Property	Without Compatibilizer	With CPE	With CSM
1. 50% Cure, T 50, min	14.71	14.66	14.69
2. 90% Cure (optimum cure time), T 90, min	5.88	5.87	5.88
3. Scorch time, TS 1.00, min	2.46	2.67	2.58
4. Scorch time, TS 2.00, min	3.96	4.66	4.37

<sup>a</sup> Determined in RPA-2000 at a temperature of 160°C, frequency of 100 cpm, and strain of 0.5°.

Table III	Physico-Mechai	nical Properties o	of
the Vulcar	nizates		

	Blend Type		
Property	Without Compatibilizer	With CPE	With CSM
Tensile strength, Kg/cm <sup>2</sup>	26.2	62.9	44.3
Elongation at break, %	300	475	325
Modulus at 100% elongation, Kg/cm <sup>2</sup>	11.9	19.7	13.7
Hardness, shore A	57	64	60
Compression set at 70°C for 24 h at 25% deflection, %	85	77	80

tomer blends. Ultrasonic velocity measurements in the determination of miscibility and evaluation of thermal properties, e.g., thermo-gravimetric analysis (TGA), dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) of isobutylene-*co*-isoprene rubber (IIR) and CR blends have recently been reported by Setua et al.<sup>22,23</sup>

In the present article, we attempt to evaluate the compatibility of NBR and EPDM blends and the effect of addition of compatibilizers by various analytical techniques, e.g., ultrasonic interferometry, FTIR, processing characteristics in rubber process analyzer (RPA), atomic force microscopy (AFM), thermo-mechanical analysis (TMA), and determination of the physico-mechanical properties.

### **EXPERIMENTAL**

Both NBR and EPDM were masticated, dissolved in toluene, and solution blends in various blend ratios were prepared. Compatibilizing agents, wherever used, were compounded with EPDM at  $80^{\circ}$ C for 2 min in a two-roll mixing mill. The ultrasonic velocity measurements were performed in these solutions by ultrasonic interferometer (M-84, Mittal Enterprises, India) at room temperature ( $25 \pm 2^{\circ}$ C) and at a frequency of 5 MHz. Cast films of the individual elastomers and blends were prepared from the solutions on glass slides by evaporating the solvent at room



**Figure 1** Variation of ultrasonic velocity with blend ratio and effect of addition of compatibilizers.

temperature followed by drying in an oven at 100°C. Nicolet Magna-750 FTIR was used for structural analysis of these films. Rubber compounds were prepared in a two-roll mill, as per formulations given in Table I. Master batches of EPDM and compatibilizers were prepared and mixed with NBR along with other ingredients. The rheological characteristics for these compounds were evaluated utilizing RPA-2000 (Table II). The mixes were cured to their respective optimum cure time in a hydraulic press at 160°C and at 4.5 MPa pressure. Thermo-mechanical properties were evaluated on the vulcanizates in a thermo-mechanical analyzer (TMA 2940) of TA Instruments (New Castle, DE) under static load (10 gm), rate of heating 10°C per min and under constant nitrogen flow rate of 100 ml per min. ASTM procedures were adopted to determine the physico-mechanical properties of the vulcanizates as enumerated in Table III. Atomic force microscopy (AFM) images were obtained using a nanoscope scanning probe microscope of Digital Instruments (Santa Barbara, CA) in tapping mode on surfaces of the samples previously chilled followed by cutting with a razor blade.

### **RESULTS AND DISCUSSION**

# Determination of Compatibility Through Ultrasonic Velocity Measurements of Solutions of NBR and EPDM and the Effect of Compatibilizers

Figure 1(A) shows the variation of the ultrasonic velocity of the blends in solution in varied blend ratios. Ultrasonic waves were found to propagate randomly because of immiscibility between NBR and EPDM. Up to 30% concentration of NBR, the velocity was increased followed by a drop and the trend was repeated again in the region between 50 to 90% NBR. Sudden increase or decrease in the ultrasonic velocity generated an S-shaped plot which might be due to varied phase morphology of different blends in the polymer-polymer-solvent system. NBR, at lower concentration formed the dispersed phase in an EPDM matrix, whereas exceeding NBR concentration beyond 50 wt % phase reversal took place via formation of cocontinuous morphology. Detailed investigation on evolution of phase morphology with respect to mixing parameters, e.g., temperature, mixing



Figure 2 FTIR spectrums of NBR, EPDM, and their blends in varied blend ratios.



**Figure 3** FTIR spectrums of NBR-EPDM blends without a compatibilizer (A) and that of the blend containing CPE (B) and CSM (C).

time, rate of homogenization, and effect of variation of blend ratios for NBR-EPM blends have already been reported by Setua and White.<sup>1</sup> Variation of average dispersed phase size with different blend ratios for solution casted films of immiscible IIR-CR blends have been described earlier.<sup>22</sup> The information thus obtained could easily be extrapolated to explain the random variation of ultrasonic velocity through polymer solutions containing NBR and EPDM.

The addition of either CPE or CSM caused remarkable changes in the ultrasonic properties. Polar-polar interaction between NBR with chlorinated polyethylene (CPE) or chlorosulphonated polyethylene (CSM) and phase coalescence of the polyethylene (PE) segment of these compatibilizers with NBR and EPDM due to structural similarity of the main chain (e.g., polybutadiene of NBR and EPDM as a whole), in such cases, were reported to result in compatibilization which also reduced the scale of dispersed NBR globules inside EPDM.<sup>2,3</sup> Ultrasonic velocity in these cases, Figure 1(B) [NBR + (EPDM + CPE)] and Figure 1(C) [NBR + (EPDM + CSM)], were found to vary linearly with composition and a marked increase in the absolute velocity compared with those of the blends without a compatibilizer. However, the addition of CPE with higher chlorine content (36

mol % chlorine) compared with CSM (29 mol % chlorine) resulted in greater compatibilization efficacy and steeper slope of the ultrasonic velocity vs. composition plot in the former case. Capability of either CPE or CSM to act as potential compatibilizer for the NBR-EPDM and NBR-EPM blends have also been reported by Johnson.<sup>24</sup>

### Evidence of Immiscibility and Physico-Chemical Process of Compatibilization

Lack of miscibility between NBR and EPDM was also confirmed by FTIR technique. Figure 2 shows the characteristic IR peaks of solvent cast films of individual elastomers as well as blends in various blend ratios. Peaks at 2237 cm<sup>-1</sup> (acrylonitrile), 1444 cm<sup>-1</sup> (—CH<sub>2</sub>—), 975 cm<sup>-1</sup> (—CH—CH—; 1,4 addition) and at 926 cm<sup>-1</sup> (—CH—CH<sub>2</sub>; 1,2 vinyl addition) groups of NBR and at 1460 cm<sup>-1</sup> (—CH<sub>2</sub>—CH<sub>3</sub>), 1373 cm<sup>-1</sup> (—CH<sub>3</sub>), 962 cm<sup>-1</sup> (—CH—CH—) and at 725 cm<sup>-1</sup> (—CH<sub>2</sub>—) of EPDM were found to be present with relative peak intensities as per their weight averages in each system indicating complete immiscibility.

Occurrence of miscibility because of addition of compatibilizers were further evident in FTIR spectrums of the 50 : 50 blends of NBR : EPDM without a compatibilizer [Fig. 3(A)] and for the



Figure 4 Rheological characteristics of the mixes in frequency sweep.

blends containing either CPE [Fig. 3(B)] or CSM [Fig. 3(C)]. Interactions among acrylonitrile and vinyl groups of NBR with electronegative chlorine of CPE were evident in variations of peak intensities of these groups. Interaction among the PE part of CPE, the polybutadiene part of NBR and EPDM, caused the appearances of stretched peaks between  $1370-1100 \text{ cm}^{-1}$  and  $920-650 \text{ cm}^{-1}$  due to merger of several peaks of the elastomers. In the case of CSM, as expected, changes in the peak intensities as well as peak stretchings were different than CPE.

# Processing Characteristics of the Blends and the Effect of Addition of Compatibilizer

A Rubber Process Analyzer (RPA-2000) was used in the evaluation of dynamic mechanical rheological characteristics viz., elastic torque (S'), viscous torque (S'') and tan delta of the uncured rubber compositions. The different types of subtests programmed were frequency sweep (Fig. 4, strain and temperature constant while fre-

quency was varied), strain sweep (Fig. 5, frequency and temperature constant while strain was varied), and cure time test (Table II, frequency, strain, and temperature were fixed with respect to time). Previous works done by Dick and Pawlowski<sup>25</sup> showed that both frequency sweep and strain sweep could distinguish various types of styrene butadiene rubber (SBR), e.g., hot emulsion, cold emulsion, oil-extended emulsion, solution SBRs, and also of the same SBR from different sources. Our studies in RPA in both these modes also responded effectively to characterize compatibility with changes in the micro and macro properties of the blends containing CPE or CSM. Setua and White<sup>1,3</sup> had also reported earlier the torque development during mixing of EPM and NBR in the presence of different compatibilizers. The addition of either CPE or CSM was found to improve the adhesion between the phase components, generation of finer phase morphology, and associated viscosity increase elevated the final torque while mixing in a Haake laboratory internal mixer.



Figure 5 Rheological characteristics of the mixes in strain sweep.

#### **Thermo-Mechanical Properties of the Vulcanizates**

Establishment of an interphase across the phase boundary due to the addition of CPE or CSM also caused marked changes in the thermo-mechanical properties (Fig. 6). Comparatively small NBR particles as well as their uniform dispersion inside EPDM matrix, in these cases, resulted in a closer packing order and a corresponding reduction in free volume. Blends of NBR and EPDM containing either CPE or CSM, therefore, did not show any marked dimensional changes near to the glass transition temperatures of the individual elastomers. The derivative of dimensional changes in these cases also showed peak shifts toward the middle and formation of a broad plateau.

### **Physico-Mechanical Properties**

Physico-mechanical properties of the vulcanizate without a compatibilizer were poor (Table III). These, however, observed to be improved remarkably due to the addition of CPE or CSM. As expected, CPE always offered better mechanical properties because of enhanced compatibility compared with CSM.

### Surface Topography

AFM images of the rubber vulcanizates were obtained in tapping mode because these materials were rather soft and could possibly be damaged in contact AFM mode. A drop of amplitude of an oscillating probe (oscillation frequency in the 150–350 KHz range) because of tip sample force interaction was used for surface imaging. The AFM approach was superior to either SEM or TEM in the sense that it did not need either a conductive coating (SEM) or any staining/chemical etching (TEM) to provide compositional maps or surface topography of polymer samples.

Surface regions of the blend without a compatibilizer, as is shown in Figure 7, had rough topography with corrugations higher than 1  $\mu$ m. There was also a variety of structures with fibrils and more dense segments. A number of brighter grains were also seen by zooming in on the flat region within this area (Fig. 8). The height image obtained by lower tip-sample force resembled closely to sample topography and helped to visualize tiny nanofibrils that most likely were nanostructural elements of this surface.

Surface topography of the blend with CPE (Fig. 9) showed direct indication of formation of a su-



Figure 6  $\,$  TMA plots of NBR-EPDM blends and the effect of the addition of CPE or CSM.



Figure 7 AFM photograph of NBR-EPDM blend without a compatibilizer.



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Data type Z range	Height 100.0 пм	Data type Z range	Phase 6.01 de

 $Figure \ 8$  Magnified view of surface topography of NBR-EPDM blend without a compatibilizer.



Figure 9 AFM photograph of NBR-EPDM blend with CPE.



Figure 10 AFM photograph of NBR-EPDM blend with CSM.

perior composite structure with differences in the phase contrast between component phases. The regions (dark contrast) with fibrillar-like structure had brighter inclusions that also had smaller brightest grains. Several oval-like inclusions with dimensions in the micron and submicron range were easily seen in this phase image.

Surface topography of the blend with CSM (Fig. 10) was in general similar to that obtained on the sample containing CPE and was also composite in nature. However, the phase image with tiny inclusions/dispersed phase which were embedded into the matrix were seen to be larger than similar domains in Figure 9. An interface region between two domains with bright and dark contrast was also evident.

# **CONCLUSIONS**

- 1. Copolymers of NBR and EPDM are immiscible in all proportions. However, these two elastomers were made compatible by the addition of either CPE or CSM as compatibilizers.
- 2. Ultrasonic velocity measurements in solution, FTIR studies on thin films, evaluation

of thermo-mechanical properties by TMA, rheological characteristics by RPA and phase morphology by AFM technique were found to be useful tools to evaluate compatibility and also helped to explain the mechanism of compatibilization.

3. Compatibilized vulcanizates showed marked improvement in the physico-mechanical properties compared with the uncompatibilized system and are expected to receive greater attention of rubber technologists for wider usage and newer applications.

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