Moving die rheometry and dynamic mechanical studies on the effect of reinforcing carbon black filler on ionomer formation during crosslinking of carboxylated nitrile rubber by zinc oxide

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The results of moving die rheometry studies show that in contrast to sulfur vulcanization of carboxylated nitrile rubber (XNBR), where the loss component of the torque (S'') decreases with curing time, the zinc oxide (ZnO) crosslinking of XNBR is accompanied by a gradual increase in S'', which becomes more pronounced in the presence of reinforcing high abrasion furnace carbon black filler. In dynamic mechanical studies, the sulfur-vulcanized XNBR shows a single peak around −5°C. The peak height reduced in the presence of the reinforcing filler with no shift in the peak position. However, the ZnO-vulcanized XNBR shows one extra peak around 54°C, in addition to the main transition around −5°C. Incorporation of reinforcing filler causes lowering of the peak height of the main transition, while the peak height of the high-temperature transition gradually increases. For the crosslinking system consisting of both sulfur and ZnO, the characteristics of the high-temperature transition are retained. These results have been explained on the basis of the formation of ionomers of XNBR during crosslinking by ZnO. Reinforcing carbon black filler favours the stabilization of these ionomers.

(Keywords: moving die rheometer; dynamic mechanical analyses; carboxylated nitrile rubber; ionomer; carbon black)

INTRODUCTION

The introduction of a small number of ionic groups into polymer chains can result in profound changes in the physical properties of the modified polymers, also known as ionomers[1,2]. Depending on the concentration of these ionic groups, the ionic aggregates can exist as multiplets which function as physical crosslinks or as clusters consisting of both ion pairs and hydrocarbon chains, often leading to microphase separation.

Dynamic mechanical measurements have been used to study such ionic aggregate structures[3]. Ionomers based on polyethylene, polystyrene and partially sulfonated polystyrene have been studied by several authors[1,2,4,5]. Weiss and coworkers[6,7] have studied the viscoelastic behaviour of lightly sulfonated polystyrene ionomers and observed that such behaviour depends on the nature of the plasticizer incorporated in the matrix. The role of ionic plasticizers like zinc stearate in the dynamic mechanical behaviour of sulfonated ethylene–propylene terpolymers has also been studied[8]. Several researchers have reported the characterization of these ionomers[9]. Blends of ionomers with other polymers have also been reported[10,11]. Paeglis and O'Shea studied thermoplastic elastomer compounds from sulfonated EPDM ionomers[12].

While studying the vulcanization of carboxylated nitrile rubber (XNBR) by different crosslinking systems, we observed that ionic clusters can be generated when XNBR is mixed with ZnO and moulded at a temperature around 150°C. The present paper reports the results of moving die rheometry and dynamic mechanical studies on ionomers of carboxylated nitrile rubber formed during its moulding with ZnO

EXPERIMENTAL

Details of the materials used are given in *Table 1* and the formulations used are given in *Table 2.*

Table 1 Details of materials used

Material	Characteristics	Source
Carboxylated acrylonitrile–butadiene rubber (XNBR)	KRYNACX 7.50 grade; Mooney viscosity (ML_{1+4} at 100°C) 57	Bayer Polysar, France
Zinc oxide (ZnO)	Rubber grade; specific gravity 5.4	Local market
High abrasion furnace black (HAF)	N-330; surface area 80 $m^2 g^{-1}$; pH 7.6	Philips Carbon Black Ltd, India
N-cyclohexylbenzothiazyl sulfenamide (CBS)	Rubber grade	ICI Ltd, India
Tetramethylthiuram disulfide (TMTD)	Rubber grade	ICI Ltd, India

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Preparation of rubber mixes

The compounding ingredients were mixed with rubber in a laboratory size (325 mm x 150 mm), two-roll mixing mill at a friction ratio of 1:1.19 according to ASTM D 3182, with careful control of temperature, nip gap, time of mixing and a uniform cutting operation. The temperature range for mixing during filler loading was 60–75°C. The order and time period of mixing were as follows: 0–2 min, mastication; 2–3 min, addition of stearic acid; 3–15 min, addition of filler; and 15–20 min, addition of curing agents.

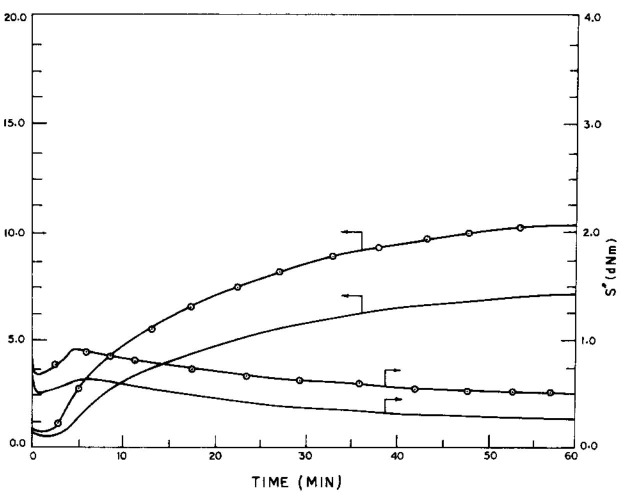

Figure 1 Rheographs at 150°C for the XNBR-sulfur system: (——) mix X_{s0}; (○) mix X_{s20}

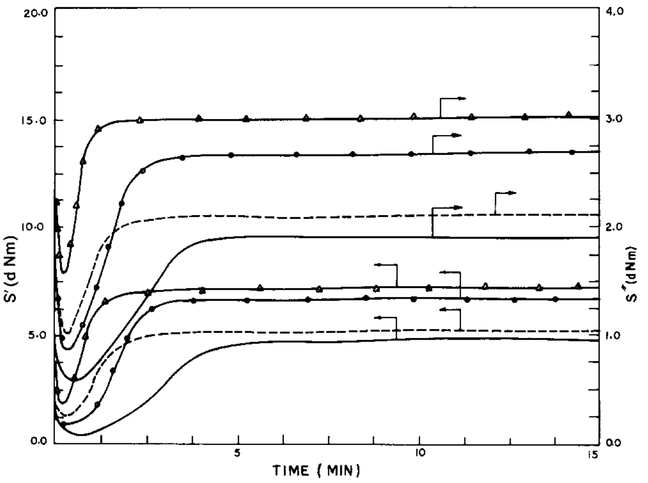

Figure 2 Rheographs at 150°C for the XNBR–ZnO system: (——) mix X_{z0}; (– – –) mix X_{z10}; (○) mix X_{z20}; (△) mix X_{z30}

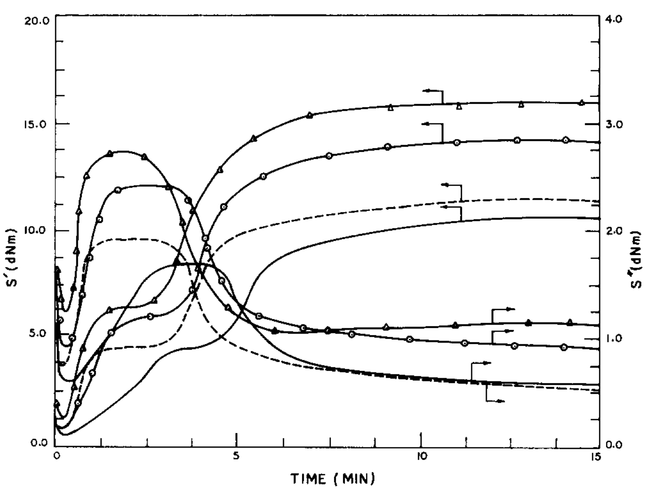

Figure 3 Rheographs at 150°C for the XNBR–ZnO/sulfur system: (——) mix X_{sz0}; (– – –) mix X_{sz10}; (○) mix X_{sz20}; (△) mix X_{sz30}

The rubber compounds were moulded at 150°C in an electrically heated hydraulic press to the optimum cure time (i.e. 90% of the maximum cure) obtained from a moving die rheometer.

Moving die rheometry

The moving die rheometry experiments were conducted using an MDR-2000 (Monsanto Company, USA) at 150°C with an arc of oscillation of ±0.5°. The instrument was programmed so that the rheographs registered both the in-phase (or elastic) response (S') and the out-of-phase (or viscous) response (S'') of the torque as curing proceeded.

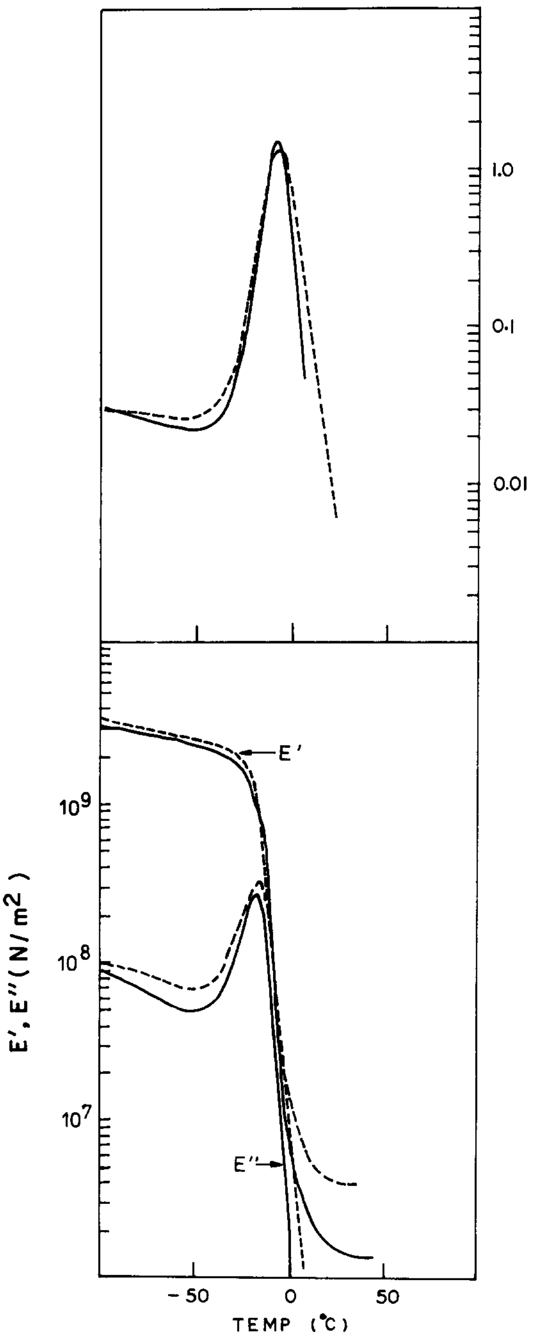

Figure 4 Plots of E', E'' and $\tan \delta$ *versus* temperature for the XNBR–sulfur system: (——) mix X_{s0}; (– – –) mix X_{s20}

Table 2 Formulations of the mixes

Mix number	X_{s0}	X_{s20}	X_{z0}	X_{z10}	X_{z20}	X_{z30}	X_{sz0}	X_{sz10}	X_{sz20}	X_{sz30}
XNBR	100	100	100	100	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1	1	1	1	1
HAF	0	20	0	10	20	30	0	10	20	30
CBS	3	3	–	–	–	–	3	3	3	3
TMTD	1	1	–	–	–	–	1	1	1	1
S	1	1	–	–	–	–	1	1	1	1
ZnO	–	–	12	12	12	12	12	12	12	12

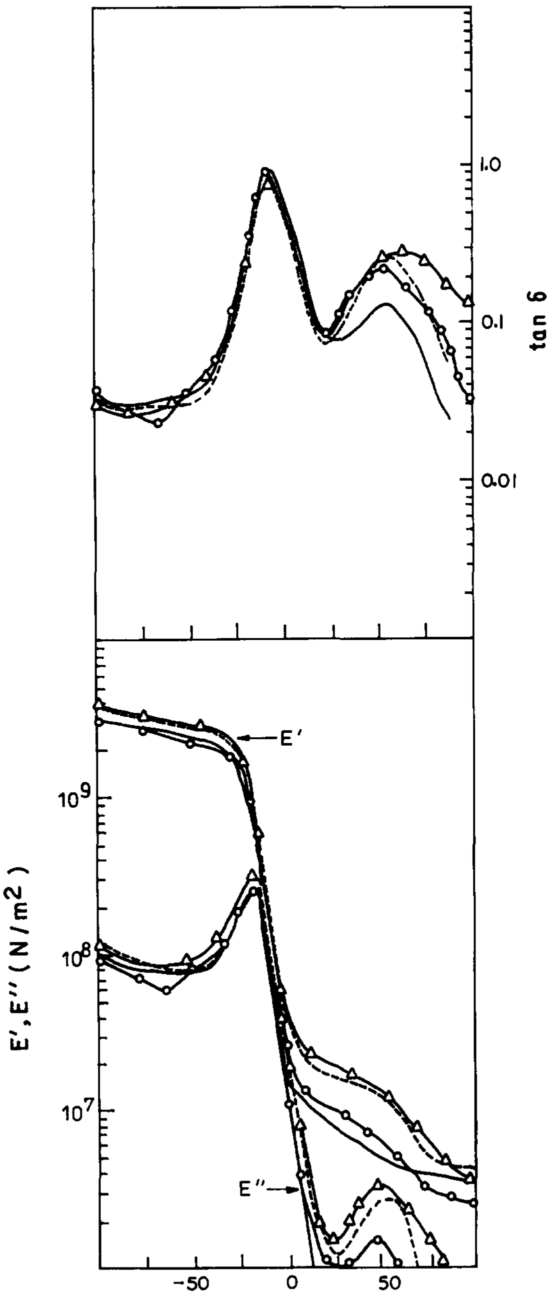

Figure 5 Plots of E', E'' and tan δ *versus* temperature for the XNBR–ZnO system: (——) mix X_{z0}; (○) mix X_{z10}; (– – –) mix X_{z20}; (△) mix X_{z30}

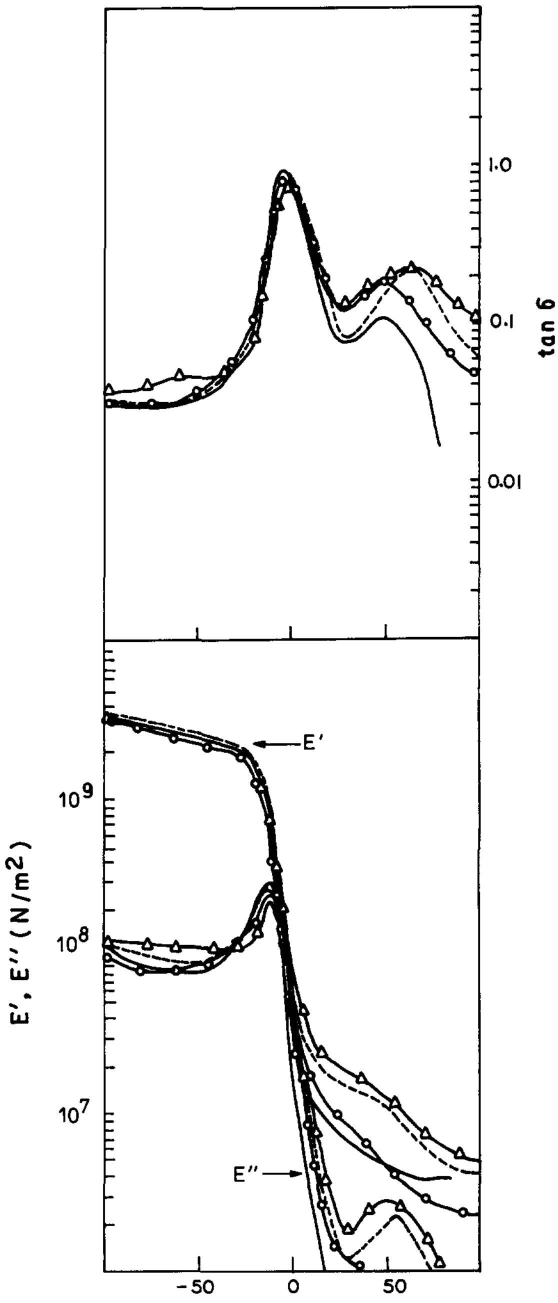

Figure 6 Plots of E', E'' and tan δ *versus* temperature for the XNBR–ZnO/sulfur system: (——) mix X_{sz0}; (○) mix X_{sz10}; (– – –) mix X_{sz20}; (△) mix X_{sz30}

Dynamic mechanical study

Dynamic mechanical analyses were performed with a Rheovibron DDV-III-EP viscoelastomer (Orientec Corporation, Japan) with a computer system for control and data analysis. Cooling was accomplished with liquid nitrogen. Isochronal dynamic moduli measurements were made from −100 to 100°C at a frequency of 3.5 Hz. Rectangular samples (6.5 mm × 4.5 mm × 2 mm) were used. Testing was carried out in tension mode. The linear rise of temperature was $2°C\,min^{-1}$.

RESULTS AND DISCUSSION

Figure 1 shows the MDR-2000 rheographs of both unfilled and filled XNBR in the presence of the sulfur vulcanizing system at 150°C. It is evident that with the progress of curing, S' increases but S'' decreases. Similar observations have been reported in the crosslinking of other rubbers by sulfur, peroxide and vulcanizing systems producing covalent bonds in the network[13]. Incorporation of reinforcing high abrasion furnace (HAF) carbon black increases both S' and S'' components of the torque. *Figure 2* shows the rheographs of unfilled and filled XNBR in the presence of the ZnO curing system at 150°C. Although S' increases as expected with the progress of curing, S'' unexpectedly increases with curing time. An increase in S'' has been observed in the case of the formation of networks consisting of ionic crosslinks[13]. In the case of the mixed crosslinking system containing both sulfur and ZnO, the variations in S' and S'' occur in two stages (*Figure 3*). For example, S' increases in two steps, the first step due to ionic crosslinking and the second step due to covalent sulfur crosslinking. S'', however, first increases due to the formation of an ionic network and then decreases due to covalent network formation[13]. Incorporation of reinforcing HAF carbon black causes an increase in both S' and S'', but the increase is more prominent in the case of S''. Furthermore, the increase in S' and S'' is found to be more pronounced in the case of the ZnO curing system. The ionic crosslinks formed in the ZnO system are of the zinc ion–carboxylate ion type ($^{-}$OOC Zn^{2+} COO^{-})[14].

Figures 4 to *6* show the effect of carbon black filler on the variations in E', E'' and $\tan\delta$ with temperature for XNBR vulcanized by the three curing systems, namely sulfur, metal oxide and mixed sulfur–metal oxide. The results of the dynamic mechanical analyses are summarized in *Table 3*. *Figure 4* shows the plots of E', E'' and $\tan\delta$ *versus* temperature for the sulfur curing system. A single and sharp glass–rubber transition in the $\tan\delta$ *versus* temperature plot occurs at −7°C. The incorporation of HAF carbon black filler does not cause a shift in the transition temperature but the peak height decreases due to the formation of an absorbed shell on the active filler surface[15]. As expected, the loss modulus peak height at the transition zone increases due to filler incorporation and the storage modulus at room temperature increases due to strong polymer–filler attachments.

Figure 5 shows similar plots for the ZnO curing system. The results are different in the sense that the transition occurs here in two stages. Besides the first relaxation observed around −5°C, a high-temperature relaxation is observed around 54°C. This second transition is prominent in the $\tan\delta$ *versus* temperature plot. It is believed that the second transition arises because of the ionomers formed during the crosslinking of XNBR by ZnO[6,7].

It is surprising to note that the existence of the two-phase structure becomes prominent in the presence of reinforcing fillers like HAF carbon black. Furthermore, as the filler loading increases, the high-temperature transition peak height gradually increases along with the broadening of the peak. This is seen in the plots of E', E'' and $\tan\delta$ *versus* temperature. The two loss peaks indicate that the ZnO-vulcanized XNBRs have two phases, consisting of ion-rich, microphase-separated domains or clusters within a predominantly hydrocarbon matrix. These clusters act as multifunctional crosslinks and give rise to the high-temperature second transition. Although the role of the reinforcing filler in such ion-cluster formation is not clearly understood, it is believed that the surfaces of carbon black particles can act as multifunctional active sites[16,17]. The physical crosslinks from ionic clusters seem to be stabilized in an environment of multifunctional carbon black filler particles.

In the mixed crosslinking system, the characteristics of the high-temperature transition due to ionic clusters are retained and the effect is prominent in the presence of the reinforcing filler, particularly at high loading (*Figure 6*).

Table 3 Summary of dynamic mechanical properties of unfilled and filled XNBR cured with different vulcanizing systems

Vulcanization system	Filler loading (phr)[a]	$10^{-8}E''_{max}$ ($N\,m^{-2}$)	Temperature corresponding to E''_{max} (°C)	$\tan\delta_{max}$	Temperature corresponding to $\tan\delta_{max}$ (°C)
Sulfur/accelerator	0	2.720	−17.3	1.477	−7.2
	20	3.320	−15.4	1.258	−7.2
ZnO	0	2.490	−17.2	0.920	−5.2
				0.138	54.7
	10	2.490	−17.2	0.87	−9.2
		0.016	46.6	0.223	52.7
	20	2.590	−17.3	0.791	−7.3
		0.030	50.7	0.263	56.7
	30	3.100	−17.6	0.757	−7.2
		0.034	48.6	0.263–0.268	58.4–70.7
Sulfur/accelerator/ZnO	0	2.780	−15.2	0.964	−5.2
				0.115	46.7
	10	2.430	−13.2	0.898	−3.2
				0.164	42.6–52.7
	20	2.970	−11.3	0.793	−1.3
		0.023	56.6	0.217	66.6
	30	2.480	−13.4	0.754	−3.2
		0.032	46.7	0.224	56.7–66.7

[a] phr, Parts per hundred parts of rubber

CONCLUSIONS

Crosslinking of XNBR by ZnO results in a two-phase material registering two transitions in the variation of dynamic mechanical properties with temperature. The high-temperature transition is believed to be due to multifunctional crosslinks of carboxyl ionomers, the formation of which is favoured in the presence of multifunctional active sites of reinforcing HAF carbon black filler.

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