

Improved Mechanical Properties of NR/EPDM and NR/Butyl Blends by Precuring EPDM and Butyl

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SYNOPSIS

Ethylene-propylene-diene rubber (EPDM) and isobutylene-isoprene rubber (IIR) were compounded, precured to a low degree, and then were blended with natural rubber (NR). The compounding ingredients for NR were then added and the final curing was done. NR/EPDM and NR/IIR blends, prepared using this method, were found to possess much improved mechanical properties as compared to their conventional counterparts. The optimum precuring crosslink density that has to be given to the EPDM and IIR phases has been determined. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The utilization of polymer mixtures to achieve a desired combination of properties has an obvious attraction, when compared with the economical and technical uncertainties associated with synthesizing new polymeric materials. Blending of two elastomers is done with specific objectives, such as enhancement of physical properties and improvement of resistance to the action of heat, oxygen, and ozone, and the improvement of processing characteristics. Such blends, however, usually show inferior mechanical properties as compared to the average properties of the constituent elastomers. Such deterioration in mechanical properties is most pronounced in blends, such as NR (natural rubber)/EPDM (ethylene propylene-diene-rubber and NR/IIR (butyl rubber). These pairs are different in the unsaturation of their constituents, resulting in widely differing cure rates. The constituents of these blends also are different in the solubility of curing agents.¹⁻⁵ The bulk of the curing agent is hence taken by the more unsaturated elastomer, leading to undercure in the other (slow curing) rubber. Both rubbers are not cured to their optimum crosslink densities, nor do they attain a covulcanized state, which is the prom-

inent reason for the less than average mechanical properties of the blends.⁶⁻¹⁰

NR possesses excellent physical properties and good processing characteristics. But its resistance to heat, oxygen, and ozone is not good and, hence, it is not employed in demanding applications. Blending with EPDM or IIR is an attractive way of improving the resistance of NR to heat, oxygen, and ozone, if moderate mechanical properties can be achieved.^{11,12} In this article, we report the effect of precuring the slower curing rubber (EPDM in NR/EPDM and butyl in NR/Butyl) as a possible route to attain a covulcanized state in NR/EPDM and NR/butyl blends, so as to improve their mechanical properties. The optimum level of precuring that has to be given to EPDM and butyl rubbers is determined and the mechanical properties of NR/EPDM and NR/butyl blends, prepared from precured EPDM and butyl, are compared with conventional blends.

EXPERIMENTAL

Materials

NR: ISNR-5; Mooney viscosity ML (1 + 4) 100°C-85.3 (Rubber Research Institute of India).

EPDM: ML (1 + 4) 100°C-52 (JSR-EP 33).

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Table I Formulations

Natural Rubber	100.0	—	—
Butyl Rubber	—	100.0	—
EPDM	—	—	100.0
Zinc Oxide	5.0	4.0	4.0
Stearic Acid	2.0	2.0	2.0
MBTS	0.6	0.6	0.6
TMTD	0.2	1.0	1.0
Carbon Black (HAF N-330)	50.0	50.0	50.0
Naphthenic Oil	8.0	8.0	8.0
Sulfur	2.5	1.5	1.5

Butyl rubber: 0.8 mol % unsaturation; ML (1 + 8) 100°C-50 (Exxon 065).

Rubber Additives

The zinc oxide, stearic acid, dibenzthiazyl disulfide (MBTS), tetramethyl thiuram disulphide (TMTD), sulfur, carbon black (HAF N-330), and naphthenic oil used were rubber grade.

Determination of Optimum Pre curing Levels

The optimum levels of pre curing that have to be given to the EPDM or butyl phase were determined from the variation of tensile properties of blends of NR/EPDM and NR/Butyl, with variation of pre curing. EPDM and butyl compounds were prepared on a laboratory mixing mill (6 × 12"), according to ASTM D 3182 (1982), as per formulations presented in Table I. These compounds were sheeted out from the mixing mill at a thickness of about 3 mm and then were pre cured for different times at different temperatures, varying from 120-160°C in a laboratory air oven. The crosslink densities of the pre cured EPDM and butyl rubber were evaluated by swelling measurement in toluene.¹³⁻¹⁵ The pre cured compounds were then blended with masticated NR in various compositions on the mill and compounding ingredients for NR were then added. The compounds were vulcanized to the respective optimum cure times and the tensile properties of the vulcanizates were determined.

Mechanical Properties of NR/EPDM and NR/Butyl Blends

EPDM and butyl rubbers, pre cured to the optimum levels, were blended with masticated NR at various percentages. The compounding ingredients required for NR were then added. The optimum cure times (time to reach 90% of the maximum torque) were

determined on a Goettfert elastograph model 67.85, as per ASTM D 1646 (1981). The compounds were then vulcanized to their optimum cure times in an electrically heated laboratory hydraulic press at 150°C. Dumbbell-shaped tensile test specimens were punched out of these compression-molded sheets along the mill grain direction. The tensile properties were measured on a Zwick Universal testing machine model 1445, using a crosshead speed of 500 mm/min, as per ASTM D 412-80.

Angular test specimens were punched out of the compression-molded sheets and tear resistance of the blends was measured on a Zwick UTM, according to ASTM D 624. Samples for abrasion resistance, compression set, hardness, and resilience were molded and tested as per relevant ASTM standards. The aging resistance of the vulcanizates was studied after aging the samples at 100°C for 24 h in a laboratory air oven.

Scanning Electron Microscope (SEM) Studies

The SEM observations of the tensile fracture surfaces of the conventional and modified 50/50 NR/EPDM and NR/IIR blends were made using a scanning electron microscope model JEOL JSM 35C.

The fracture surfaces of the test specimens were carefully cut from the test pieces and were then sputter coated with gold within 24 h of testing. The gold coated surfaces were examined through the scanning electron microscope.

RESULTS AND DISCUSSION

Figures 1 and 2 show the variation in tensile strength of a 50/50 NR/EPDM and NR/IIR blend with an amount of pre curing in the EPDM or IIR rubbers. In both cases, the tensile strength initially increases with the amount of pre curing, reaches a maximum, and decreases thereafter. In the case of the NR/EPDM blend, a maximum in tensile strength is observed at a pre curing crosslink density of 1.427×10^{-5} gm mole/cc in the EPDM phase and in the case of NR/IIR blends, when the crosslink density of pre cured IIR is 0.4311×10^{-5} gm mole/cc. Similar curves were obtained for other blend compositions, but maximum tensile strength was observed at slightly different crosslink densities. This shows that there is an optimum crosslink density, to which the EPDM or butyl rubber should be pre cured, to attain a maximum advantage in the mechanical behavior of their blends with NR; inhomogeneity develops in

the blends thereafter. Table II shows the effect of temperature on precuring of EPDM and butyl in 50/50 blends of NR/EPDM and NR/butyl. For attaining a certain degree of crosslinking, different times are required at different temperatures. Maximum tensile strength is not affected much by the temperature of precuring. Aging resistance of the blends is also not affected by the change of precuring temperature. Further studies on NR/EPDM and NR/butyl blends were done by precuring the EPDM and butyl phase up to the optimum level at 140°C.

Figures 3 and 4 show a variation of optimum precuring crosslink density in the EPDM and butyl phases with blend composition. The optimum precuring crosslink density decreases with an increase in EPDM or butyl rubber. This behavior throws light on the co-crosslinking of the blends. For developing moderate mechanical strength, a certain level of crosslinking may be necessary in both the elastomer phases and in the interface. The optimum level of crosslinking in EPDM or butyl is thus a compromise between the degree of crosslinking in these phases and at the interface with NR. When EPDM or butyl forms the continuous phase, the optimum crosslink density in it has to be lower in order to form a homogeneous blend with NR. The precuring in the EPDM or butyl phase possibly reduces the migration of the curing agents out of EPDM and butyl into the NR phase. Figure 5 shows the variation in tensile strength of NR/precured EPDM (hereafter referred to as modified blends) with the composition compared to that of the conventional NR/EPDM blends. The modified blends show better tensile

strength as compared to the conventional blends. The aging resistance is also found to be superior for the modified blends. Figure 6 shows the variation of tensile strength of the modified and conventional NR/Butyl blends, which also shows a behavior that is similar to the NR/EPDM blends. Figure 7 shows the elongation at break (EB) of the modified and conventional NR/EPDM blends. Modified blends show higher EB as compared to the conventional blends before and after aging. Since NR has higher EB as compared to EPDM, these values may be more influenced by the crosslink density in the NR phase. In the conventional curing of the blends, NR receives a higher proportion of the curing agents, resulting in overcure. The improved EB, in the case of modified NR/EPDM blends, points towards optimum crosslink densities in both the NR and the EPDM phases. Similar trends are shown by NR/Butyl blends as well (Fig. 8).

The variation of tear strength with blend composition for modified and conventional NR/EPDM and NR/Butyl blends is shown in Figure 9. The modified blends show better tear strength as well. The tear strength improvement with modification is even more pronounced than that of the tensile strength, since the tear strength is more sensitive to optimum crosslink densities in both rubber phases.¹⁶

Hardness, compression set, and abrasion resistance of the modified and conventional NR/EPDM and NR/Butyl blends are shown in Tables III and IV. The results are comparable for the modified and conventional blends. The cure characteristics of the

Table II Effect of Precuring Temperature and Time on the Tensile Strength of 50/50 NR/EPDM and NR/Butyl Blends

	Temperature of Precuring (°C)	Time (min)	Tensile Strength (N/mm ²)	Tensile Strength Retention After Aging at 100°C for 24 h (%)
50/50 NR/EPDM Blend	—	—	7.51	86
	120	120	16.52	72
	130	80	15.65	75
	140	40	17.70	72
	150	20	17.01	74
	160	15	17.40	75
50/50 NR/IIR Blend	—	—	8.60	86
	120	120	15.64	61
	130	70	17.91	60
	140	40	15.61	63
	150	25	16.63	60
	160	20	17.34	61

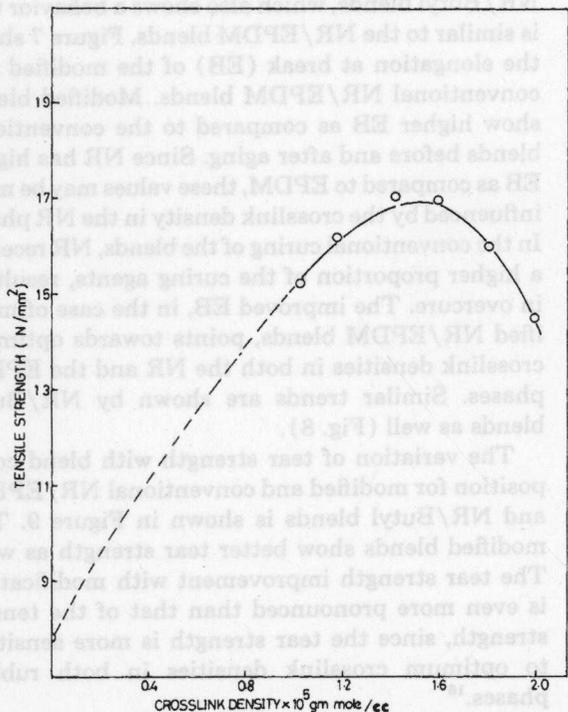


Figure 1 Variation of tensile strength of 50/50 NR/EPDM blend with precuring of EPDM rubber.

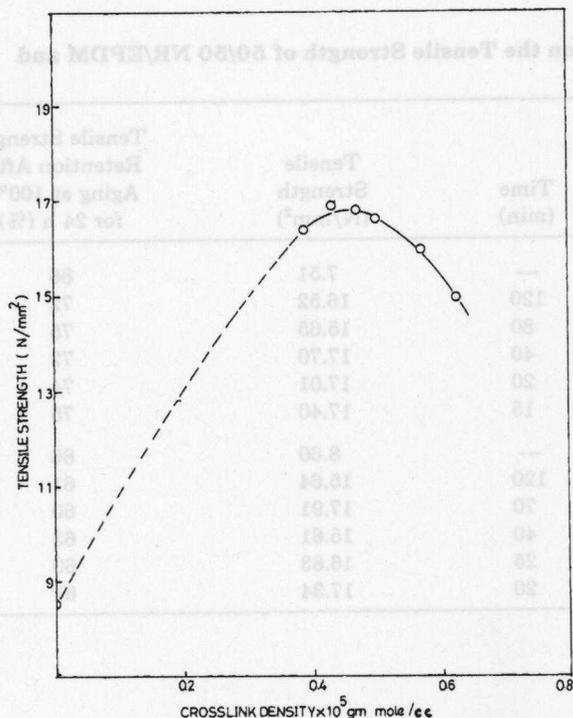


Figure 2 Variation of tensile strength of 50/50 NR/Butyl blend with precuring of butyl rubber.

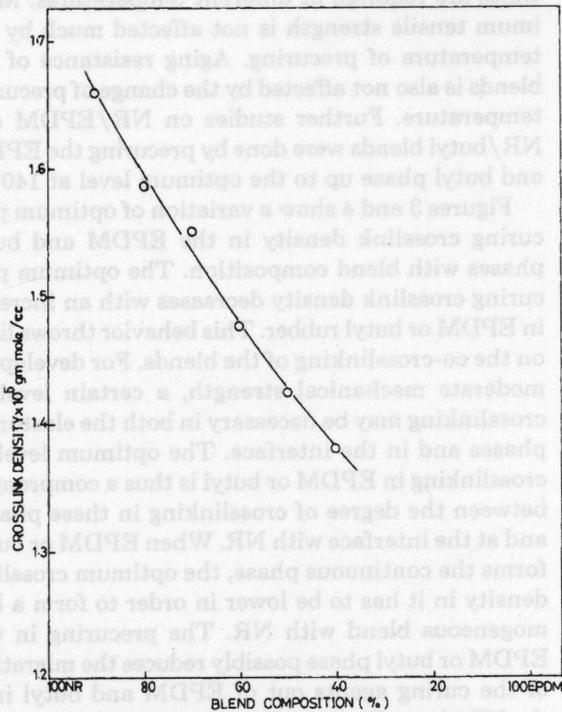


Figure 3 Variation of optimum crosslink density in EPDM phase vs. blend composition in NR/EPDM blends.

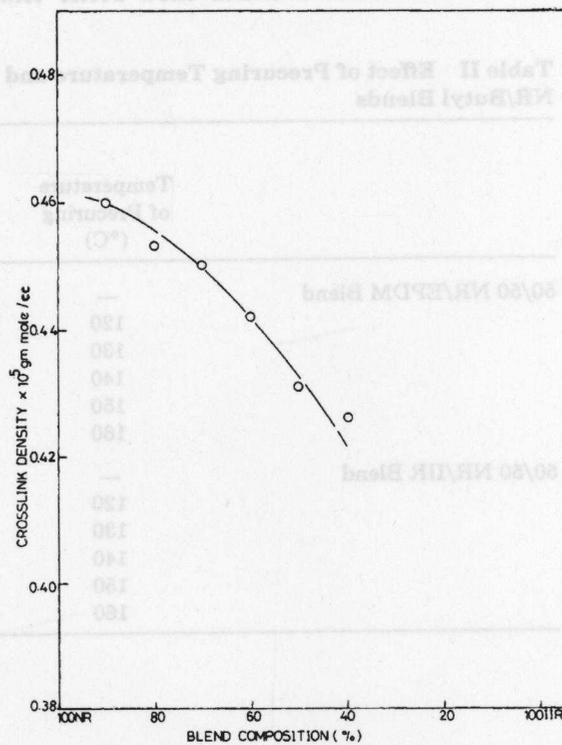


Figure 4 Variation of optimum crosslink density in butyl phase vs. blend composition in NR/Butyl blends.

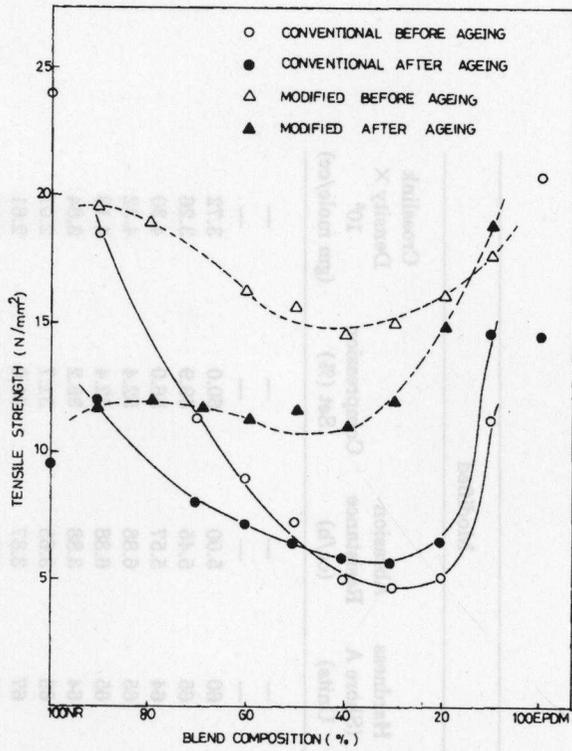


Figure 5 Tensile strength vs. blend composition of NR/EPDM blends.

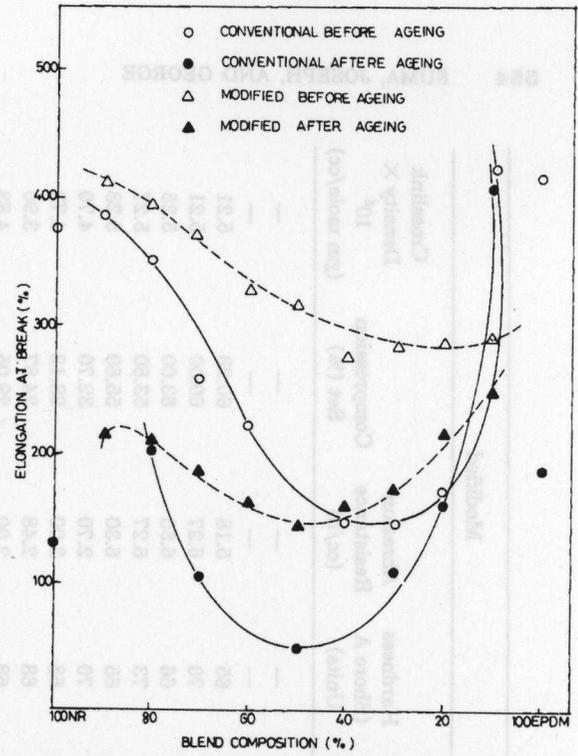


Figure 7 Elongation at break vs. blend composition of NR/EPDM blends.

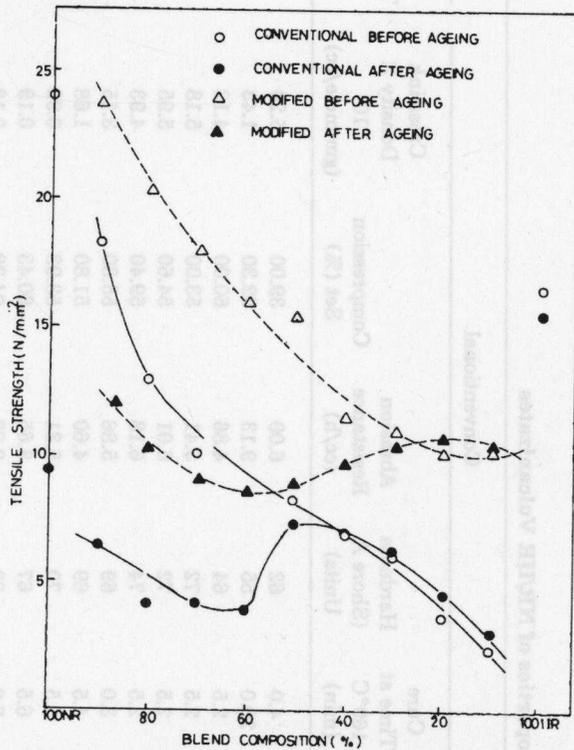


Figure 6 Tensile strength vs. blend composition of NR/Butyl blends.

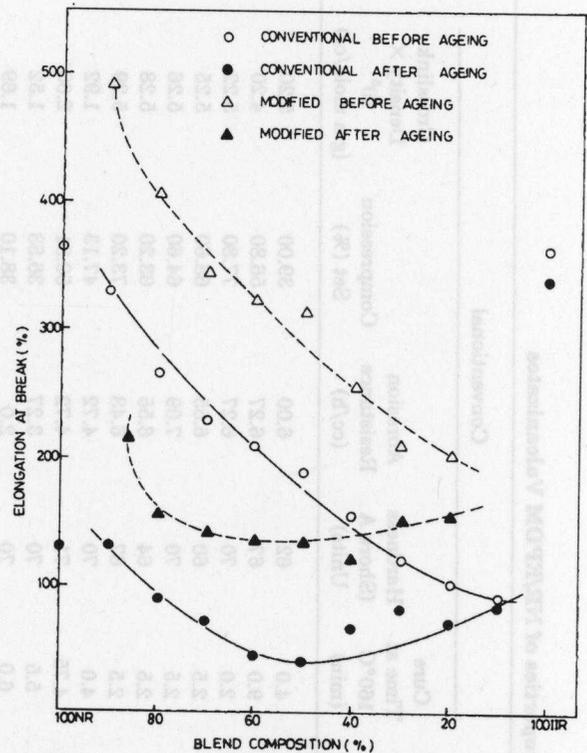


Figure 8 Elongation at break vs. blend composition of NR/Butyl blends.

Table III Properties of NR/EPDM Vulcanizates

NR	EPDM	Conventional					Modified				
		Cure Time at 160°C (min)	Hardness (Shore A Units)	Abrasion Resistance (cc/h)	Compression Set (%)	Crosslink Density $\times 10^6$ (gm mole/cc)	Cure Time at 160°C (min)	Hardness (Shore A Units)	Abrasion Resistance (cc/h)	Compression Set (%)	Crosslink Density $\times 10^6$ (gm mole/cc)
100	—	4.0	62	6.00	39.00	5.20	—	—	—	—	
—	100	9.0	67	6.27	56.80	4.20	—	—	—	—	
90	10	2.0	70	6.27	77.80	5.22	2.5	65	5.18	60.20	
80	20	2.5	60	6.55	68.60	5.25	3.0	70	6.27	60.00	
70	30	2.5	70	7.09	64.60	5.26	3.0	66	6.55	63.00	
60	40	2.5	64	6.55	63.20	5.28	3.5	73	6.27	53.80	
50	50	2.5	67	6.48	73.20	5.29	4.0	65	6.30	55.60	
40	60	4.0	70	4.72	47.13	1.92	4.0	70	2.70	32.70	
30	70	4.75	71	4.72	50.31	2.00	4.0	68	3.00	28.12	
20	80	5.5	70	3.27	36.53	1.52	5.0	68	2.48	24.87	
10	90	6.0	70	2.0	38.10	1.69	5.0	68	2.00	29.05	

Table IV Properties of NR/IIR Vulcanizates

NR	IIR	Conventional					Modified				
		Cure Time at 160°C (min)	Hardness (Shore A Units)	Abrasion Resistance (cc/h)	Compression Set (%)	Crosslink Density $\times 10^6$ (gm mole/cc)	Cure Time at 160°C (min)	Hardness (Shore A Units)	Abrasion Resistance (cc/h)	Compression Set (%)	Crosslink Density $\times 10^6$ (gm mole/cc)
100	—	4.0	62	6.00	39.00	5.20	—	—	—	—	
—	100	20.0	55	9.13	62.30	1.43	—	—	—	—	
90	10	2.5	64	4.86	60.00	4.12	3.0	60	5.00	60.0	
80	20	2.5	72	5.41	53.00	5.18	3.0	65	5.45	59.9	
70	30	2.5	72	6.01	54.60	5.95	3.5	64	5.57	56.0	
60	40	2.5	74	6.18	59.40	4.93	3.5	65	6.88	52.4	
50	50	3.0	69	5.86	55.80	3.15	3.5	65	6.88	52.4	
40	60	4.5	69	4.60	51.80	1.68	4.0	64	3.88	35.2	
30	70	5.5	70	5.81	53.93	0.90	5.0	65	3.65	31.7	
20	80	6.5	67	8.65	60.43	0.19	6.0	67	3.87	31.0	
10	90	7.0	63	8.93	64.32	0.18	6.0	66	6.06	30.7	

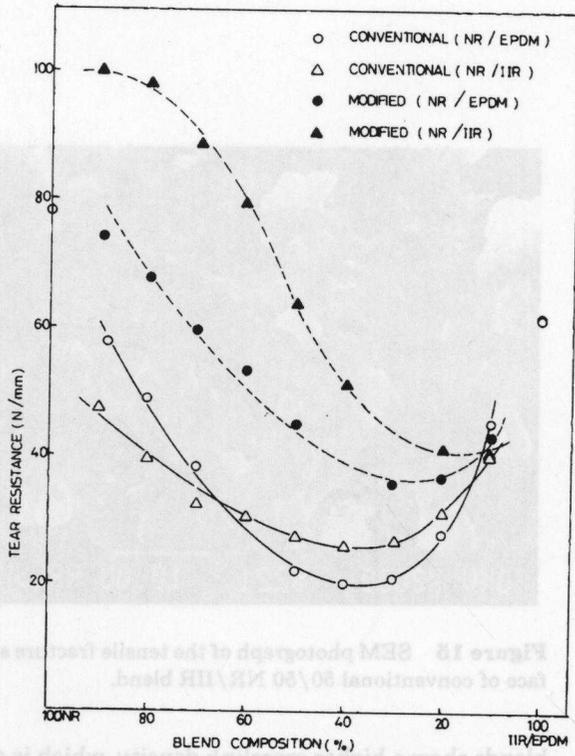


Figure 9 Tear strength vs. blend composition of NR/EPDM and NR/Butyl blends.

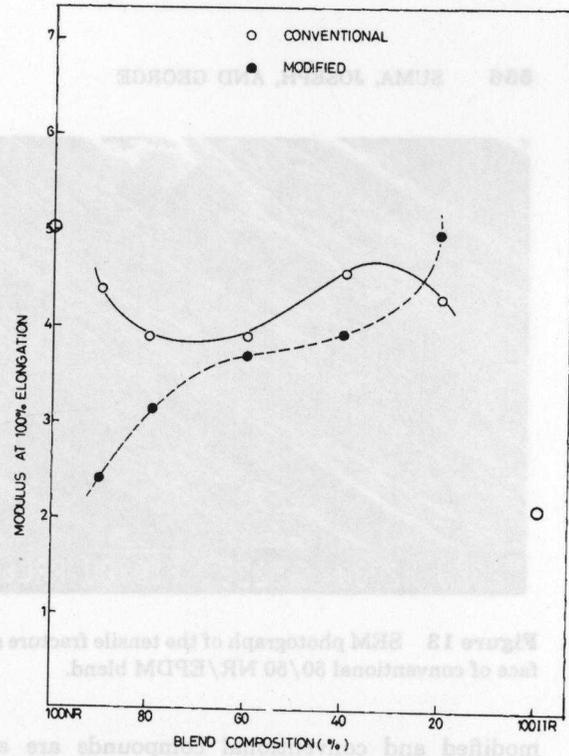


Figure 11 Variation of modulus at 100% elongation with blend composition of NR/Butyl blends.

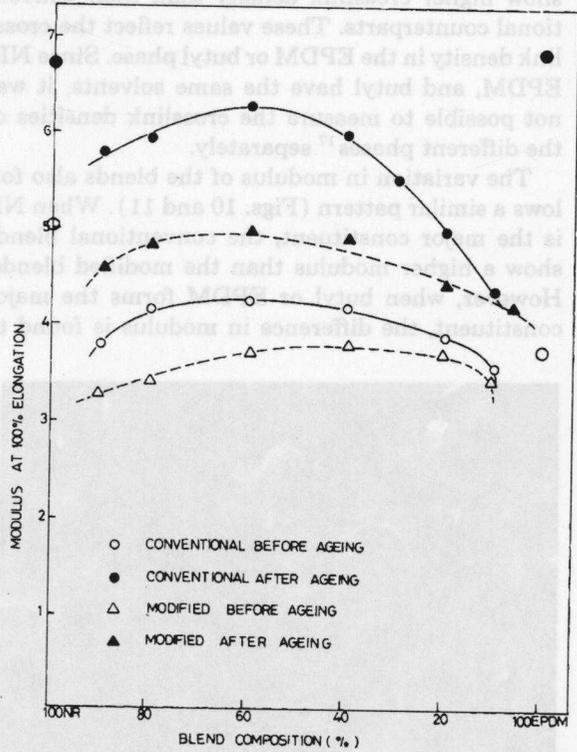


Figure 10 Variation of modulus at 100% elongation with blend composition of NR/EPDM blends.

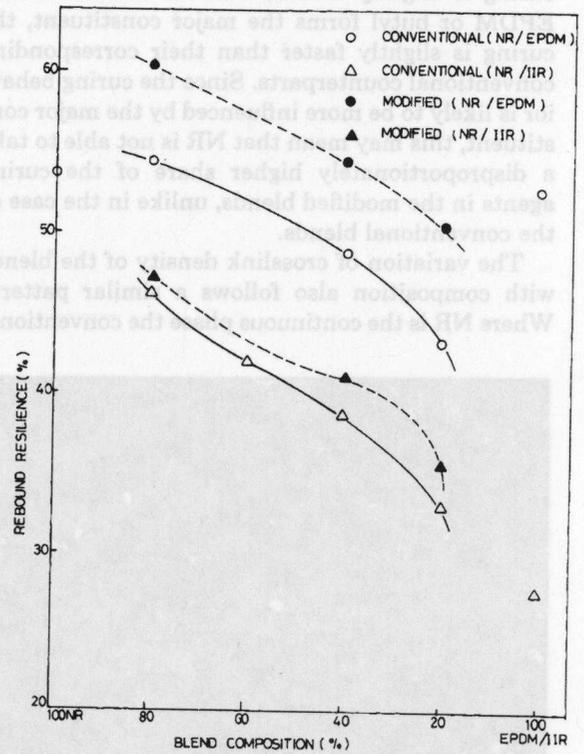


Figure 12 Rebound resilience vs. blend composition of NR/EPDM and NR/Butyl blends.

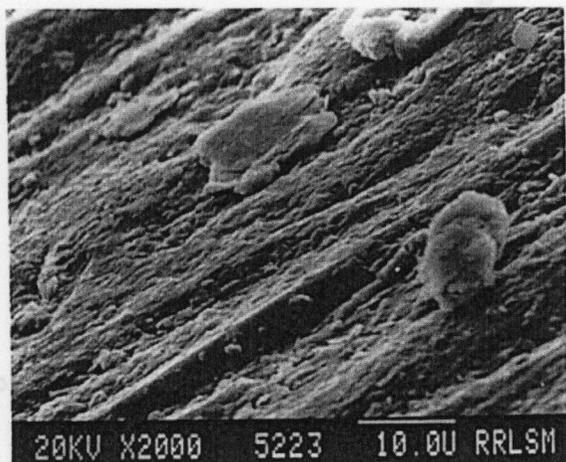


Figure 13 SEM photograph of the tensile fracture surface of conventional 50/50 NR/EPDM blend.

modified and conventional compounds are also shown in the Tables III and IV. In the modified blends, when NR forms the major constituent, the curing is slightly slower, whereas in cases where EPDM or butyl forms the major constituent, the curing is slightly faster than their corresponding conventional counterparts. Since the curing behavior is likely to be more influenced by the major constituent, this may mean that NR is not able to take a disproportionately higher share of the curing agents in the modified blends, unlike in the case of the conventional blends.

The variation of crosslink density of the blends with composition also follows a similar pattern. Where NR is the continuous phase the conventional

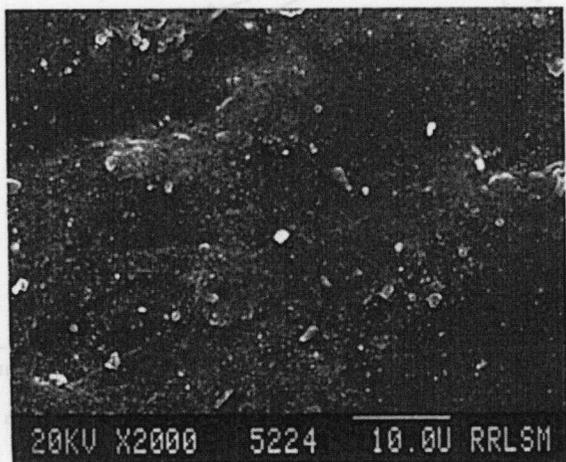


Figure 14 SEM photograph of the tensile fracture surface of modified 50/50 NR/EPDM blend.

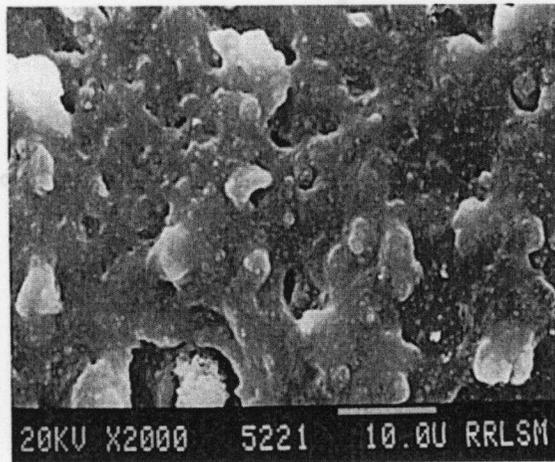


Figure 15 SEM photograph of the tensile fracture surface of conventional 50/50 NR/IIR blend.

blends show a higher crosslink density, which is obviously more influenced by NR. But when EPDM or butyl is the larger constituent, the modified blends show higher crosslink density than their conventional counterparts. These values reflect the crosslink density in the EPDM or butyl phase. Since NR, EPDM, and butyl have the same solvents, it was not possible to measure the crosslink densities of the different phases¹⁷ separately.

The variation in modulus of the blends also follows a similar pattern (Figs. 10 and 11). When NR is the major constituent, the conventional blends show a higher modulus than the modified blends. However, when butyl or EPDM forms the major constituent, the difference in modulus is found to

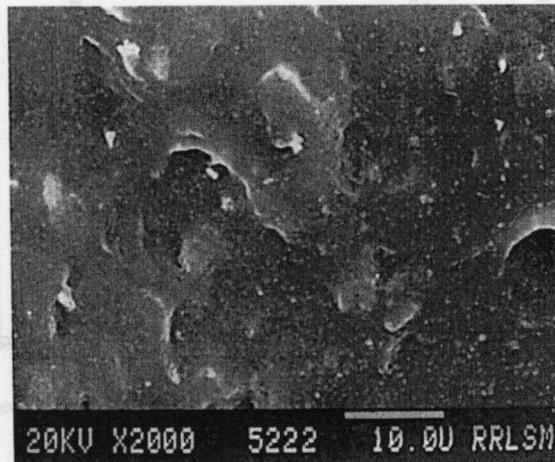


Figure 16 SEM photograph of the tensile fracture surface of modified 50/50 NR/IIR blend.

be marginal. This behavior is expected, since the modulus is directly proportional to the crosslink density. The variation of rebound resilience also follows a similar pattern (Fig. 12).

Figures 13 and 14 show SEM photographs of the fracture surfaces of conventional and modified 50/50 NR/EPDM blends. The fracture surfaces of the modified blend show a more smooth and homogeneous pattern, justifying its higher tensile strength. The same behavior is shown by 50/50 NR/IIR blends (Figs. 15 and 16).

CONCLUSIONS

1. A low degree of precuring in the EPDM phase in NR/EPDM blends and in the butyl phase in NR/butyl blends helps to attain a covulcanized state in these blends after the final curing.
2. Mechanical properties, which are influenced by the crosslink densities in both the phases and in the interface, are remarkably improved by the precuring.

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