

# Unsaturated Polyester as Compatibilizer for Styrene–Butadiene (SBR)/Acrylonitrile–Butadiene (NBR) Rubber Blends

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**ABSTRACT:** The effect of the addition of 5 and 10 phr of unsaturated polyester resin (UPE) on the compatibility and physicomechanical properties of styrene–butadiene (SBR) and acrylonitrile–butadiene (NBR) rubber blends was studied. Differential scanning calorimetry (DSC), scanning electron microscopy (SEM), electrical, and ultrasonic techniques were used to determine the degree of the compatibility (DC). The results obtained revealed that, by the addition of 10 parts per hundred parts of rubber (phr) UPE as a compatibilizer for SBR/NBR blends, the degree of compatibility was greatly enhanced. The rheological and mechanical properties of the blends were also improved. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2314–2321, 2002

**Key words:** compatibility; styrene–butadiene/ acrylonitrile–butadiene (SBR/NBR) blends; unsaturated polyesters

## INTRODUCTION

Rubber blends are frequently used in the rubber industry to obtain the best compromise in the physical properties, processability, and cost. Therefore, there is a real need to know which types of rubber can be successfully blended and what factors may influence the final blend properties. Recently, the blending of polymers became an increasingly important area of research work. Many rubber producers are developing new blended products because they offer a convenient and less expensive alternative to developing totally new polymers. Blends can be tailored to meet the requirements of specific applications.<sup>1,2</sup> However, the degree of compatibility or miscibil-

ity of these blends greatly depends on the microstructure of the constituent rubbers in the blends. Many rubber blends are incompatible. Therefore, it is necessary to introduce a compatibilizing agent to the rubber blend, which can act as an interface between the rubber constituents of the blend.

A variety of experimental and theoretical methods have been used to study the blend compatibility.<sup>3</sup> These methods include viscometric measurements, dynamic mechanical analysis, electron microscopy,<sup>4</sup> differential scanning calorimetry (DSC),<sup>5,6</sup> infrared spectroscopy (IR), and electrical<sup>7</sup> and ultrasonic measurements.<sup>8–11</sup>

The effect of the polyester resins on the properties of many kinds of rubber has been extensively studied.<sup>12–16</sup>

The main aim of this work is to study the effect of unsaturated polyester resin (UPE) on the properties and the compatibility of styrene–butadiene

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**Table I Rheometric Characteristics and Physicomechanical Properties of SBR/NBR Blends Without Compatabilizer**

Property	SBR	SBR/NBR					NBR
	100	75/25	60/40	50/50	40/60	25/75	100
Rheometric characteristics at $142 \pm 1^\circ\text{C}$							
$M_L$ (dN · m)	12	8	10	8	8	8	6
$M_H$ (dN · m)	100	83	97	80	80	68	66
$T_{c90}$ (min)	33	33.25	32	35	35	34	35
$T_{s2}$ (min)	2	3	3	3	3	3	3.5
CRI ( $\text{min}^{-1}$ )	3.23	3.31	3.45	31.3	3.13	3.23	3.17
Physicomechanical properties of the vulcanizates							
Tensile strength (MPa)	1.04	1.97	2.68	2.4	2.69	3.49	1.4
Elongation at break (%)	78	104	114	142	170	250	210
Equilibrium swelling (%)	108	102	89	146	129	138	108

(SBR) and acrylonitrile–butadiene (NBR) rubber blends.

## EXPERIMENTAL

### Materials and Blend Preparation

The materials used to prepare the samples investigated in this work are (i) styrene–butadiene rubber (SBR 1502; styrene content,  $\sim 23.5\%$ ) with specific gravity of  $0.945 \pm 0.005$  and Mooney viscosity (ML4) of  $\sim 52$  at  $100^\circ\text{C}$ ; (ii) acrylonitrile–butadiene rubber (NBR; Krynac 34-52; acrylonitrile content,  $\sim 33\%$ ), with specific gravity of  $0.990 \pm 0.005$  and Mooney viscosity (ML4) of  $\sim 45$  at  $100^\circ\text{C}$ ; and (iii) the unsaturated polyester resin (UPE) is based on the reaction of *p*-carbethoxy phthalinic acid, maleic anhydride, and ethylene glycol with acid value  $7.7$  mg KOH/g was prepared in a previous work by the authors;<sup>16</sup> and (iv) dicumyl peroxide [bis(1-methyl-1-phenylethyl) peroxide] was obtained from Aldrich Company.

The mixing was carried out in a Brabender Plasticorder at  $140^\circ\text{C}$  and a rotor speed of 30 rpm for 5 min. Different ratios of SBR and NBR were mixed without and with 5 and 10 phr (part per hundred parts of rubber) of the prepared UPE. The dicumyl peroxide (4 phr) was then added as curing agent on a laboratory two roll mill of outside diameter 470 mm, working distance 300 mm, speed of slow roll 24 rpm, and gear ratio 1:1.4. After completing the mixing, the rubber mixes were subjected to sheeting on the mill. The vul-

canization was carried out in a heated flatten press under a pressure of  $\sim 40$  kg/cm<sup>2</sup> and temperature of  $142 \pm 1^\circ\text{C}$ . The optimum cure time ( $T_{c90}$ ) is shown in Tables I, II, and III. The investigated samples were cut and prepared with dimensions that best suit each testing technique.

### Testing Techniques

The determination of the rheometric characteristics, maximum torque  $M_H$ , minimum torque  $M_L$ , scorch time  $t_{s2}$ , and optimum cure rate index (CRI), were done using a Monsanto oscillating disc rheometer 100 according to ASTM D 1646 (1996). The mechanical properties were measured at room temperature using a tensile testing machine (Zwick 1101) according to ASTM D 412 (1998). Swelling in toluene was carried out for 24 h at room temperature.<sup>17</sup> The permittivity ( $\epsilon'$ ) at 5 kHz was measured using an LCR meter type AG-4311B Ando electric LTD. The cell was calibrated using standard samples with known permittivity. For accurate determination of the glass transition temperature  $T_g$ , differential scanning calorimeter measurements (DSC) were carried out using Shimadzu DSC-50. The specimen was rapidly cooled to  $-100^\circ\text{C}$ , and DSC was recorded on heating up to  $100^\circ\text{C}$  at a rate of  $5^\circ\text{C}/\text{min}$ .

Ultrasonic measurements were performed using an ultrasonic flaw detector of type Krautkrämer-Branson USD10. The technique used was the pulse-echo immersion technique.<sup>18</sup> All measurements were carried out at ultrasonic frequency of 5 MHz and constant temperature of  $20^\circ\text{C}$ . Ethyl alcohol was chosen as the immersion liquid because of its

**Table II Rheometric Characteristics and Physicomechanical Properties of SBR/NBR Blends with 5 phr UPS as Compatibilizer**

Property	SBR	SBR/NBR					NBR
	100	75/25	60/40	50/50	40/60	25/75	100
Rheometric characteristics at 142 ± 1°C							
$M_L$ (dN · m)	12	10	10	8	10	6	6
$M_H$ (dN · m)	101	85	87	87	88	82	76
$T_{c90}$ (min)	37	38.5	37	37	36	36	35.5
$T_{s2}$ (min)	2.5	2.5	2.5	2.5	2.5	2.5	2
CRI (min <sup>-1</sup> )	2.9	2.8	2.82	2.82	3.08	2.99	2.99
Physicomechanical properties of the vulcanizates							
Tensile strength (MPa)	1.14	2.06	2.31	3.08	3.09	3.34	1.95
Elongation at break (%)	130	156	226	212	270	235	360
Equilibrium swelling (%)	166	130	127	150	171	151	111

negligibly small ultrasonic attenuation (0.45 dB/cm) compared with that of rubber (100–140 dB/cm). The velocity of waves in alcohol at the same temperature was 1244 m/s. For velocity and attenuation measurements in rubber samples using the immersion technique, the sample was immersed in alcohol. The time of flight for a round trip and the decibel difference with the sample immersed and then removed were measured and used to calculate the velocity and the attenuation in rubber using the following equations<sup>18</sup>

$$V_r = \frac{2LV_a}{[2L - V_a(t_1 - t_2)]} \quad (1)$$

$$\exp(-2\alpha_r L) = R \exp(-2\alpha_a L) \times \left[ \left( \frac{\rho_a V_a}{4\rho_r V_r} \right) + \left( \frac{\rho_r V_r}{4\rho_a V_a} \right) + \frac{1}{2} \right] \quad (2)$$

where the subscripts 'a' and 'r' stand for alcohol and rubber, respectively,  $V$  is the ultrasonic velocity,  $L$  is the specimen thickness,  $t_1$  and  $t_2$  are the times of flight of ultrasonic waves in a round trip with the specimen removed and immersed, respectively,  $\alpha$  is the attenuation coefficient,  $\rho$  is the density, and  $R$  is the ratio of the received amplitudes when the specimen is removed and immersed. The average of the densities of different rubber blends was 970 kg/m<sup>3</sup>. The density of

**Table III Rheometric Characteristics and Physicomechanical Properties of SBR/NBR Blends with 10 phr UPS as Compatibilizer**

Property	SBR	SBR/NBR					NBR
	100	75/25	60/40	50/50	40/60	25/75	100
Rheometric characteristics at 142 ± 1°C							
$M_L$ (dN · m)	9	5	5	6	6	5	4
$M_H$ (dN · m)	100	94	86	84	80	76	64
$T_{c90}$ (min)	33	33.5	33	31.5	33.5	33	29
$T_{s2}$ (min)	2	2	2	2	2	2	3
CRI (min <sup>-1</sup> )	3.45	3.17	3.23	3.39	3.17	3.17	3.85
Physicomechanical properties of the vulcanizates							
Tensile strength (MPa)	1.68	2.15	3.6	3.82	4.14	4.61	5.54
Elongation at break (%)	47	42	77	131	140	158	162
Equilibrium swelling (%)	55	93	73	62	93	83	90

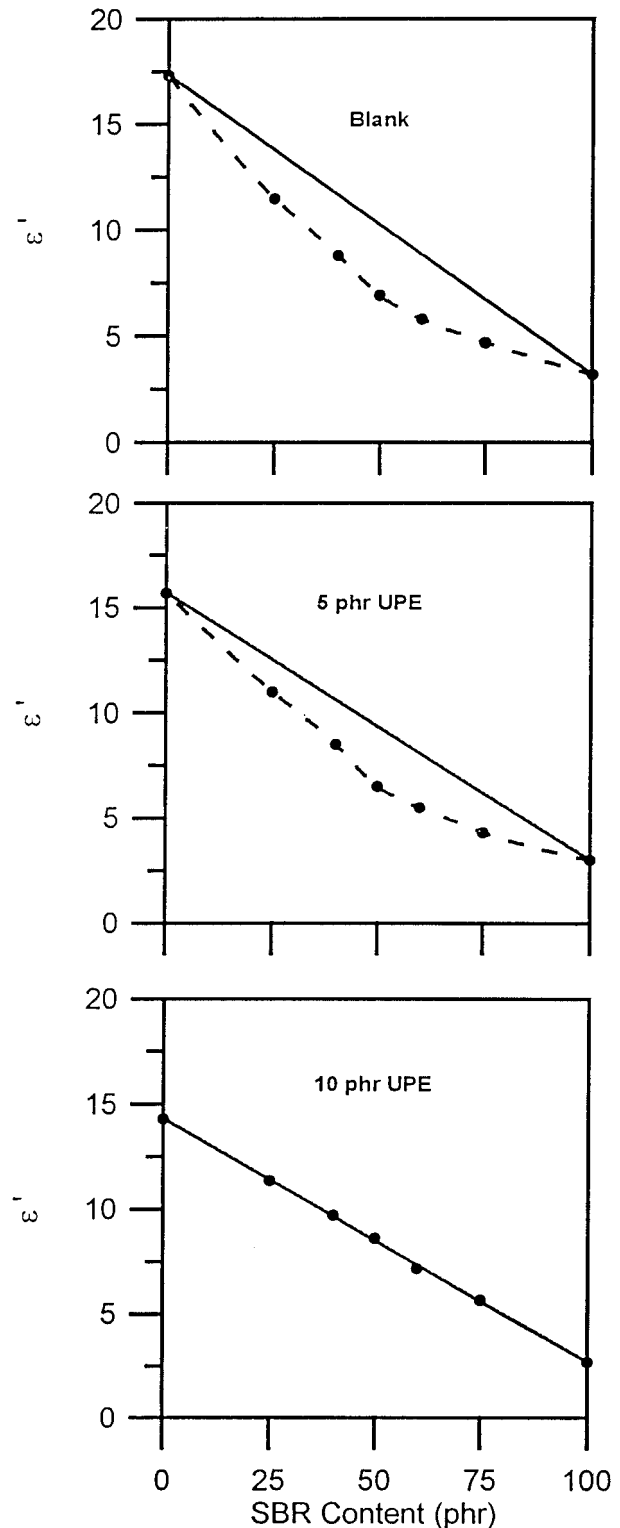
alcohol was  $805 \text{ kg/m}^3$ .<sup>19</sup> The accuracy of measuring the velocity was 1.5 m/s, which corresponds to a percentage error of 0.1%. The error in measuring the attenuation in rubber does not exceed 5%.

A scanning electron microscope (SEM; JMS-T 20, JEOL, Japan), with an applied voltage of 20 kV, was used to analyze the morphology of the blends. To prepare the specimen for SEM, the samples were fractured and the fractured surfaces were coated with gold.<sup>20</sup>

## RESULTS AND DISCUSSION

The effect of addition of 5 and 10 phr UPE on the physicomechanical properties and the compatibility of SBR/NBR blends was studied. A summary of the rheological characteristic and mechanical properties of the rubber mixes with and without the UPE is given in Tables I–III. It is clear from the rheological data that the increase of NBR content in all rubber mixes, with and without the UPE, decreased the maximum and minimum torque ( $M_H$  and  $M_L$ , respectively). The addition of 10 phr UPE in all rubber mixes decreased the minimum torque ( $M_L$ ), as shown in Table III. This result may be due to its plasticizing effect. The results in Table I indicate that the tensile strength and the elongation at break for the rubber mixes increased as the NBR content increased. Comparing data from Tables II and III with that in Table I, it is clear that the addition of 5 phr UPE increased the tensile strength, the elongation at break, and the equilibrium swelling (Table II). At 10 phr UPE, the tensile strength increased and the elongation at break decreased. The percentage of equilibrium swelling in toluene decreased dramatically, which can be attributed to the increase in the degree of crosslinking via the unsaturation of UPE.

The effect of the UPE as a compatibilizing agent on degree of compatibility of different rubber blends was studied by measuring the dielectric permittivity, by DSC, by determining the ultrasonic attenuation and velocity, and with the scanning electron microscope. The dependence of the dielectric permittivity ( $\epsilon'$ ) at 5 kHz on the SBR content in the blends is shown in Figure 1. It is clear that the values of  $\epsilon'$  in the blank blends (with 0 phr of UPE) do not coincide with the straight line connecting the values of  $\epsilon'$  of the two individuals SBR and NBR. This result indicates that the two types of rubber are incompatible because the deviation from that line is  $\sim 30\%$ ,



**Figure 1** Relation between the dielectric permittivity  $\epsilon'$  and SBR content in blank SBR/NBR blends and in blends containing 5 and 10 phr of UPE.

**Table IV DSC Results for SBR, NBR, and Their Blends**

SBR/NBR Ratio	$T_g$ , °C
100/0	-49
0/100	-22
50/50	-43
	-22
50/50 + 5 phr UPE	-49
	-20
50/50 + 10 phr UPE	-45
	-24

which is considered to be higher than the permissible experimental error. By the addition of 5 phr UPE to the rubber blends, this deviation decreased to 25%, which indicates slight improvement in the degree of compatibility. Finally the addition of 10 phr UPE reduced the deviation from linearity to <2%, which indicates that this concentration of UPE acts successfully as a compatibilizer for SBR/NBR blends.<sup>21</sup>

The glass transition temperatures of SBR and NBR samples and their blends, measured by the DSC technique, are shown in Table IV. The glass transition temperatures detected in the pure rubber types were -22 and -49 °C for NBR and SBR, respectively. The addition of 10 phr UPE reduced the difference between the two transition temperatures. The degree of compatibility may thus be enhanced by the addition of 10 phr UPE. The presence of two glass transition temperatures does not imply complete incompatibility of the two components;<sup>22</sup> that is, the two phases could be present with some degree of compatibility, with the first phase possibly rich in one component and the second is rich in the other.

The variations of ultrasonic velocity and ultrasonic attenuation coefficient with SBR content in blank specimens and in specimens containing 5 and 10 phr UPE are shown in Figures 2 and 3, respectively. The ultrasonic velocity  $V$  and attenuation coefficient  $\alpha$  decreased with increase of SBR content. By the addition of UPE, both  $V$  and  $\alpha$  increased with UPE concentration, but only in blends containing SBR. In pure NBR specimens,  $V$  and  $\alpha$  remained unchanged with addition of UPE. The same observation was obvious in a recent work<sup>16</sup> in which the main attenuation relaxation peak in SBR, corresponding to the glass transition, shifted to higher temperatures with addition of 5 phr UPE, whereas the shift in the

same peak for NBR was very slight. The least square linear fittings are also shown in Figures 2 and 3 as solid lines. The correlation coefficient  $r$  is often used as a statistical quantity that varies between -1 and 1 and provides a measure of how data measured between two variables can be closely related to a straight-line regression. For  $N$  data points, the correlation coefficient is defined as follows:<sup>23</sup>

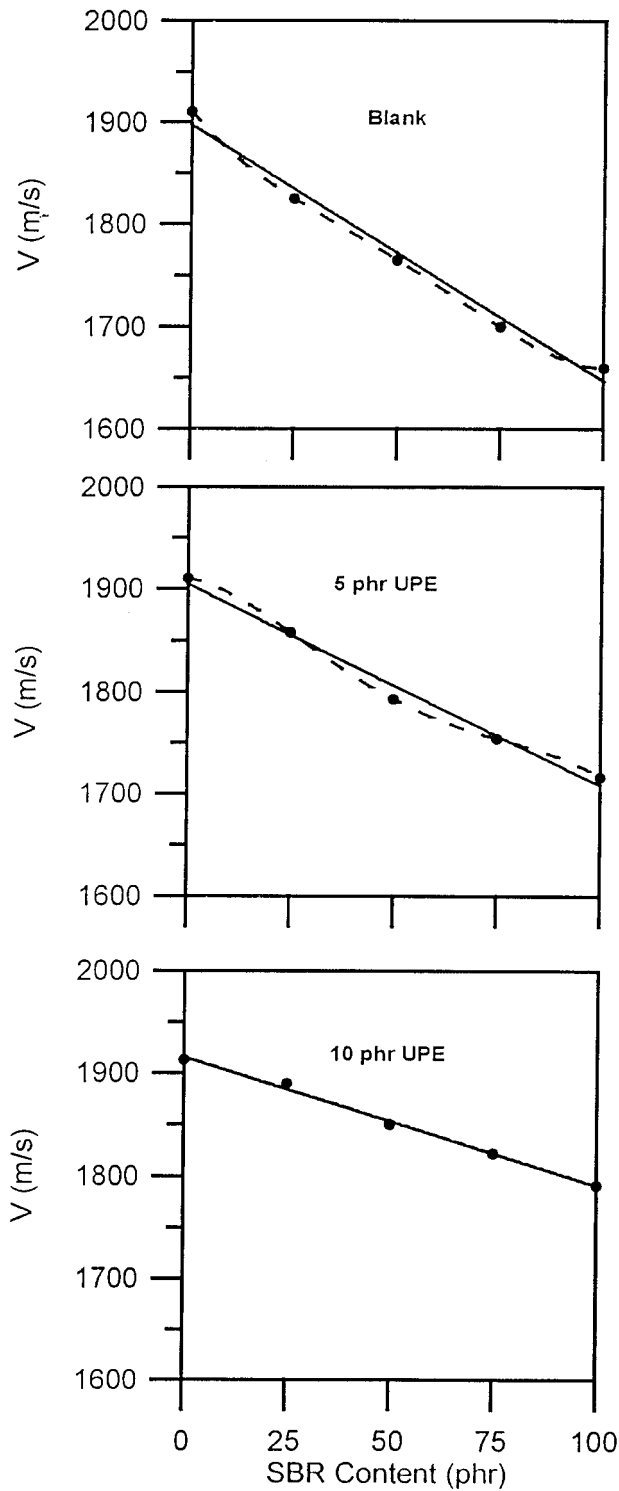
$$r = \frac{\sum X_i Y_i - (\sum X_i)(\sum Y_i)/N}{\{[\sum X_i^2 - (\sum X_i)^2/N][\sum Y_i^2 - (\sum Y_i)^2/N]\}^{1/2}} \quad (3)$$

where the summation covers the range  $i = 1-N$ . Because the correlation coefficient has the same sign as the slope of the line, it is preferable to use the square of the correlation coefficient as a quantitative measure of how experimental points fit well to the linear regression. The values of  $r^2$ , which may range from 0 to 1, of the linear fittings are listed in Table V. It is well known<sup>10,24</sup> that good linear fitting and high  $r^2$  values indicate a high degree of compatibility. Introducing 5 phr UPE improved DC to some extent, whereas 10 phr UPE improved DC considerably. The slopes of the different linear fittings,  $(-dV/dC)$  and  $(-d\alpha/dC)$  are listed in Table V. The slopes decrease with increase of UPE concentration. This inverse relationship indicates that the limiting values of attenuation and velocity, for blank SBR and blank NBR, approach each other mainly because of changes in attenuation and velocity of SBR and not in those of NBR.

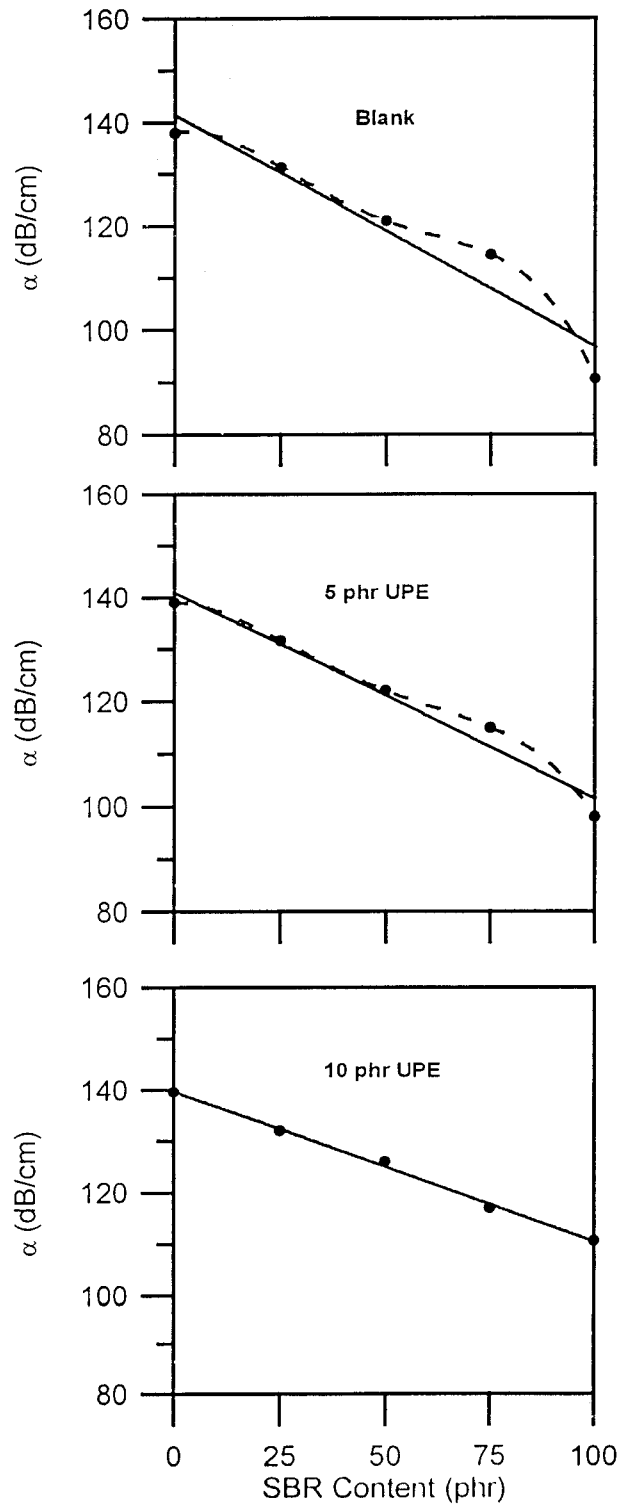
Scanning electron microscopy was used to determine the fine structure of SBR/NBR blends. SEM micrographs of SBR/NBR (50/50) with 5 and 10 phr UPE are compared with micrographs of the specimen without compatibilizer in Figure 4. These micrographs clearly indicate that the fine

**Table V Square of Correlation Coefficient ( $r^2$ ) and Slopes of Different Fittings of Velocity and Attenuation for Different UPE Concentrations**

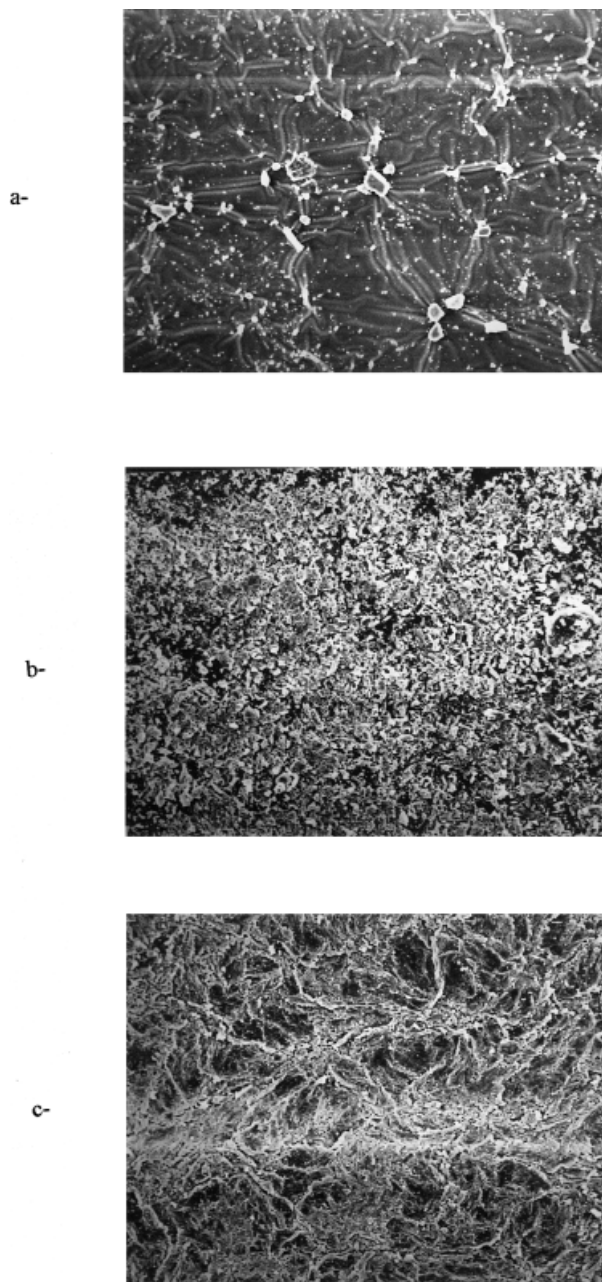
UPE Concentration	Velocity		Attenuation	
	$r^2$	$-dV/dC$	$r^2$	$-d\alpha/dC$
Blank	0.986	2.51	0.928	0.45
5 phr	0.988	1.96	0.970	0.39
10 phr	0.995	1.25	0.997	0.29



**Figure 2** Variation of ultrasonic velocity at 5 MHz and 20 °C with SBR content in blank SBR/NBR blends and in blends containing 5 and 10 phr of UPE.



**Figure 3** Variation of ultrasonic attenuation coefficient at 5 MHz and 20 °C with SBR content in blank SBR/NBR blends and in blends containing 5 and 10 phr of UPE.



**Figure 4** Scanning electron micrograph with 200 $\times$  magnification of (a) SBR/NBR = 50/50, (b) SBR/NBR = 50/50 + 5 phr UPE, (c) SBR/NBR = 50/50 + 10 phr UPE.

morphology is generated by the compatibilizer. Generally, the compatibilizer used here reduces the domain size and increases the interconnection between the phases of the blend.<sup>25</sup>

## CONCLUSION

It may be concluded that the addition of 10 phr UPE concentration in all rubber mixes decreases

the minimum torque ( $M_L$ ). In addition, the tensile strengths are improved by the addition of UPE. Finally, the percent of equilibrium swelling in toluene decreases considerably at 10 phr UPE because of the increase of the degree of crosslinking. In summary, the electrical, DSC, ultrasonic, and SEM data indicate that the addition of 10 phr UPE as a compatibilizing agent for SBR/NBR blends enhances the degree of compatibility.

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