EPDM/CIIR BLENDS: RHEOLOGY, AIR PERMEABILITY, THERMAL STABILITY AND THERMAL DIFFUSIVITY

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Abstract: Blends of two commercially important synthetic elastomers (Ethylene Propylene Diene Monomer rubber (EPDM) and chlorobutyl rubber (CIIR)) were prepared using two-roll mill mixing. Effect of nature and degree of crosslinking with different vulcanizing agents as well as the composition of blends on their rheological characteristics and processability were examined using a capillary rheometer. To explore their possible applications, the air permeability at varying temperatures is measured. We also report on the thermal diffusivity of EPDM/CIIR blends being investigated using photo thermal deflection technique. Results of the thermal diffusivity and thermal degradation resistance reveal that the blends are suitable for high temperature applications such as in the manufacturing of curing envelopes.
Key words: EPDM, CIIR, Rheology, Air permeability, Thermal diffusivity.

1. Introduction

Our ability to engineer novel materials has led to unprecedented opportunities in polymer science and technology. It has fueled rapid development in polymer blends and alloys for the past several decades leading to the creation of new materials with interesting properties. In the framework of this development, the domain of elastomer blends is attracting more and more researchers; both academic and industrial. The purpose of alloying or blending of two or more polymers or copolymers is to gain synergistic improvement in properties at both micro and macro levels[1].

Ethylene Propylene Diene Monomer rubber (EPDM) is a commercially important synthetic rubber having wide range of applications, mainly because of their physical properties such as high heat resistance, ozone resistance, and cold and moisture resistance. Because of the low gas and moisture permeability, good weathering resistance and high thermal stability of chlorobutyl rubber (CIIR), blends of EPDM with CIIR will be attractive for several commercial applications.

Considerable amount of work has been reported by our group on blends of EPDM and CIIR under varying curing conditions[2-5]. However, for a specific application it is necessary to tailor-make a composition having the desired rheological behavior and physico-mechanical properties. It has been reported that the flow behaviour of polymer systems depends mainly on molecular characteristics, flow geometry and processing conditions such as temperature, shear rate or frequency[6-12]. In the present investigation, we report on the processability of blends of EPDM and CIIR for use in envelopes for precured retreading. Rheological characteristics at different blend compositions over a wide range of temperatures, shear rates and various curing conditions are investigated. The extrudate die swell is also noted to correlate with the elastic behaviour of the blends. Air permeation characteristics of EPDM/CIIR blends that are vulcanized under sulphur curing, pre-curing and resin curing conditions are also reported. We have also studied the thermal diffusivity of EPDM/CIIR blends under varying curing conditions along with the effect of blending on the thermal stability.

2. Experimental

2.1 Materials

EPDM rubber with ethylidene norbornene (NDR 4640), having a Mooney viscosity [ML(1+8)@100 ºC] 53.4, ethylene/propylene weight ratio 55/45 and iodine value 16.0, was supplied by Nodal Dupont. EPDM with dicyclopentadiene as diene (301 T), having a Mooney viscosity [ML(1+8)@100 °C] 47.8, ethylene/propylene weight ratio 68/32 and iodine value 10.5, was supplied by Herdillia Unimers; Chlorobutyl rubber (Exxon Chlorobutyl 1066) having Mooney viscosity [ML(1+8)@100 ºC] 56.3, iodine value 8.4 and chlorine content 1.2%, was supplied by Exxon Chemical Company. Neoprene rubber (MC 30 Butachlor) was supplied by Enichem Elastomers. The light cream flakes had a specific gravity 1.23, volatile matter 1.3% and Mooney viscosity [ML(1+8)@100 °C] 46. Rubber additives such as zinc oxide, stearic acid, zinc chloride, methylol phenol resin (methylol content 9%), dibenzthiazyl disulphide (MBTS), tetramethyl thiuram disulphide (TMTD), zinc diethyl dithio carbamate (ZDC), 2-(4-morpholinyl mercaptobenzthiazole) (MOR), sulphur, carbon black (HAF-N330), paraffinic oil and antioxidant (accinox ZC) used in the study were of commercial grade.

Table 1. Formulation of the compounding ingredients

Ingredients	Recipe* (phr)			
	Resin curing		Sulphur curing	
	EPDM	CIIR	EPDM	CIIR
EPDM	95.0	-	100	-
CIIR	-	95.0	-	100
Neoprene	5.0	5.0	-	-
Reactive phenolic	10.5	10.5	-	-
resin	2.0	-	-	-
$ZnCl_2$	-	-	1.0	-
MBT	-	-	0.5	-
TMTD	-	-	0.5	-
ZDC	-	-	-	1.0
MOZ	-	-	1.0	1.5
Sulphur	7.0	5.0	7.0	5.0
Paraffinic oil				

*All the compounds contain ZnO at 4 phr, stearic acid at 1.5 phr, carbon black at phr and antioxidant at 1 phr

2.2 Methods

The blend compounds for sulphur curing and resin curing were prepared according to ASTM-D 3182 on a laboratory two-roll mixing mill (16 × 33 cm) at a friction ratio of 1:1.25 as per the formulations given in Table 1. In the precuring method (where sulphur has been used as the curing agent), chlorobutyl is compounded, precured to 20% of its optimum cure time and is then blended with compounded EPDM[4]. The rheological measurements were carried out using a capillary rheometer MCR 3210 attached to the Universal Testing Machine (Shimadzu-AG1). From the recorded force and the cross head speed of the plunger, shear stress, shear rate and the shear viscosity were calculated. The diameter of the extrudate after 48 hours of extrusion and the swelling index were determined. The cure curves of the mixes were taken at 170 °C using a Rubber Process Analyzer (RPA 2000, Alpha Technologies). The compounds were then vulcanized up to their respective optimum cure times on an electrically heated laboratory hydraulic press at 170 °C. Permeability measurements were carried out according to ASTM D 1434 (1982) using air at a flow rate of 500 ml/min. Test

specimens of thickness 2 mm were moulded and used for measurements at 40 and 70 °C. The equipment used was Lyssy Manometric Gas Permeability Tester (L 100-2402). Thermal stability of the blends was studied using thermogravimetric analyzer (TGA Q-50, TA Instruments). Analyses were carried out under nitrogen atmosphere and samples were subjected from 30 to 600 °C at a heating rate of 10 °C/min. A constant sample weight was used in all cases. Thermal diffusivity of the materials was determined by photo thermal deflection (PTD) technique in which samples of 2 mm thickness and 1 cm diameter were used. Effect of thermal ageing at 100 °C for 24 and 48 hours on thermal diffusivity was also studied. To improve the thermal diffusivity of the blends, 1 phr of boron nitride was added and its subsequent effect on thermal diffusivity is also studied.

3 Results and discussion

3.1 Processability characteristics

Processability characteristics such as shear viscosity and extrudate die swell at different blend compositions over a wide range of temperatures, shear rates and various curing conditions are studied using a capillary rheometer and the results obtained are discussed below.

Figure 1 shows the plots of shear viscosity versus shear rate at 100 °C for filled 50/50 EPDM/CIIR blends under sulphur curable, partially precured and resin curable conditions. For all systems the shear viscosity falls sharply with increasing shear rate, confirming pseudoplastic flow behaviour of the systems. As expected, the partially precured blend exhibits highest shear viscosity as it contains partially cured chlorobutyl. The slightly higher values for resin curable blends when compared to the sulphur curable counterparts are attributed to the presence of entangled long chain resin molecules.

Figure 2 is a plot of shear viscosity against shear rate of sulphur curable 50/50 EPDM/CIIR blends at different temperatures. In all cases the viscosity drops with shear rate showing typical pseudoplastic behaviour. At high shear rates the temperature has little effect on the viscosity and all the points converge to a small area. The convergence occurs at around 1000 s^{-1}. Hence it is evident that at high shear rate (above 1000 s^{-1}), temperature is not a critical parameter for controlling the flow properties of blends of EPDM and CIIR. This is due to the fact that at higher shear rates, the stress alignment of the long and coiled chains occurs; thereby reducing the resistance to flow and thus lowering down the viscosity.
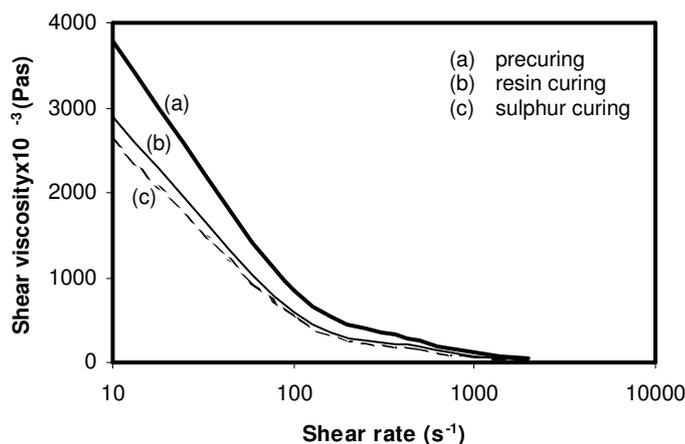
Figure 1. Variation of shear viscosity with shear rate for 50/50 EPDM/CIIR blends at 100 ºC
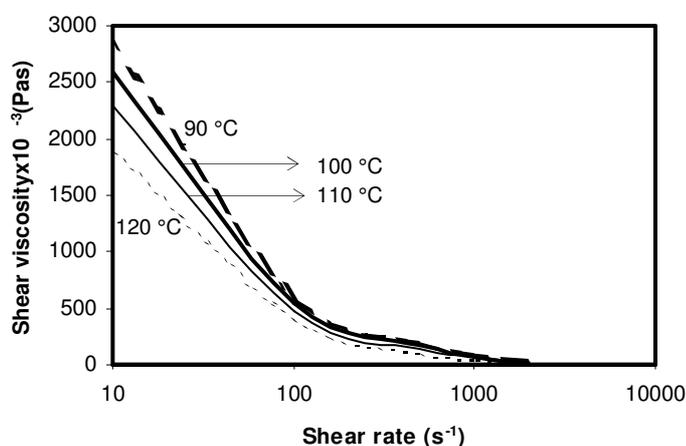

Figure 2. Shear viscosity against shear rate of sulphur curable 50/50 EPDM/CIIR blends at different temperatures

This effect is much predominant over the effect of temperature. Similar trend has been observed irrespective of the curing agent/method adopted. This might help to process the blends at high shear rates but at low temperature, still achieving the desired viscosity, thereby avoiding the possible thermal decomposition.

Figure 3 shows the effect of blend ratio on shear viscosity of sulphur curable blends at two different shear rates. At both shear rates, the viscosity increases with EPDM content and show maximum value for 100 % EPDM. Viscosities of the blends fall in between that of pure components which further indicates the compatible behaviour of the blends. The change in viscosity with shear rate is dominant where EPDM content is high. This was very well expected because EPDM possesses higher viscosity than CIIR and is attributed to the severe wall slip mechanism in the case of EPDM[8].
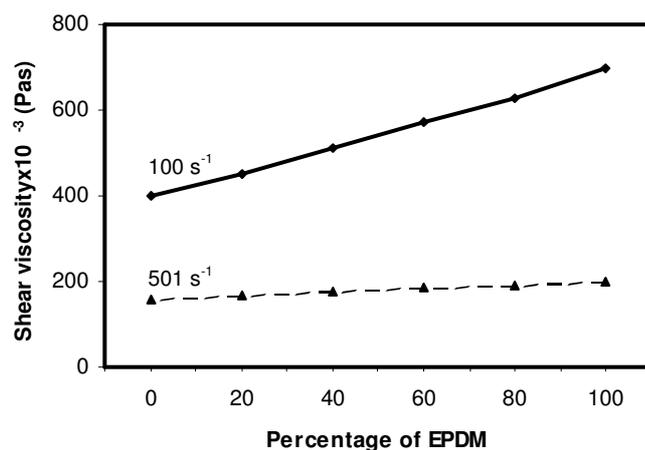
Figure 3. Variation of shear viscosity of EPDM/CIIR blends with percentage of EPDM at 100 °C

The extrudate swell characteristics at 100 °C for sulphur curable, resin curable and partially precured 50/50 EPDM/CIIR blends at varying shear rates are shown in Figure 4. It is evident from the figure that die swell is maximum for sulphur curable blend and minimum for the partially precured blend. Due to the partial crosslinking of the CIIR phase, the latter exhibits better dimensional stability. The lower swelling of resin curable blend when compared with that of sulphur curable one can be attributed to the presence of entangled resin molecules.

Figure 5 shows the variation of extrudate die swell with EPDM content for sulphur curable blends at 100 °C at different rates of extrusion. At low shear rates, the die swell increases marginally with increase in EPDM content in the blends. But at high rate of extrusion, a reverse trend results; the die swell decreases with increasing EPDM content in the blends. This may be due to the fact that the elastic response of CIIR is much higher than that of EPDM and is more predominant at high shear rates. This response gives rise to high die swell at high rate of extrusion for pure CIIR and blends containing higher amount of CIIR.
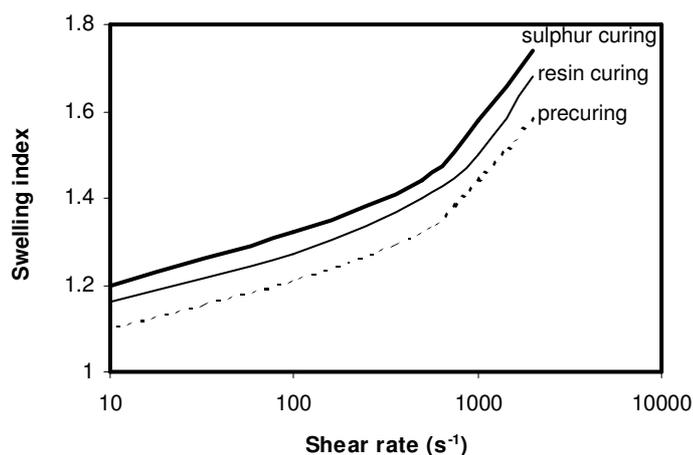
Figure 4. Extrudate swelling index against shear rate of 50/50 EPDM/CIIR blends at 100 °C under varying curing conditions
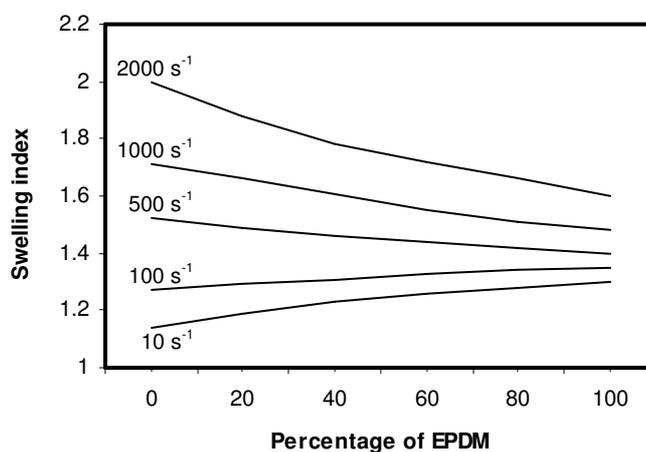

Figure 5. Extrudate swelling index of EPDM/CIIR blends with percentage of EPDM at different shear rates

3.2 Air permeability

The basic requirement for a pneumatic tube or an envelope is that it must be highly impermeable to air. Several methods have been adopted for developing such materials for commercial applications including the synthesis of new polymers, copolymerization and blending of miscible polymers etc.[13]. Permeation properties are sensitive to changes in membrane structure such as crystallinity, crosslinking, additives and phase morphology[14-17]. The air permeabilities of sulphur cured, precured and resin cured EPDM/CIIR blends at 40 °C for varying blend compositions are given in Figure 6.
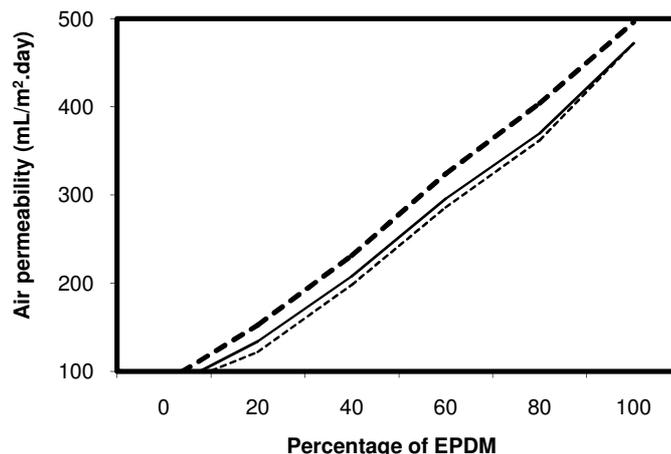
Figure 6. Variation of air permeability at 40 °C for EPDM/CIIR blends under varying curing conditions (from top to bottom: resin curing, sulphur curing, precuring)

There is an almost linear variation in permeability with blend composition with highest permeability for resin cured vulcanizate and lowest for the precured one. The air permeation behaviour for the various vulcanizates follows the order: resin cured > sulphur cured > precured. In both sulphur cured and precured vulcanizates, efficient vulcanizing system is used resulting in the formation of higher percentage of stable monosulphidic crosslinks. By precuring, the curative migration is reduced to a large extent resulting in vulcanizates with increased crosslink density. This results in stable and compact structure when compared with the sulphur cured blends. For the resin-cured vulcanizates, the crosslink density is comparatively low. Moreover the percentage free volume is more due to the bulkier phenolic resin linkages. As the number of crosslinks per unit volume of the polymer molecules increases, it becomes very difficult for the gas molecules to pass through the tightly crosslinked system in the case of sulphur curing and precuring. Therefore, crosslink density and partly the nature of crosslinks, influence the gas permeation behaviour.

3.3 Thermal response

Thermal resistance of polymers is another important parameter for testing the suitability of the material for retreading envelope. Fabrication of a variety of articles and their end uses need a detailed understanding of the thermal behavior of polymers.[18] For products like curing envelope, curing diaphram etc. the thermal conductivity is a significant parameter because it is the heat generated within the envelope/diaphram that is transferred to the tyre during vulcanization. In this study, photo thermal deflection (PTD) technique is used to determine the thermal diffusivity of compounds[19].

Figure 7 shows the variation of thermal diffusivity of sulphur cured EPDM/CIIR blends under unaged conditions and after 24 and 48 hours of ageing. Even though CIIR is slightly polar, the thermal conductivity, which is directly proportional to the measured thermal diffusivity, is maximum for EPDM and blends containing higher percentage of EPDM possibly due to the increased extent of interaction between EPDM and carbon black. The thermal diffusivity values increase marginally with ageing. This is probably due to the post vulcanization reaction, which strengthens the network thereby making the structure more rigid and compact so that the thermal vibrations can more easily pass through the material.
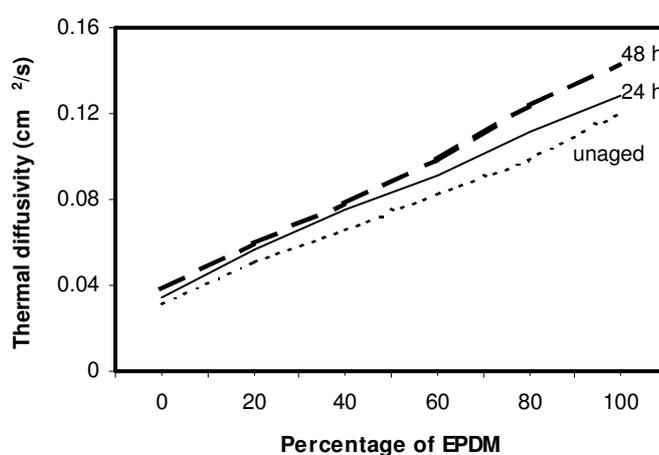
Figure 7. Variation of thermal diffusivity of EPDM/CIIR blends with percentage of EPDM under different conditions of thermal ageing

The effect of addition of 1 phr of boron nitride on thermal diffusivity of the blend compounds is shown in Figure 8. As seen from the figure, the addition of boron nitride increases the thermal diffusivity of all the compounds abruptly. The highest fluctuation is shown by EPDM. Boron nitride resembles graphite in its structure and the presence of free electrons enhances the thermal diffusivity of the samples. These results are highly attractive, especially for products like curing diaphragms, envelopes etc. where the increased thermal diffusivity not only enhances the green tyre curing rate but also may reduce the extent of bladder degradation.
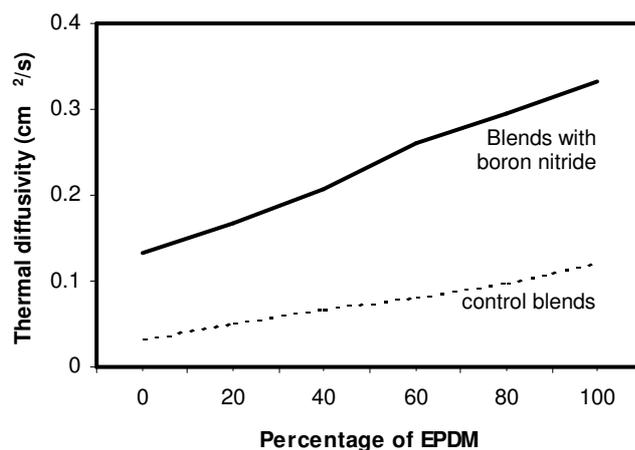
Figure 8. Effect of boron nitride on thermal diffusivity of EPDM/CIIR blends
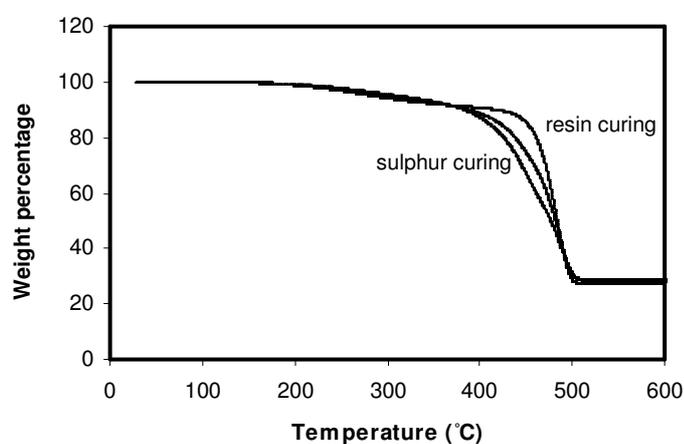

Figure 9. TGA curves for sulphur cured, precured and resin cured 50/50 EPDM/CIIR blends showing the highest thermal degradation resistance for resin cured and lowest for sulphur-cured vulcanizates

Figure 9 shows the TGA curves of sulphur cured, precured and resin cured 50/50 EPDM/CIIR blends. The onset of thermal degradation (temperature of 10 % degradation) and the peak degradation temperature (from the DTG curves) are found to be highest for resin cured and lowest for sulphur cured vulcanizates. On comparing the decomposition pattern, resin cured blends exhibit the highest degradation resistance, followed by precured and finally for sulphur cured blends. The enhancement in thermal stability of precured blends than the conventional sulphur cured blends may be due to the improved compatibility of the component elastomers caused by the reduced curative migration. The superior thermal stability of resin crosslinked vulcanizates is due to the formation of C-O-C linkages, which

are more thermally stable than C-S-C linkages in conventional sulphur cured and precured vulcanizates.

4. Conclusions

Studies on rheological behaviour of EPDM/CIIR blends using a capillary rheometer showed that the viscosity of the blends decreases with increase of shear rate and with increase of temperature but at higher shear rates temperature is not a critical parameter for controlling the flow properties of the blends. Moreover, with increase of the EPDM content, the shear viscosity also increases. The extrudate die-swell characteristics reveal that precuring method leads to minimum die swell. The air permeation behaviour of the blends follows the order precured > sulphur cured > resin cured, which is correlated to the flexibility of crosslinks as well as the crosslink density. A comparison of air permeability with respect to the blend composition shows that permeability of the blends to air decreases with increasing CIIR content, which is due to the inherent compact structure of CIIR. The effects of blend composition on the thermal diffusivity of the blends were analysed and was found highest for EPDM and blends containing higher percentage of EPDM, which is due to the increased extent of interaction between EPDM and carbon black. The thermal diffusivity can be significantly improved by the addition of low concentrations of boron nitride. On comparing the thermal degradation pattern, resin cured blends exhibit the highest degradation resistance, followed by precured and was least for sulphur cured blends.

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