EPDM/CIIR blends: improved mechanical properties through precuring

Sunil T. Jose · Anoop K. Anand · Rani Joseph

Abstract Precuring of one of the blend components is a promising strategy in order to improve the mechanical properties of elastomer blends and thereby broadening their application spectra. In the present work, the effect of precuring chlorobutyl (CIIR) on the properties of its blends with ethylene–propylene–diene monomer rubber (EPDM) is discussed. The optimum precuring that has to be given to the CIIR phase was determined on the basis of the variation of blend mechanical properties. It was observed that without affecting the processing safety of the blends, precuring of the CIIR phase substantially improves the mechanical properties of EPDM/CIIR blends as compared to their conventionally cured blend counterparts. Morphological studies using scanning electron microscopy substantiate the results.

Keywords Blends · Elastomers · Precuring · Mechanical properties

Introduction

More than ever before, today, there is increased technological interest in the use of blends of dissimilar rubbers [1–3]. However such blends generally show inferior mechanical properties compared to the average properties of the components. This can be attributed to three types of incompatibility, which exist between dissimilar elastomers viz., viscosity mismatch, thermodynamic incompatibility and cure mismatch [4]. As a result of the incompatibility, after mixing, the curatives migrate

S. T. Jose · A. K. Anand · R. Joseph (✉)
Department of Polymer Science and Rubber Technology,
Cochin University of Science and Technology, Cochin 682022, India
e-mail: rani@cusat.ac.in

A. K. Anand
e-mail: anoopnair24@gmail.com

to the more unsaturated or more polar rubber, which cures faster than the slow curing rubber causing the latter remaining undercured [5–7]. This phenomenon leads to poor mechanical properties of the blends. Such migration can also occur due to the difference between the reactivities of elastomers or due to the difference between the solubilities of curatives in elastomers [8–10]. Several methods have been suggested to overcome these problems and to improve the mechanical properties of elastomer blends. For example, it has been reported that lead oxide activated curing and the use of long chain hydrocarbon dithiocarbamate accelerators is beneficial in sulphur curing of blends of EPDM with highly unsaturated or more polar rubbers such as nitrile rubber [11]. Approaches for the chemical modification of slow curing phase or binding of accelerators to the polymer backbones etc. have also been proposed [12].

Preblending of curatives into respective elastomers at optimal concentrations prior to blending can improve the blend cross-link distribution, although the usual practice is to incorporate the curatives at the last stage in order to avoid scorch problems. To reduce the diffusion of curatives from one phase to the other, so as to improve the adhesion between the component elastomers, an attractive method is to partially prevulcanize one of the blend components and then mixing the prevulcanized elastomer with the other component [13–15].

EPDM possesses better physical properties such as high heat resistance, ozone resistance, cold and moisture resistance, high resistance to permanent deformation, very good resistance to flex cracking and impact. Because of the low gas and moisture permeability, good weathering resistance and high thermal stability of CIIR, blends of EPDM with CIIR may be attractive, if sufficient mechanical strength can be developed.

In this study, one of the component elastomers in EPDM/CIIR blends has been partially cured to a low level prior to blending. This would significantly reduce curative migration from one phase to another which improves co-curing and thereby the blend properties. Mechanical properties of the blends prepared by this novel route are compared with those prepared by the conventional mixing method.

Experimental

Materials

EPDM with dicyclopentadiene as the diene (301 T, Mooney viscosity [ML(1 + 8) at 100 °C] 47.8, ethylene/propylene weight ratio 68/32 and iodine value 10.5) was supplied by Herdillia Unimers; Chlorobutyl [CIIR 1066 having Mooney viscosity [ML(1 + 8) 100 °C] 56.3, iodine value 8.4 and chlorine content 1.2%], was purchased from Exxon. Rubber additives such as zinc oxide, stearic acid, carbon black (High abrasion furnace, HAF-N330), paraffinic oil, mercapto benzthiazole (MBT), tetramethyl thiuram disulphide (TMTD), zinc diethyl dithiocarbamate (ZDC), N-cyclohexyl-2-benzothiazole sulphenamide (CBS) and sulphur used in the study were of commercial grade.

Table 1 Compounding recipe

Ingredients	Concentration (phr)	
	EPDM phase	CIIR phase
ZnO	4.0	4.0
Stearic acid	1.5	1.5
MBT	1.0	–
TMTD	0.5	–
ZDC	0.5	–
CBS	–	1.0
Carbon black	40	40
Paraffinic oil	7.0	5.0
Sulphur	1.0	1.5
Antioxidant	1.0	1.0

Determination of optimum level of precuring

The optimum precuring required for the slow curing CIIR phase for developing blends with EPDM was determined on the basis of the mechanical properties of their 50/50 blends, with the CIIR phase precured to different extents. CIIR was compounded according to ASTM-D 3182 on a laboratory size two-roll mixing mill at a friction ratio of 1:1.25 as per the formulations given in Table 1. The compound was sheeted out from the mill at a thickness of 3 mm and was precured in an air oven for different periods viz. 10, 20, 30 and 40% of the optimum cure time at a temperature of 170 °C (as determined using a Rubber Process Analyser (RPA 2000, Alpha Technologies). These precured samples were blended with masticated EPDM on the mill and then compounding ingredients for EPDM were added. The compounds were cured up to their respective optimum cure time at 170 °C in an electrically heated laboratory hydraulic press.

The tensile properties of the blends were evaluated and the optimum precuring time was determined by comparing the mechanical strength. In a similar manner, EPDM was compounded as per the standard formulation, precured to different levels, blended with CIIR followed by the addition of its curatives, vulcanized and the tensile properties of the resulting blends were compared.

Determination of cure characteristics and cross-link density

The total cross-link density of the vulcanizates was determined from the swelling data in toluene [16]. Individual cross-link densities of EPDM and CIIR could not be measured because both have common true solvents [17]. The concentration of chemical cross-links was estimated from the equilibrium swelling data as follows: Samples of ~ 1 cm diameter and ~ 0.2 cm thickness were punched out from the vulcanizate sheet and was allowed to swell in toluene. The swollen sample was taken out of the solvent after 24 h and weighed. Solvent was then removed in vacuum and the sample weighed again. The volume fraction of rubber (V_r) in

the swollen network was then calculated by the method reported by Ellis and Welding [18, 19]. Cross-link density ($\frac{1}{2}M_C$) was then determined using Flory–Rehner equation [20]:

$$\frac{1}{2}M_C = -\frac{\left[\ln(1 - V_r) + V_r + \chi V_r^2\right]}{2\rho_r V_s (V_r)^{1/3}} \qquad (1)$$

where V_s = molar volume of solvent; V_s (toluene) = 106.2 cm^3/mol and χ = parameter characteristic of interaction between rubber and solvent (for CIIR–toluene, $\chi = 0.57$, for EPDM–toluene, $\chi = 0.49$). ρ_r represents the density of rubber. The densities of EPDM and CIIR obtained were 0.856 and 0.917 g/cm^3 respectively. Densities of the blends were calculated by taking into consideration the weight fraction and the density of each components [16, 21].

Physical properties

Dumbbell shaped tensile test specimens were punched out of the compression moulded sheets along the mill direction. Tensile properties of the vulcanizates were measured as per ASTM D 412 at a cross head speed of 500 mm/min on a Shimadzu Universal Testing machine (AG1). Tear resistance of the angular test pieces was measured on the UTM according to ASTM D 624. The hardness of the vulcanizates was determined according to ASTM 2240 and expressed in shore A units. Samples for abrasion resistance were moulded and weight loss/h was determined on a DIN abrader according to DIN 5351. Samples for compression set, flex crack resistance and rebound resilience were moulded and tested as per relevant ASTM standards. The ageing resistance and tension set of vulcanizates were determined after ageing the samples at 100 °C for 24, 48, and 72 h in a laboratory air oven. Steam ageing resistance of the vulcanizates was also studied after ageing the specimens in a steam chamber for 6, 18 and 36 h.

Morphological studies

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. The acceleration voltage used for image acquisition was 15 kV.

Results and discussion

Optimization of precuring of individual components

In the conventional method of blend preparation, due to the differences in viscosity and cure rate between EPDM and CIIR, the chances of curative migration between

Fig. 1 Variation of **a** tensile and **b** tear strength of 50/50 EPDM/CIIR vulcanizates with percentage curing time
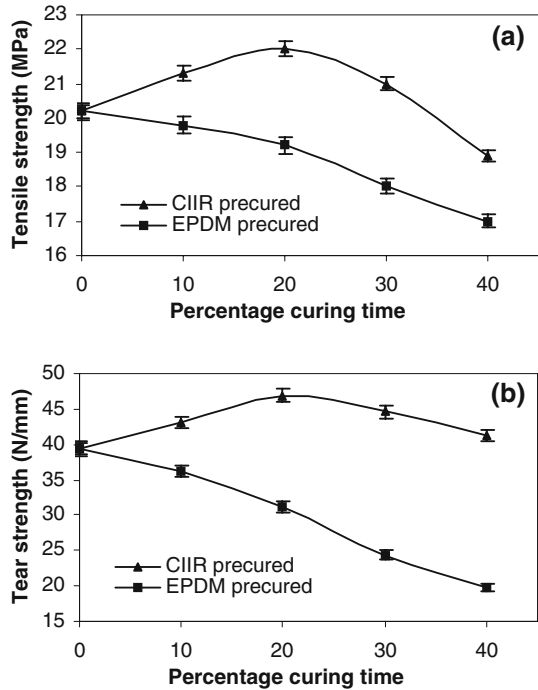
the phases is more, leading to inferior physical properties. Fixing the curatives from the phase where it migrates by partially curing that phase prior to blending can considerably reduce this migration. Figure 1a shows a plot of tensile strength of 50/50 EPDM/CIIR blends (in which the EPDM phase is precured) versus percentage curing time (various percentage of the optimum cure time, the EPDM phase has been maintained in air oven at 170 °C). The results indicate that, with increase in state of precuring of EPDM, the tensile strength of the blend decreases.

In the normal 50/50 EPDM/CIIR blend, owing to the low viscosity and more unsaturated nature of EPDM when compared with CIIR, the curatives and carbon black prefer to diffuse to the EPDM phase leading to slight overcuring. Hence in the case of the blend consisting precured EPDM, the EPDM phase gets overcured leading to poor interfacial linking. Secondly, in the resulting blend the CIIR phase remains undercured which also contribute to the inferior properties.

On the other hand, the variation in tensile strength of the blends in which the CIIR phase is precured indicates a gradual increase with the state of precuring of the CIIR phase. It is also evident that with an initial hike, the strength reaches a peak at 20% precuring and then decreases. It can be seen from Fig. 1b that the variation of tear strength is very similar to that observed in the case of tensile strength. This behaviour shows that precuring the CIIR phase up to a certain degree of cross-linking assists co-cross-linking but non-homogeneity develops in the blend at higher precuring levels. In other words, after the optimum level of precuring, chlorobutyl phase gets further cured and then it acts similar to an overcured or scorchy rubber

leading to poor interfacial linking. Blends prepared by partially precuring chlorobutyl rubber to a predetermined level (20% of the actual cure time at 170 °C) and then blending with EPDM are hence expected to possess better general properties. These blends are hereafter referred as 'modified' blends to distinguish from those prepared by blending the components by conventional method.

Cure characteristics and cross-link density

Further studies on EPDM/CIIR blends were carried out by precuring the CIIR phase up to 20% of the optimum cure time at 170 °C. Cure characteristics of the blends are shown in Table 2.

When EPDM forms the major constituent, there is no significant change in the cure time between the conventional and modified blends. As chlorobutyl content increases, cure time decreases for modified blends. This is expected, because the curing behaviour is likely to be more influenced by the major constituent [22, 23]. Reduction in cure time for modified blends indicates that there is no significant curative migration to the EPDM phase and curatives are trapped in the chlorobutyl phase itself due to precuring. The modified blends show marginally higher torque and cure rate, which is related to the homogeneity of the modified blends. The processing safety of the modified compounds remains unaltered by precuring, as there is no significant variation in scorch time.

Cross-link densities of the conventional and modified blends are shown in Fig. 2. The modified blends show a higher cross-link density than the corresponding conventional blends as determined from swelling experiments in toluene. Higher cross-link density values on modification are due to the equal distribution of

Table 2 Cure characteristics of conventional and modified EPDM/CIIR blends

EPDM (%)	20	40	60	80	20	40	60	80
CIIR (%)	80	60	40	20	–	–	–	–
Modified CIIR (%)	–	–	–	–	80	60	40	20
Cure time (min)	12.2	14.6	18.8	13.0	10.5	12.3	19.1	13.2
Scorch time (min)	1.01	1.32	1.41	1.23	1.01	1.31	1.40	1.21
Torque$_{max}$ (Nm)	0.34	0.30	0.33	0.32	0.39	0.35	0.38	0.36
Torque$_{min}$ (Nm)	0.042	0.036	0.034	0.038	0.082	0.064	0.048	0.04

Fig. 2 Variation of cross-link density of EPDM/CIIR blends with EPDM content. *Filled triangle* modified and *filled squares* conventional blends
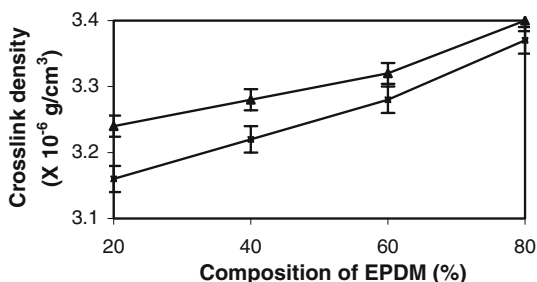
cross-links owing to reduced curative migration. Improvement in values is more significant in the case of 20/80 EPDM/CIIR blend. In this case the cross-link density of chlorobutyl, which is the major component, is low due to curative migration. But on modification, curative imbalance is reduced resulting in uniform cross-linking in the component elastomers and at the interphase.

Comparison of physical properties of conventional and modified blends

Table 3 shows the variation in mechanical properties of the modified and conventional blends. The modified blends show better tensile strength compared to the conventional blends. This improvement is attributed to the optimum cross-link densities in both EPDM and CIIR phases and in the interphase [24]. Improvement is found to be more pronounced in 20/80 EPDM/CIIR blend which shows that it was this composition that was comparatively most affected due to curative migration in conventional blending leading to the EPDM phase to get overcured whereas CIIR phase remains undercured. Ageing resistance of the modified and conventional blends is also given in the table. Results reveal that the ageing resistance is also better for the modified blends. This clearly shows the superiority of precured CIIR in resisting curative migration and in getting optimally cured at the final curing stage along with EPDM.

The modified EPDM/CIIR blends show higher elongation compared to the conventional blends (Table 4). Since elongation is controlled by the continuous elastomer phase, the lower value in the case of conventional blends might be due to the overcure of the continuous elastomer phase. In the conventional curing method, EPDM gets a higher proportion of curing agents resulting in its overcure. The 20/80 EPDM/CIIR blend shows higher elongation at break since chlorobutyl is the major component. The same trend was observed in the case of tear strength as well.

The variation in tear strength for conventional and modified blends under unaged and aged conditions is given in Table 5. The modified blends show superior tear strength compared to conventional blends before and after ageing. This observation is similar to what observed in the case of tensile strength. The tear strength improvement with modification is more pronounced, since tear strength has stronger correlation with optimum cross-link densities in both rubber phases and in the interphase [25]. Further reasons for the improved strength may be attributed to the

Table 3 Variation of tensile strength with ageing for conventional and modified EPDM/CIIR blends

Percentage of EPDM	Tensile strength of conventional blends (MPa)				Tensile strength of modified blends (MPa)			
	Unaged	24 h	48 h	72 h	Unaged	24 h	48 h	72 h
20	18.2	17.2	16.0	14.6	19.4	17.8	16.3	14.8
40	19.5	19.1	18.2	17.2	20.5	19.6	18.4	17.4
60	21.1	21.4	20.6	19.8	21.8	21.7	20.8	19.8
80	22.0	22.8	21.3	20.5	22.4	23.0	21.4	20.5

Table 4 Variation of elongation at break with blend composition for conventional and modified blends

Percentage of EPDM	Elongation at break of conventional blends (%)				Elongation at break of modified blends (%)			
	Unaged	24 h	48 h	72 h	Unaged	24 h	48 h	72 h
20	687	570	472	418	712	582	480	422
40	788	676	584	532	802	685	591	536
60	885	812	718	654	896	818	722	659
80	958	864	786	708	964	870	790	713

Table 5 Variation of tear strength with blend composition for conventional and modified EPDM/CIIR blends under unaged and aged conditions

Percentage of EPDM	Tear strength of conventional blends (*N*/mm)				Tear strength of modified blends (*N*/mm)			
	Unaged	24 h	48 h	72 h	Unaged	24 h	48 h	72 h
20	33.4	30.1	28.5	24.8	39.2	36.8	31.1	26.4
40	37.0	33.6	30.7	28.0	42.4	39.6	34.2	31.2
60	41.2	38.8	35.0	32.1	45.6	43.2	38.9	36.4
80	43.4	41.4	40.8	37.2	46.8	45.1	41.4	39.2

uniform filler distribution due to the reduction in the viscosity mismatch between EPDM and CIIR phases in the case of modified blends due to precuring.

Figure 3a–d indicate the variation of abrasion loss, hardness, compression set and rebound resilience with blend composition for the modified and conventional blends. The modified blends show better abrasion resistance than the conventional blends. This is due to the uniform filler distribution in the two elastomer components which results from the better viscosity matching of the precured CIIR and EPDM [26, 27]. Hardness is also found to be superior for modified blends due to the uniform cross-linking and filler distribution in both phases. Figure 3c and Table 6 gives the variation of compression set and tension set respectively. As the chlorobutyl content increases compression set and tension set decreases for both conventional and modified blends, which is an inherent property of CIIR, but the modified blends owing to the better homogeneity, display lower set values compared to conventional blends. Precured blends show lower resilience compared to conventional blends. This is attributed to two reasons; one is higher cross-link density of the vulcanizate and second is the uniform distribution of the filler in the matrix, both due to the partial precuring. Flex crack resistance (Fig. 4) also exhibits improvement with precuring, again due to the increased homogeneity in the blends because of precuring [28]. In the conventional blend, the reinforcing filler, carbon black, gets distributed more in the EPDM phase due to the low viscosity of EPDM. By precuring, migration of the filler is considerably reduced and this results in the
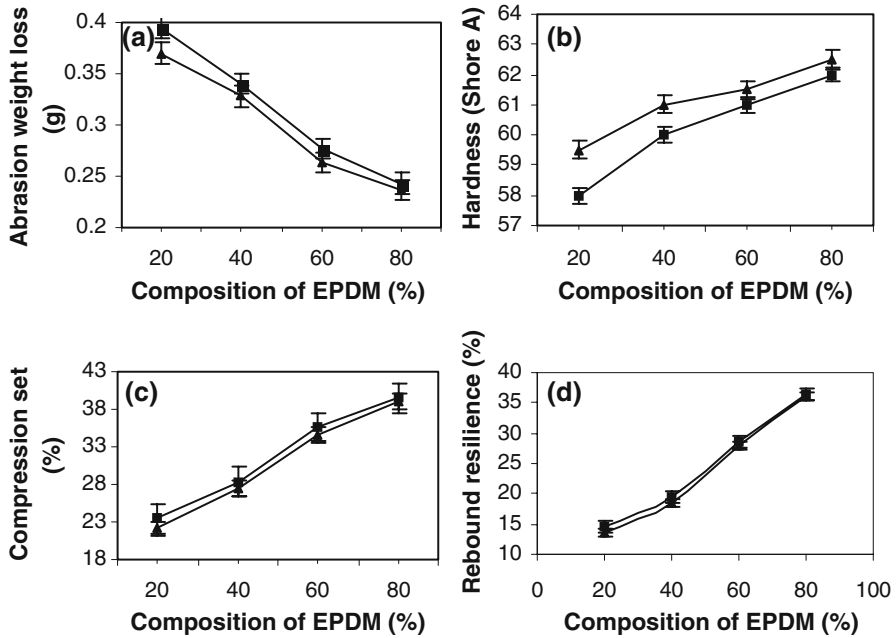
Fig. 3 a–d Variation of physical properties with blend composition for modified and conventional blends. *Filled triangles* modified and *filled squares* conventional blends

Table 6 Variation of tension set with ageing for conventional and modified EPDM/CIIR blends

Percentage of EPDM	Tension set for conventional blends (%)			Tension set for modified blends (%)		
	24 h	48 h	72 h	24 h	48 h	72 h
20	76	–	–	64	–	–
40	102	–	–	95	118	–
60	116	125	–	109	121	138
80	123	131	144	118	127	142

uniform distribution of active sites. Hence, when the two phases come into molecular contact, adsorption takes place in addition to the bonds formed by cross-linking. These bonds can absorb high stress before rupture leading to better flex crack resistance for the modified blends.

Steam ageing resistance of the conventional and modified vulcanizates is shown in Table 7. The modified blends show only a marginal improvement in steam ageing resistance compared to the usual sulphur cured blends. This was pretty much expected as steam ageing resistance depends mainly on the nature of the component elastomers. Chlorobutyl rubber when exposed to steam degrades easily due to dehydrochlorination resulting in inferior properties even after precuring [29, 30].

Fig. 4 Variation of increment
in cut length of conventional and
modified blends at a selected
blend composition. *Filled
triangles* modified and *filled
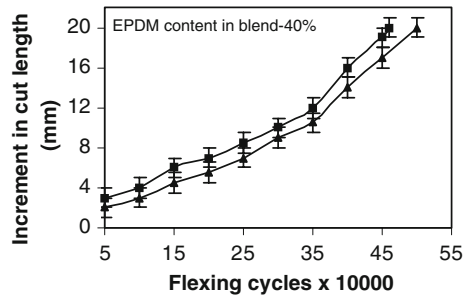squares* conventional blends

Table 7 Variation of steam ageing resistance with blend composition for conventional and modified
EPDM/CIIR blends

Percentage of EPDM	Tensile strength of conventional blends after steam ageing (MPa)			Tensile strength of modified blends after steam ageing (MPa)		
	6 h	18 h	36 h	6 h	18 h	36 h
20	17.4	16.1	14.2	18.1	17.2	15.8
40	18.3	17.3	16.1	19.2	18.4	17.4
60	19.6	18.8	17.5	20.3	19.6	18.5
80	21.3	20.8	19.7	22.2	21.9	21.0

Scanning electron microscopy

In order to substantiate our observations on improvement in mechanical properties,
we have studied the fracture surface morphology of the blends. SEM images of the
tensile fractured surfaces of blends of EPDM with precured CIIR at various
compositions are shown in Fig. 5 in comparison to that of the conventional ones
shown in Fig. 6. The images project a smoother and homogeneous pattern for the
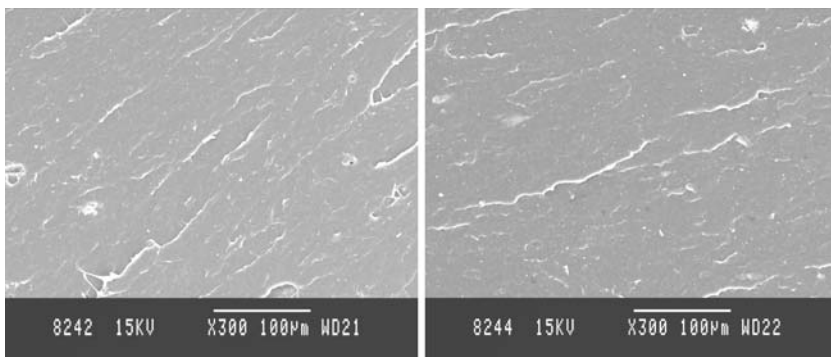

Fig. 5 SEM images of cryofractured surfaces of modified EPDM/CIIR blends containing 40 (*left*) and
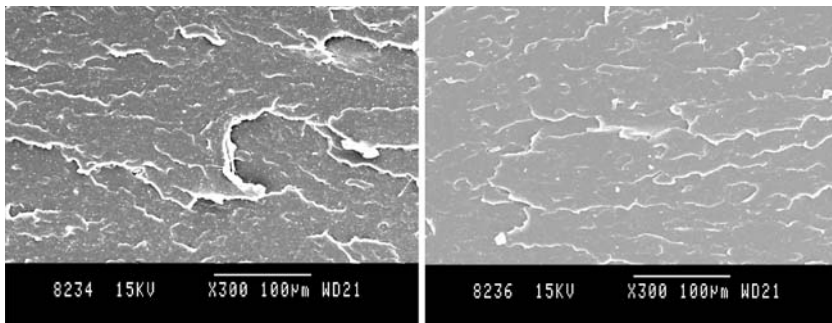60% EPDM (*right*)

Fig. 6 SEM images of cryofractured surfaces of conventional EPDM/CIIR blends containing 40 (*left*) and 60% EPDM (*right*)

modified blends, justifying their higher tensile strength and other mechanical properties.

Conclusions

Precuring of chlorobutyl to a predetermined level followed by blending with EPDM and then curing the blend is an efficient way of obtaining optimum cross-link density in both the elastomer phases and at the interphase. This novel route is found to reduce the curative migration from one phase to another and hence improve the mechanical properties of EPDM/CIIR blends significantly over their conventional counterparts. SEM studies confirm the results. The processing safety of the blend compounds is not affected by partial precuring.

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