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Dynamic mechanical spectroscopic studies on the miscibility of polychloroprene–epoxidized natural rubber blend in presence of carbon black filler

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Blends of polychloroprene (CR) and epoxidized natural rubber (ENR) are crosslinked during high temperature moulding for a prolonged time. As studied by dynamic mechanical spectroscopy, the 30/70 CR/ENR-50 blend is miscible and its miscibility is unaffected by the incorporation of high abrasion furnace carbon black filler. The 50/50 CR/ENR-50 blend is miscible, but its miscibility is adversely affected on incorporation of carbon black filler and the tan δ peak broadens and is shifted towards higher temperature. The 70/30 CR/ENR-50 blend is not miscible showing microheterogeneous characteristics, and incorporation of carbon black filler causes phase separation. It is believed that the microheterogeneity of the blend with high CR content, as in 70/30 CR/ENR-50, arises due to the furanization of the ENR chain induced by HCl liberated from CR during high temperature moulding. Carbon black catalyses HCl liberation from CR and the consequent furanization of ENR in the blend, causing phase separation at high filler loading. Since the probability of two adjacent epoxy groups in ENR-25 is less than in ENR-50, such phase separation in CR/ENR-25 blends does not occur.

(Keywords: polychloroprene; epoxidized natural rubber; carbon black filler)

INTRODUCTION

Nagode and Roland have reported that polychloroprene (CR) and epoxidized polyisoprene blends are miscible in all ratios when the blends are prepared by solvent casting from carbon tetrachloride solution[1]. Alex *et al.* observed that CR and epoxidized natural rubber (ENR) are crosslinked when the mill mixed blend is moulded for a prolonged time at high temperature[2]. This type of blend, which undergoes crosslinking due to reaction between the reactive sites of the individual polymers in the absence of any crosslinking agent, is often referred to as a 'self-crosslinkable blend'[2–4]. The physical properties of such blends are comparable to rubbers vulcanized by conventional curing agents and they can be reinforced by fillers[5,6]. While working on the development of a broad damping rubber formulation, CR/ENR blend systems appeared promising. Since fillers are used in almost all practical rubber formulations, the effect of fillers on the miscibility of blends was considered worth investigating. This paper reports the results of dynamic mechanical studies on the miscibility of CR/ENR blends with special reference to the effect of high abrasion furnace (HAF) carbon black filler.

The effects of mineral filler on the compatibility of polymer blends have been studied by Lipatov and co-workers[7–11]. Recently it has been reported that the introduction of a filler enhances the thermodynamic compatibility of a blend of polyethylene and polyurethane[11]. Another report indicates that addition of filler to a mechanically compatible binary blend near its miscibility region leads to an incompatible blend[12]. Based on their studies on dynamic mechanical spectroscopy, Mallick *et al.* reported that incorporation of carbon black filler to an incompatible poly(acrylic acid) (PAA)/ENR blend, results in an increase in the apparent homogeneity of the blend[6].

EXPERIMENTAL

Two grades of ENR were obtained from Kumpulan Guthrie Berhard, Malaysia under the trade names Epoxyprene-50 (containing 50 mol% oxirane ring) and Epoxyprene-25 (containing 25 mol% oxirane ring). The CR (AD-20) was obtained from Du Pont Ltd, UK and the HAF carbon black filler (N-330) was obtained from Phillips Carbon Black Ltd, India. Blending was carried out in a laboratory-sized two-roll mill for 4 min. Prior to blending, CR and ENR were premasticated for 1 min. Carbon black was added to the mill-mixed blend in a Brabender Plasticorder (PLE-330) at room temperature and at a rotor speed of 60 rev min^{-1}. The total mixing cycle was ~9 min. Finally the carbon black filled blend was sheeted out in a two-roll mill.

A Monsanto R-100 rheometer was used to study the cure characteristics at 170°C and the blends were

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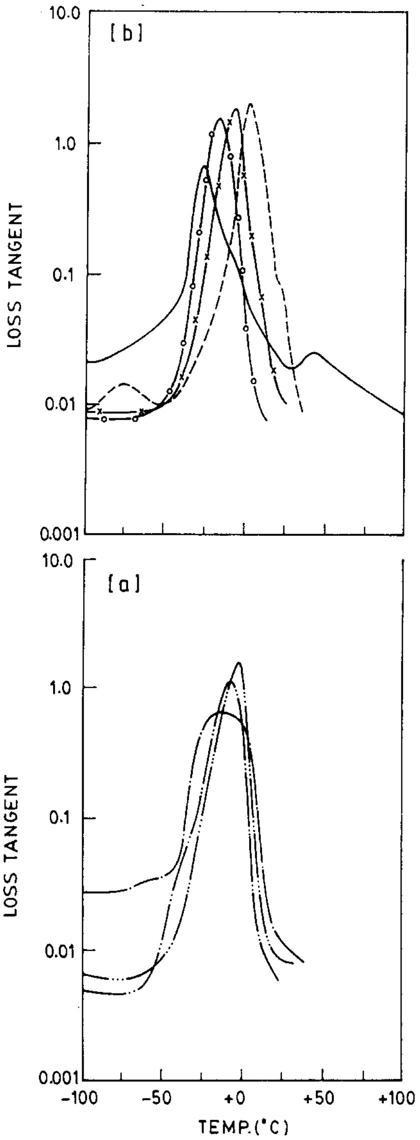

Figure 1 Loss tangent *versus* temperature plots of: (a) 30/70 CR/ENR-50 (—··—); 50/50 CR/ENR-50 (—·—); 70/30 CR/ENR-50 (—·—); (b) 100/0 CR/ENR-50 (——); 0/100 CR/ENR-50 (---); 50/50 CR/ENR-50 in the presence of Na_2CO_3 (— × —) and 70/30 CR/ENR-50 in the presence of Na_2CO_3 (—○—)

moulded at the same temperature. Moulding was carried out in a hydraulic press at a pressure of 10 MPa. After curing, the samples were cooled down to room temperature under pressure by circulating cold water through the platens.

For dynamic mechanical analysis (d.m.a.), samples (3 cm × 0.6 cm × 0.2 cm) were cut from the moulded sheets. D.m.a. of the samples was carried out in a Rheovibron DDV-III-EP (Orientec Corp., Japan) at a double strain amplitude of 0.166% and a frequency of 3.5 Hz. The measurements were taken over a temperature range of −100°C to +100°C at a heating rate of $2^\circ C\ min^{-1}$.

RESULTS AND DISCUSSION

Figures 1a and *b* show the loss tangent *versus* temperature plots of CR, ENR-50 and 30/70, 50/50 and 70/30 CR/ENR-50 blends. It is apparent that while the single rubbers, 30/70 and 50/50 CR/ENR-50 blends show sharp glass transitions, the 70/30 CR/ENR-50 blend shows a broad transition which, however, becomes narrow when sodium carbonate is incorporated into it. During moulding of the CR/ENR-50 blend, intermolecular crosslinking between CR and ENR takes place through the formation of an ether-type linkage[2]. In blends with high CR content, high moulding temperature causes thermovulcanization of CR occurring through intramolecular dehydrochlorination via allylic chlorine atoms[13,14]. The hydrogen chloride liberated from CR causes structural changes in ENR which lead to the formation of furanized ENR[15–17]. Therefore, the microstructure of the moulded 70/30 CR/ENR-50 blend consists of thermovulcanized CR, furanized ENR and self-crosslinked CR/ENR, apart from unreacted CR and ENR. The broad transition in the 70/30 CR/ENR-50 blend could be attributed to the superposition of different relaxation processes due to these species. In blends with lower CR content, crosslinking between CR and ENR takes place in preference to side reactions like thermovulcanization of CR and furanization of ENR. When Na_2CO_3 is incorporated into the 70/30 CR/ENR-50 blend, the hydrogen chloride liberated during moulding is absorbed by the base and accordingly the acid-induced structural changes of ENR cannot take place. The absence of furanized ENR is the reason for the sharp transition in the Na_2CO_3 filled 70/30 CR/ENR-50 blend in d.m.a. studies.

The temperature corresponding to the tan δ maxima is taken as the glass transition temperature (T_g). The composition-dependent single glass transition of the moulded blends clearly indicates that the system is miscible at all blend ratios even after crosslinking. The 2 min moulded 70/30 CR/ENR-50 blend gives a single transition and the T_g of the blend is −15.0°C, which is the same as the T_g of the crosslinked blend (blend nos 13 and 14 in *Table 1*). Thus it can be concluded that the system is miscible in the uncured state and the miscibility is not affected on crosslinking. The compositional dependence of the blends can be obtained according to Fox's relationship[18]:

$$1/T_{g_b} = W_1/T_{g_1} + W_2/T_{g_2} \qquad (1)$$

where W is the weight fraction of the components and T_{g_b}, T_{g_1} and T_{g_2} are the glass transition temperatures of the blend and the individual components, respectively. *Figure 2* shows the variation of T_g with blend composition in the case of CR/ENR-50 blends (blend nos 1, 2, 4, 8 and 15) and also the prediction based on the Fox equation. Slight deviation from the Fox equation was observed, which is attributed to the chemical interactions between the components[19,20].

Figures 3a and *b* show the effect of incorporation of HAF carbon black filler on the tan δ *versus* temperature plot in 30/70, 50/50 and 70/30 CR/ENR-50 blends, respectively. Results are summarized in *Table 1*. It is evident from *Table 1* that in the case of 30/70 and 50/50 CR/ENR-50 blends, incorporation of HAF carbon black decreases the tan δ peak height. Medalia[21,22] suggested that the occluded rubber, bound rubber[23,24] and shell rubber[25] may overlap each other to form a complex interlinked system. Therefore, filled polymers are a complicated structure of hard absorbed rubber and bulk rubber; the former is the cause of the perturbation in the

Table 1 Tan δ peak height and peak temperature obtained from dynamic mechanical studies of CR/ENR-50 blends[a]

Blend no.	Blend composition (CR/ENR-50/filler[b]/Na_2CO_3)	Tan δ peak height	Tan δ peak temperature (°C)
1	0/100/0/0	2.067	−1.3
2	30/70/0/0	1.732	−7.2
3	30/70/30/0	1.023	−7.2
4	50/50/0/0	1.171	−9.2
5	50/50/30/0	0.522	+2.7
6	50/50/0/5	1.599	−9.6
7	50/50/30/5	1.226	−9.2
8	70/30/0/0	0.655 (0.848)[c]	−17.3 to −7.1 (−15.0)[c]
9	70/30/5/0	0.388, 0.503	−17.3, +10.6
10	70/30/10/0	0.465, 0.463	−19.3, +10.7
11	70/30/15/0	0.397, 0.456	−21.2, +10.1
12	70/30/30/0	0.269, 0.446	−25.2, +28.0
13	70/30/0/5	1.565	−17.2
14	70/30/30/5	0.975	−15.2
15	100/0/0/0	0.619	−27.3

[a] Loadings in phr (parts per hundred parts of rubber)
[b] High abrasion furnace carbon black
[c] Figures in parentheses indicate results of the 2 min moulded sample

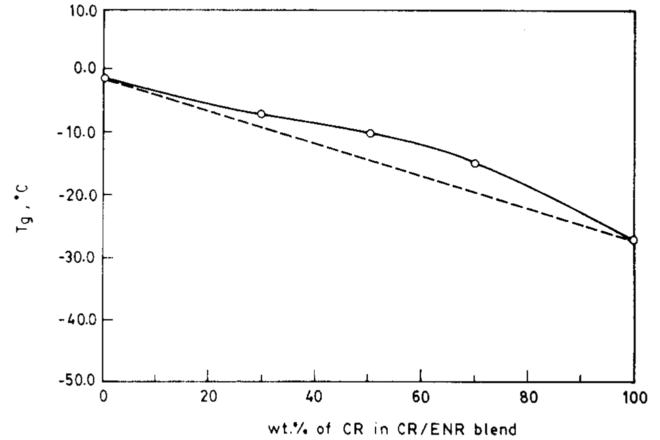

Figure 2 Variation of T_g with CR content in the CR/ENR-50 blend: (- -) experimental; (– – –) Fox equation

relaxation process and the reduction in the tan δ peak height[25]. The tan δ peak position gets broadened particularly at high filler loading. In the case of the 50/50 CR/ENR-50 blend, incorporation of HAF carbon black filler causes a shift in the tan δ peak towards high temperature which may be due to the initiation of side reactions in the ENR phase, as discussed earlier in the case of the 70/30 CR/ENR-50 blend. Addition of Na_2CO_3 to this system brings the tan δ peak to its original position, which is presumably due to the absence of side reactions in the ENR phase in the presence of Na_2CO_3. The

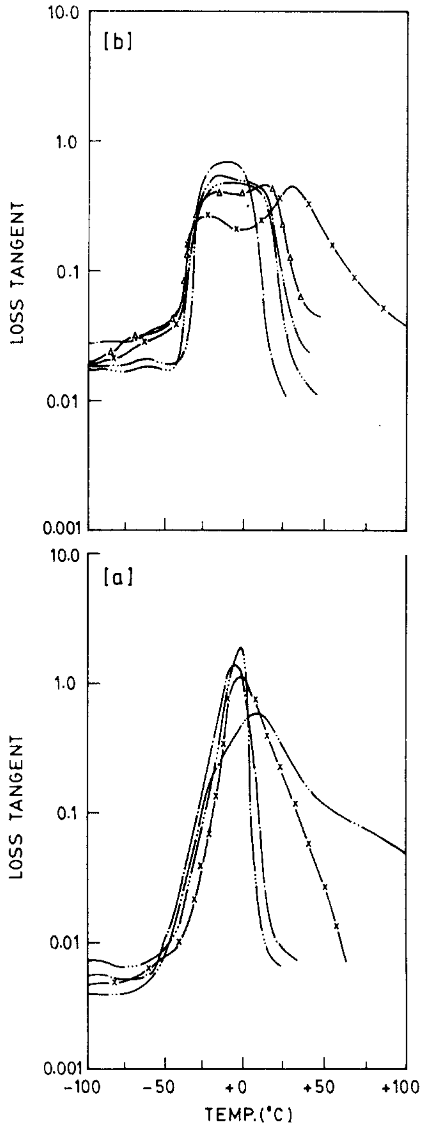

Figure 3 (a) Effect of incorporation of HAF carbon black filler on the variation of loss tangent *versus* temperature plots: 30/70 CR/ENR-50 (unfilled) (—···—); 30/70 CR/ENR-50 (30 phr black) (— × —); 50/50 CR/ENR-50 (unfilled) (—·—); 50/50 CR/ENR-50 (30 phr black) (—··—). (b) Effect of loadings of HAF carbon black filler on the plots of loss tangent *versus* temperature in the case of the 70/30 CR/ENR-50 blend: 0 phr (—·—); 5 phr (—··—); 10 phr (—···—); 15 phr (—△—); 30 phr (— × —)

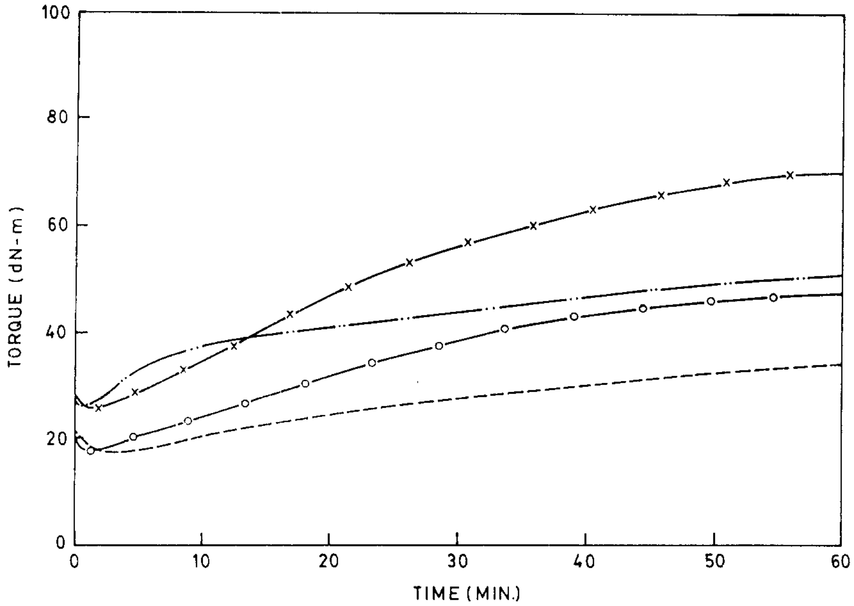

Figure 4 Monsanto rheographs at 170°C for: neat CR (– – –); CR plus 30 phr HAF carbon black (—··—); 70/30 CR/ENR-50 blend (—○—); 70/30 CR/ENR-50 blend plus 30 phr HAF carbon black (— × —)

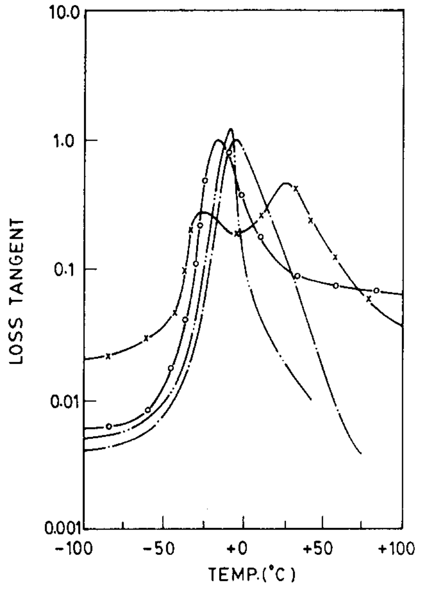

Figure 5 Effect of Na_2CO_3 on the loss tangent *versus* temperature plot in the presence of 30 phr HAF carbon black: 50/50 CR/ENR-50, no Na_2CO_3 (—·—); 50/50 CR/ENR-50 with Na_2CO_3 (—··—); 70/30 CR/ENR-50, no Na_2CO_3 (— × —); 70/30 CR/ENR-50 with Na_2CO_3 (—○—)

broadening phenomenon is more prominent in the case of the partially miscible 70/30 CR/ENR-50 blend, where it occurs even at a low filler loading of 5 phr. As filler loading increases, broadening of the tan δ peak increases gradually, resulting in the formation of two separate peaks, one occurring at the transition temperature of CR and the other occurring at a temperature higher than the transition temperature of ENR. In the case of the 70/30 CR/ENR-50 blend with 30 phr HAF black the two peaks occur at −25.2°C and 28°C, respectively, which indicates that a partially miscible 70/30 CR/ENR-50 blend becomes immiscible on incorporation of 30 phr HAF carbon black filler.

As discussed earlier, formation of furanized ENR is responsible for the breadth of the tan δ peak in the case of the 70/30 CR/ENR-50 blend. Since carbon black increases the breadth of the tan δ peak region and causes its separation into two peaks, it appears that the filler catalyses the formation of furanized ENR. Since hydrogen chloride is necessary for the furanization and ring opening reactions of ENR, filler seems to catalyse the formation of hydrogen chloride. *Figure 4* shows the Monsanto rheographs for the neat polymer, where the increase in torque is due to thermovulcanization. In the case of the CR/ENR-50 blend the increase in torque is due to crosslinking. In both systems the rate and extent of crosslinking increase, which implies more hydrogen chloride formation prior to crosslinking due to the incorporation of HAF carbon black filler. *Figure 5* shows that in presence of Na_2CO_3 the two peaks in carbon black filled 70/30 CR/ENR-50 blend merge to form a single narrow transition occurring in between the transition temperatures of CR and ENR, making it a miscible system. Na_2CO_3 absorbs the liberated HCl and prevents the side reactions in ENR[26]. It is to be noted that increase in filler loading in the case of the 70/30 CR/ENR-50 blend system causes lowering of the tan δ value at the low temperature transition (i.e. the CR transition), but the tan δ value at the high temperature transition does not drop (*Figure 3b*). In the unfilled blend and at low filler loading, the CR and ENR phases are indistinguishable. At high filler loading phase separation occurs presumably due to the formation of thermovulcanized CR and modified ENR. Since modified ENR is likely to be of higher viscosity than the CR phase, carbon black migrates preferentially to the CR phase and causes lowering of the tan δ peak value of the CR phase. In the case of the 50/50 CR/ENR-50 blend, the catalytic effect of the filler in the furanization of ENR is less and in the case of the 30/70 CR/ENR-50 blend it is not

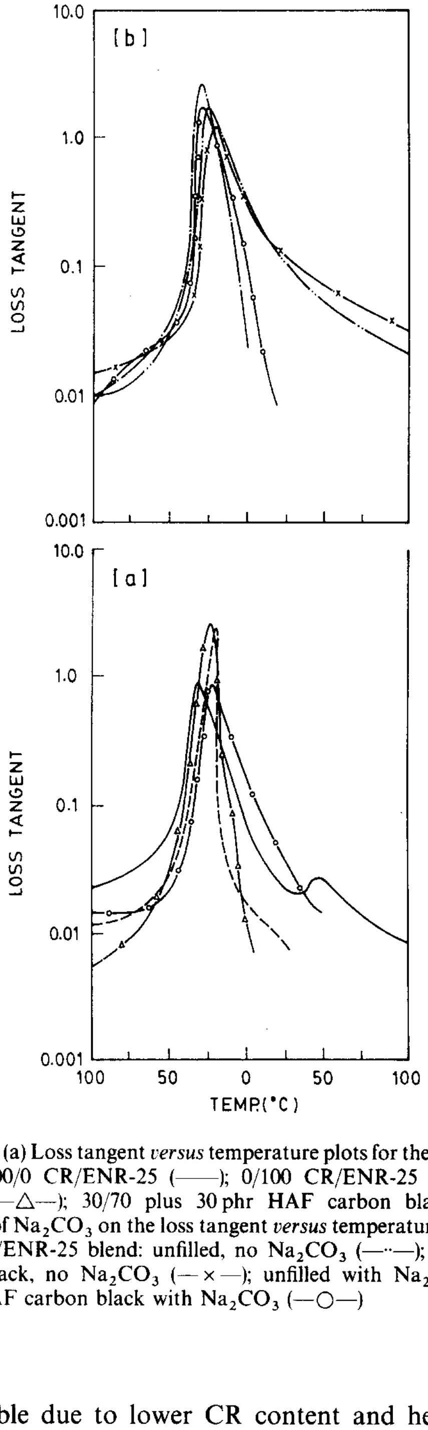

Figure 6 (a) Loss tangent *versus* temperature plots for the CR/ENR-25 blends: 100/0 CR/ENR-25 (——); 0/100 CR/ENR-25 (– – –); 30/70 unfilled (—△—); 30/70 plus 30 phr HAF carbon black (—○—). (b) Effect of Na_2CO_3 on the loss tangent *versus* temperature plot for the 70/30 CR/ENR-25 blend: unfilled, no Na_2CO_3 (—··—); 30 phr HAF carbon black, no Na_2CO_3 (—×—); unfilled with Na_2CO_3 (—·—); 30 phr HAF carbon black with Na_2CO_3 (—○—)

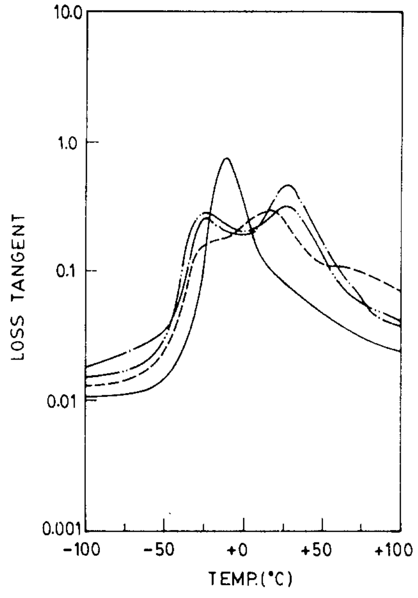

Figure 7 Effect of moulding time on the loss tangent *versus* temperature plots of the 70/30 CR/ENR-50 blend: 2 min (——); 30 min (– – –); 60 min (—·—); 120 min (—··—)

observable due to lower CR content and hence phase separation does not occur.

Figure 6a shows the effect of HAF carbon black filler on the variation of tan δ with temperature in the case of the 30/70 CR/ENR-25 blend. The 30/70 CR/ENR-25 blend is miscible and the miscibility is unaffected by incorporation of the filler. The 50/50 CR/ENR-25 blend also shows similar behaviour (not shown). In contrast to the 70/30 CR/ENR-50 blend, no phase separation occurs in the case of the 70/30 CR/ENR-25 blend, even in the presence of HAF carbon black filler (*Figure 6b*). Although the CR content remains the same in both blends, the concentration of epoxy groups is much less in ENR-25 and hence the probability of there being two adjacent epoxy rings is less. The low concentration of adjacent epoxy rings causes broadness and shift in the tan δ relaxation spectra, but this is not enough to cause phase separation. It has been established that ENR furanizes only when two epoxy groups are adjacent[27]. *Figure 6b* shows the effect of Na_2CO_3 on the plot of tan δ *versus* temperature in the case of filled and unfilled 70/30 CR/ENR-25 blend. It is apparent that in the presence of Na_2CO_3 furanization of ENR cannot take place and the blend remains miscible even in the presence of HAF carbon black filler.

Figure 7 shows the effect of moulding time on the dynamic mechanical properties of the carbon black filled 70/30 CR/ENR-50 blend. It is observed that at a moulding time of 2 min no phase separation occurs. At a moulding time of 30 min, phase separation has started which, however, becomes prominent at 60 min moulding time. At 120 min moulding time, although no further changes take place, there is a reduction in the tan δ peak height of the high temperature transition. The reduction in the tan δ peak height of the high temperature transition during prolonged moulding may be due to crosslinking in the modified ENR phase, because the gel content is believed to increase in vulcanized ENR on prolonged ageing[28].

CONCLUSIONS

Dynamic mechanical spectroscopy of CR/ENR blends reveals that blends with high CR content and with ENR containing high epoxy content show signs of microheterogeneity. This is believed to be the result of the superposition of different relaxation processes arising from the formation of furanized ENR due to HCl liberation from CR during high temperature moulding, in addition to the presence of thermovulcanized CR, crosslinked CR/ENR and unreacted polymers in the matrix. Incorporation of HAF carbon black filler catalyses the furanization reaction and increases the degree of microheterogeneity of the blends, and in the case of the 70/30 CR/ENR-50 blend the filler causes phase separation.

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