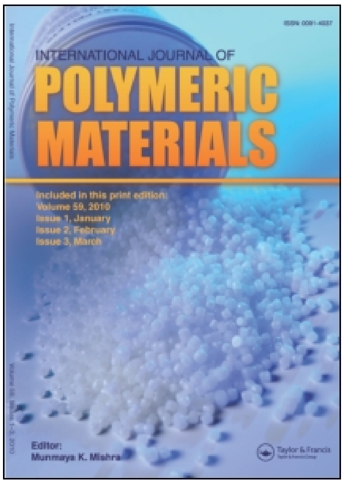

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On the Mechanical Properties of EPDM/CIIR Blends Cured with Reactive Phenolic Resin

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Blends of ethylene propylene diene monomer rubber (EPDM) and chlorinated isobutylene isoprene rubber (chlorobutyl, CIIR) with a reactive phenolic resin as the curing agent have been prepared through conventional two-roll mill mixing. The effect of resin curing on the mechanical properties of EPDM/CIIR blends was investigated and compared with conventional curing systems. The morphology of the blends as well as their thermal and steam aging resistance has also been reported. It was found that blends with a phenolic curing system exhibited superior mechanical and thermal aging properties and have potential applications in high-temperature engineered products.

Keywords blend, CIIR, cure compatibility, EPDM, mechanical properties, resin curing

INTRODUCTION

Blending two or more elastomers is carried out for specific objectives, such as the enhancement of mechanical properties, improvement of aging resistance, and for better processing characteristics. By blending different polymers, it is possible to bring some properties of the individual components to a single material [1,2]. A blend can have a set of properties that might offer it the potential of entering application areas that are not possible with either of its components [3].

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During the curing processes of blends, crosslinking forms a three-dimensional network structure, which has a strong influence on their physical properties. Many researchers have studied the important factors that determine the mechanical properties of blends [4–7]. It has been shown that for sulphur-cured EPDM/CIIR blends under certain severe conditions the properties, especially thermal and steam aging resistance, are inferior [8]. To be used for high-temperature applications such as in curing bladders, conveyor belts for hot material handling, and high-temperature service hoses, the hot air aging resistance of these blends should be improved. It is known that certain crosslinking systems, specifically the resin cure of blends, provide vulcanized networks of outstanding heat resistance [9]. This paper concerns the evaluation of physicomechanical properties of resin-cured EPDM/CIIR blends before and after aging, at various blend ratios. The improvement in the aging resistance under severe conditions and the evaluation of the technological dose threshold for industrial applications are the main goals of the present work.

EXPERIMENTAL

Materials

EPDM rubber with ethylidene norbornene (NDR 4640), Mooney viscosity [ML(1 + 8) at 100°C] 53.4, ethylene/propylene weight ratio 55/45 and iodine value 16.0 was supplied by Nodal Dupont. Chlorobutyl rubber (Exxon Chlorobutyl 1066) having Mooney viscosity [ML(1 + 8) at 100°C] 56.3, iodine value 8.4 and chlorine content 1.2(%), was supplied by Exxon Chemical Company. Polychloroprene rubber (neoprene MC 30 Butachlor) was supplied by Enichem Elastomers. The light cream flakes had a specific gravity of 1.23, volatile matter 1.3% and Mooney viscosity [ML(1 + 8) at 100°C] 46. Rubber additives such as zinc oxide, stearic acid, zinc chloride, methylol phenol resin (methylol content 9%), carbon black (HAF-N330), paraffinic oil and accinox ZC used in the study were of commercial grade.

Methods

Blends of EPDM and CIIR were prepared according to ASTM D 3182 (1982) as per the formulations given in Table 1. In this formulation phenolic resin (SP 1045) is used as the vulcanizing agent and neoprene serves as a halogen-containing activator. Zinc chloride is used as Friedel Craft's catalyst for better resin curing of EPDM [10]. Compounding was done on a laboratory two-roll mixing mill at a friction ratio of 1:1.25 with cold-water circulation. The optimum cure times of the compounds were determined using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) at 170°C at a frequency of

Table 1: Formulation of the compounding ingredients.

Ingredients	Recipe for EPDM (phr)	Recipe for CIIR (phr)
EPDM	95.0	–
CIIR	–	95.0
Neoprene	5.0	5.0
Reactive phenolic resin	10.5	10.5
$ZnCl_2$	2.0	–
ZnO	4.0	4.0
Stearic acid	1.5	1.5
Carbon black	40.0	40.0
Paraffinic oil	7.0	5.0
Antioxidant	1.0	1.0

50 cpm and a strain of 0.2 deg. The compounds were vulcanized up to their respective optimum cure times in an electrically heated laboratory hydraulic press at 170°C.

Dumbell-shaped tensile and angular tear test specimens were punched out of the compression-molded sheets along the mill grain direction and testing was carried out at a crosshead speed of 500 mm/min on a Universal Testing machine (Shimadzu, AG1) as per the relevant ASTM standards. Aging resistance and tension set of the vulcanizates were determined after aging the samples at 100°C for 24, 48, and 72 h in a laboratory air oven. Steam aging resistance of the vulcanizates was also studied using a steam chamber maintained at a pressure of one atmosphere for the time intervals 6, 18 and 36 h. Hardness of the vulcanizates was determined according to ASTM 2240 and expressed in Shore A units. Samples for abrasion resistance were molded and volume loss per hour was determined on a Zwick abrader according to DIN 53514. Samples for compression set, flex crack resistance and rebound resilience were molded and tested as per the relevant ASTM standards. The thermal stability of EPDM, chlorobutyl and their blends was studied using a thermogravimetric analyzer (TGA Q-50, TA Instruments). TGA was carried out under nitrogen atmosphere and samples were scanned from 30–600°C at a heating rate of 10°C/min. A constant sample weight was used in all cases. The microstructure of tensile fracture surfaces of the blends at varying compositions was studied using a scanning electron microscope (JEOL JSM 35C). The fracture surfaces of the test specimens were carefully cut from the test pieces and were then sputter-coated with gold before they were examined through the SEM.

RESULTS AND DISCUSSION

Cure Characteristics and Mechanical Properties

Cure characteristics of the resin-cured EPDM/CIIR blends and the physico-mechanical properties of the vulcanizates are given in Table 2. It is evident that

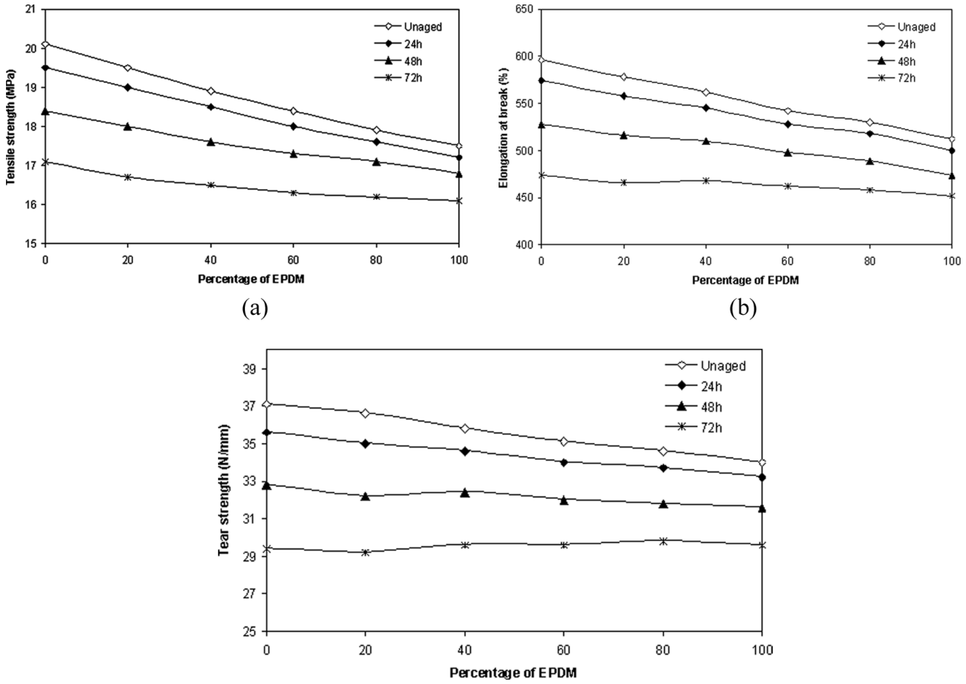
Table 2: Cure characteristics and stress-strain properties of resin-cured EPDM/CIIR blends.

Composition of EPDM (%)	Cure time (min)	Scorch time (min)	Max. torque (Nm)	Min. torque (Nm)	Tensile strength (MPa)	Elong. at break (%)	Tear strength (N/mm)
0	17.4	2.7	0.38	0.05	19.8	596	35.1
20	18.8	3.3	0.39	0.04	20.7	578	37.6
40	19.6	3.8	0.40	0.04	21.9	562	39.8
60	20.4	3.8	0.41	0.04	20.4	542	38.1
80	21.3	4.2	0.42	0.04	19.3	530	36.6
100	22.2	4.4	0.44	0.04	18.2	512	35.0

the cure times, scorch times and maximum torque of resin-cured blends increase with increased percentage of EPDM. It is generally observed that the mechanical response of the blend is closely related to its compatibility and a synergistic effect is often obtained for miscible or partially compatible blends [11,12]. Resin-cured vulcanizates exhibit remarkably high tensile and tear strength values which can be attributed to the increased extent of crosslink density and low values for elongation at break, due to the reduced elasticity of the chains due to resin curing. The possibility of curative migration from one phase to another owing to viscosity and unsaturation differences is not significant in resin-cured blends due to the larger size of phenolic resin molecules. This results in increased homogeneity of the blends, leading to better properties [13,14].

EPDM/CIIR vulcanizates at various compositions were subjected to thermal aging at 100°C for periods up to 72 h. Tensile strength, elongation at break and tear strength were determined and plotted against percentage composition of EPDM as illustrated in Figures 1a–c. As expected, the resin-cured blends exhibit outstanding heat resistance [15]. It can be seen that the tensile strength and tear strength values of pure EPDM and blends containing higher percentage of EPDM exhibit better retention in properties than that of pure CIIR and blends containing higher percentage of chlorobutyl. This is because the resin-curing system always shows a marching cure until it attains some saturation point. Chlorobutyl compound attains the saturation point faster than the EPDM compound and then it reverts [16]. The better retention in tensile and tear strength values of pure EPDM and vulcanizates containing higher EPDM content can be explained due to the increase in crosslink density because of the marching cure [17]. The elongation at break shows similar behavior due to the increased crosslink density during aging.

The effect of steam aging on tensile and tear properties of the blends is shown in Figures 2a and b. As in the case of thermal aging, the steam aging resistance is higher for blends with a higher percentage of EPDM. As expected, due to the elimination reactions occurring in halogenated



(a)

(b)

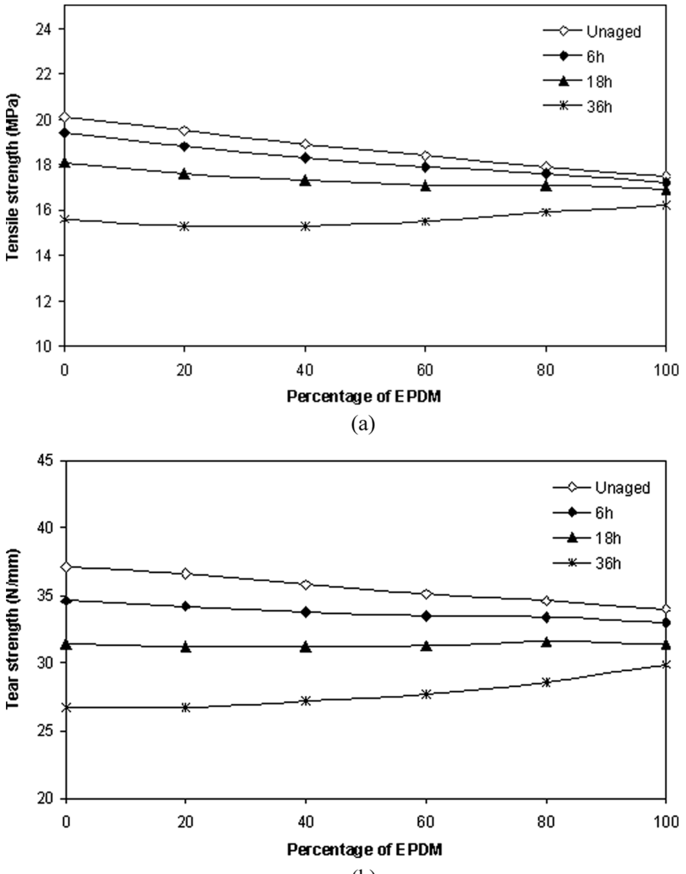
(c)

Figure 1: Variation of (a) tensile strength, (b) elongation at break and (c) tear strength of resin-cured EPDM/CIIR blends with aging.

compounds, which are severe during steam aging, there is not much retention in the properties for chlorobutyl and blends containing a higher percentage of chlorobutyl [18,19].

Table 3 shows the tension set and compression set values of the blends with composition. As the chlorobutyl content increases, the compression set decreases, which is an inherent property of chlorobutyl. Although the resin-cured blends exhibit inferior compression set properties, the low tension set, which is a major property required for a good bladder compound, is achieved by resin curing. The values are far better for blends containing a higher percentage of EPDM, which is due to the increase in crosslink density, because of the marching cure of EPDM vulcanizates, thereby strengthening the network by post curing.

Table 4 shows the variation of hardness, abrasion resistance and rebound resilience with blend composition for resin-cured EPDM/CIIR blends. On increasing the concentration of EPDM, the elasticity of rubber chains get reduced leading to increased hardness. For a given rubber compound, in addition to crosslink density, abrasion resistance is influenced by hardness of the vulcanizate [20–22]. So the abrasion resistance also increases with an



(a)

(b)

Figure 2: Effect of steam aging on: (a) tensile and (b) tear strength.

increase in EPDM content of the blend. As expected, the resilience value decreases with an increase in chlorobutyl content related to the inherent high strain energy density of chlorobutyl. The viscoelastic properties of CIIR are a

Table 3: Variation of tension set and compression set with percentage composition of EPDM.

Composition of EPDM (%)	Tension set values for resin-cured blends (%)			Compression set of resin-cured blends (%)
	24 h	48 h	72 h	
0	76	122	–	21.4
20	88	128	–	21.8
40	94	136	144	22.1
60	98	126	132	22.6
80	112	132	136	23.1
100	118	138	142	23.5

Table 4: Variation of hardness, abrasion weight loss and rebound resilience with percentage composition of EPDM.

Composition of EPDM (%)	Hardness (Shore A)	Abrasion weight loss (g)	Rebound resilience (%)
0	59.0	0. 40	11.0
20	61.0	0.35	16.5
40	63.0	0.31	22.5
60	66.0	0.25	31.0
80	68.5	0.21	40.0
100	71.5	0.16	51.0

reflection of the molecular structure of the polyisobutylene chain. This molecular chain with two methyl side groups on every other chain carbon atom possesses greater delayed elastic response to deformation [23,24].

The increment in cut length against number of flexing cycles is given in Figure 3. The results showed that the resin-cured vulcanizates have a higher cut growth resistance. In addition to the improved interaction between the rubber matrices, the crosslinking in resin curing was by activated phenolic resin so that the crosslinks formed are much more flexible compared to the S-S bonds formed by sulphur curing. With an increase in chlorobutyl content, the flex crack resistance increases which is due to the inherent high viscoelastic nature of the latter [25,26].

Thermal Degradation

Thermogravimetric plots for resin-cured EPDM, CIIR and their selected blends are given in Figure 4. As compared to the degradation of individual components, the degradation behavior of the blends was slightly different. It has been reported that improved stability can be achieved by the incorporation

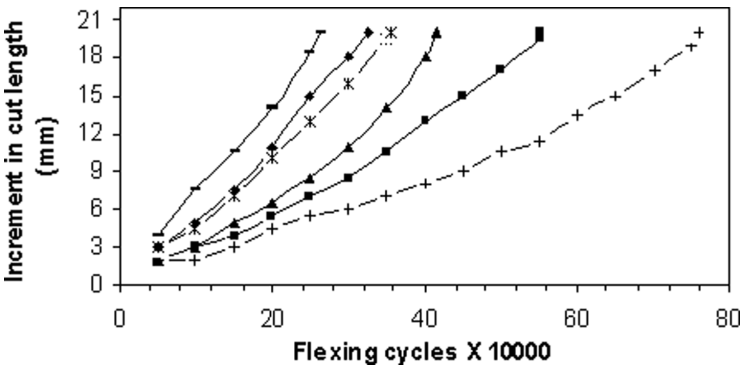


Figure 3: Increment in cut length against flexing cycles for resin-cured EPDM/CIIR blends at a precut of 2.0 mm. —, 100/0; ◆, 80/20; ж, 60/40; ▲, 40/60; ■, 20/80; +, 0/100.

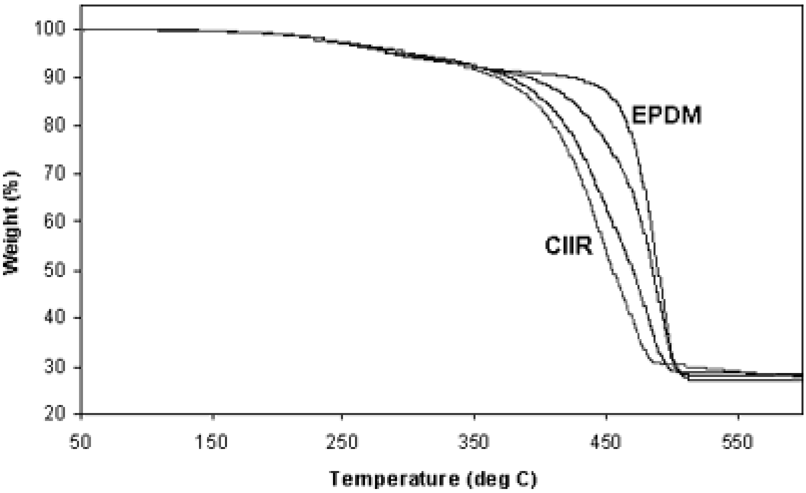


Figure 4: TGA curves of resin-cured EPDM, CIIR and their blends at two selected compositions.

of a second polymer [27,28]. This is attributed to the fact that in the pyrolysis of EPDM/CIIR blends, each component degrades in a manner different from that observed when EPDM and CIIR are degraded separately. It can be explained by assuming that radicals generated by chain scission in the first stage of

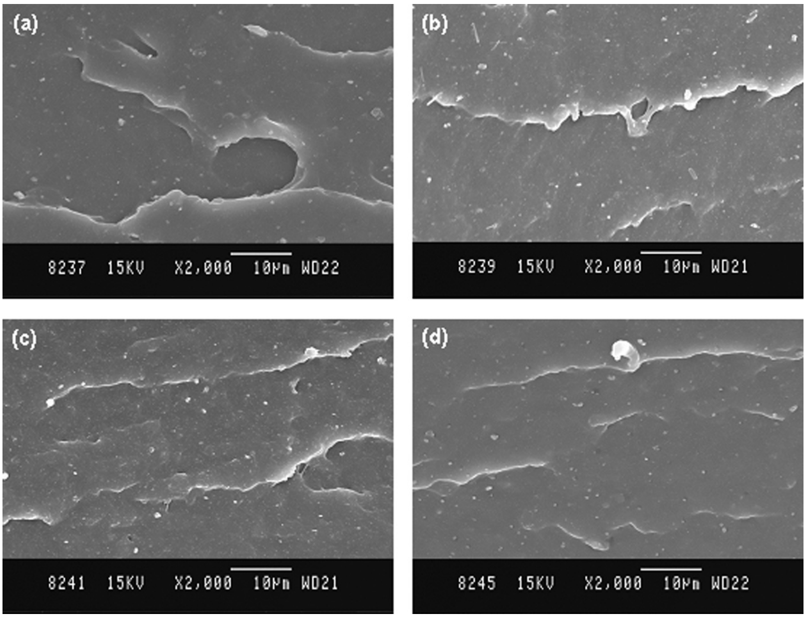


Figure 5: SEM images of tensile fracture surfaces of EPDM/CIIR blends. (a) 20/80; (b) 40/60; (c) 60/40; (d) 80/20.

degradation in one elastomer phase diffuse into the second elastomer phase, hydrogen abstraction takes place, and the radicals which would normally contribute to degradation of the elastomer phases are thus stabilized [29]. But the products of pyrolysis are identical both qualitatively and quantitatively.

Fracture Surface Morphology

Scanning electron microscopy (SEM) has been used to examine the fracture surface morphology of the blends. SEM images of the tensile fractured surfaces of blends of EPDM with CIIR at various compositions are shown in Figure 5. The images project a smoother homogeneous pattern for the blend compositions, justifying their higher aging resistance, tensile strength and other mechanical properties [30].

CONCLUSIONS

Blends of EPDM and CIIR have been prepared with reactive phenolic resin as the curing agent. Mechanical properties of these blends are seen to have improved in comparison to those with traditional sulphur curing. This is attributed to the uniform crosslinking of both phases and in the interphase, which are remarkably improved by resin curing. Phenolic resin molecules, owing to their bulky nature, prevent the migration of the curatives to a great extent. Additionally, the blends show additive behavior with respect to the ratio of the component elastomers. The fracture surface morphology of the blends exhibits co-continuous morphology, which substantiate our observations for the higher aging resistance and thermal degradation resistance along with mechanical properties. Of all the properties studied, the best performance by resin-cured vulcanizates is in the outstanding thermal aging and degradation resistance which can be used in curing envelopes and high-temperature conveyor belts, among other uses.

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