

Characterization of Network Structure of Rubber Vulcanizate by Monsanto Moving Die Rheometer (MDR 2000)

A. ROYCHOUDHURY and S. K. DE*

Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721 302, India

SYNOPSIS

While studying the curing of rubbers in a moving die rheometer, the viscous component (S'') of the measured torque increases with the formation of ionic cross-linking. But the covalent cross-linking of elastomers is manifested by a decrease in S'' . The mixed cross-linking system, however, shows an initial rise in S'' value due to ionic cross-linking, followed by a decrease in S'' due to covalent cross-linking. As curing progresses, the elastic component (S') of the measured torque in the case of a mixed cross-linking system increases in two steps: The first step is due to ionic cross-link formation, and the second step, to covalent cross-link formation. The moving die rheometer can be useful in assessing not only the extent of cross-linking, but also the type of cross-links formed during the vulcanization of rubbers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The moving die rheometer (MDR 2000) was introduced in 1988. In the MDR 2000, the force response can be separated into its in-phase (elastic) and out-of-phase (viscous) components.¹ Sezna² studied the correlation of results from curometers of different designs. DiMauro³ reported the testing of special rubber compounds on the MDR 2000 rheometer. While studying vulcanization characteristics of different rubber compounds by the MDR 2000 rheometer, we observed that the elastic and viscous components of the measured torque can provide useful information about the nature of cross-links in a vulcanizate⁴ (i.e., covalent, ionic, or mixed). In the present communication, we report the results of our rheometric studies with the MDR 2000 rheometer with carboxylated nitrile rubber (XNBR) using four different vulcanization systems, namely, dicumyl peroxide, sulfur-accelerator, zinc oxide, and a combination of zinc oxide and sulfur-accelerator. Both dicumyl peroxide and sulfur-accelerator systems

provide covalent cross-links, whereas zinc oxide gives rise to ionic-type cross-links.⁵ The combination of zinc oxide and sulfur-accelerator is known to give rise to mixed cross-linking consisting of both ionic and covalent types.⁵

EXPERIMENTAL

The carboxylated nitrile rubber (XNBR) used in the present study was Krynac X7.50, obtained from Polysar Ltd., Ontario, Canada. The formulation of the different mixes are given in the Table I. The mixing of curatives in the rubber was made on a laboratory two-roll mixing mill.

A Monsanto moving die rheometer (MDR 2000) with a 0.5° arc was used for studying the dependence of S' and S'' on cure time for the different rubber compositions (mix nos. 1–7) at the required temperature.

Dynamic mechanical studies were performed using a dynamic viscoelastometer (Rheovibron DDV III-EP, Orientec Corp., Japan) at a double-strain amplitude of 0.166% and a frequency of 3.5 Hz at room temperature. For dynamic mechanical studies, rubber compounds corresponding to mix no. 7 were cured at six different times at 140°C.

* To whom correspondence should be addressed.

Table I Formulation of the Mixes

	Mix No.						
	1	2	3	4	5	6	7
XNBR	100	100.0	100	100	100.0	100.0	100.0
ZnO	—	—	6	14	2.0	6.0	14.0
TMTD ^a	—	1.4	—	—	1.4	1.4	1.4
CBS ^b	—	4.0	—	—	4.0	4.0	4.0
Sulfur	—	1.6	—	—	1.6	1.6	1.6
DCP ^c	1	—	—	—	—	—	—

^a Tetramethyl thiuram disulfide.^b *N*-Cyclohexyl benzthiazyl sulfenamide.^c Dicumyl peroxide.

RESULTS AND DISCUSSION

Figure 1 shows the S' and S'' vs. time plots for mix nos. 1 and 2. Both dicumyl peroxide (mix no. 1) and the sulfur-accelerator system (mix no. 2) give rise to covalent cross-links. In both cases, S' increases and S'' decreases as the curing of the rubber progresses. At a very short time (generally less than 2 min), however, there occurs a decrease in S' and an increase in S'' . This is due to the initial heat softening of the rubber compound. Similar observations have also been made in the case of peroxide and sulfur vulcanization of other rubbers like natural rubber, nitrile rubber, and EPDM rubbers (results not shown here). Mix no. 2 does not contain ZnO, in order to ensure that there are no metal carboxylate cross-links in the network.

Figure 2 shows the rheographs for XNBR containing ZnO only (mix nos. 3 and 4). It is apparent that in contrast to the peroxide and sulfur-curing systems the metal oxide system in the case of XNBR registers an increase in both S' and S'' with increasing cross-linking. Both S' and S'' reach constancy around 5 min at 140°C, showing that ionic cross-link formation is fast enough to be completed in 5 min. When the ZnO concentration is increased from 6 phr (mix no. 3) to 14 phr (mix no. 4), values of both S' and S'' increase and the nature of the rheographs remains the same. It is apparent, therefore, that there is a distinct change in the nature of S'' vs. time plots when the nature of the cross-links changes from covalent cross-links (mix nos. 1 and 2) to ionic cross-links (mix nos. 3 and 4). $\text{COO}^- - \text{M}^{2+} - \text{OOC}$ linkage is labile in contrast to $\text{C}-\text{S}-\text{C}$ and $\text{C}-\text{C}$ linkages, which results in poor dynamic properties, namely, high-stress relaxation, heat buildup, and hysteresis in metal oxide-cured carboxylic elastomers.^{6-8,10,11} The lossy nature of metal carboxylate linkage is also reflected in the present case in the increase in S'' during cross-linking.

Mix no. 5 contains both zinc oxide and sulfur-accelerator curatives in order to ensure that the system produces both covalent and ionic cross-links. Figure 3 is the rheograph of mix No. 5 at 120°C. The MDR scorch time of the sulfur-accelerator system (mix no. 2) at 120°C is 52 min (the rheograph is not shown here). Therefore, sulfur cross-linking is unlikely to start at an early stage at 120°C. On the contrary, the carboxylated rubber-metal oxide

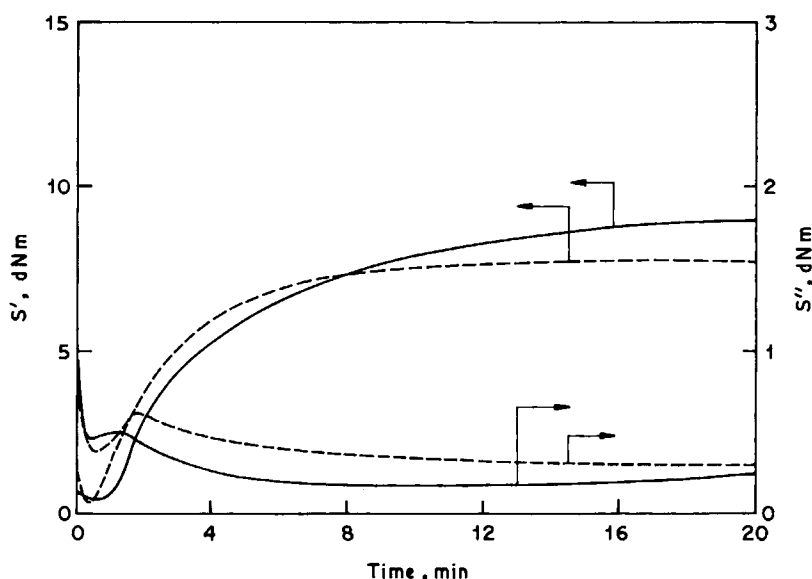


Figure 1 MDR traces (S' , S'') at 170°C of (—) XNBR-dicumyl peroxide (mix no. 1) and (----) XNBR-sulfur-accelerator (without ZnO, mix no. 2).

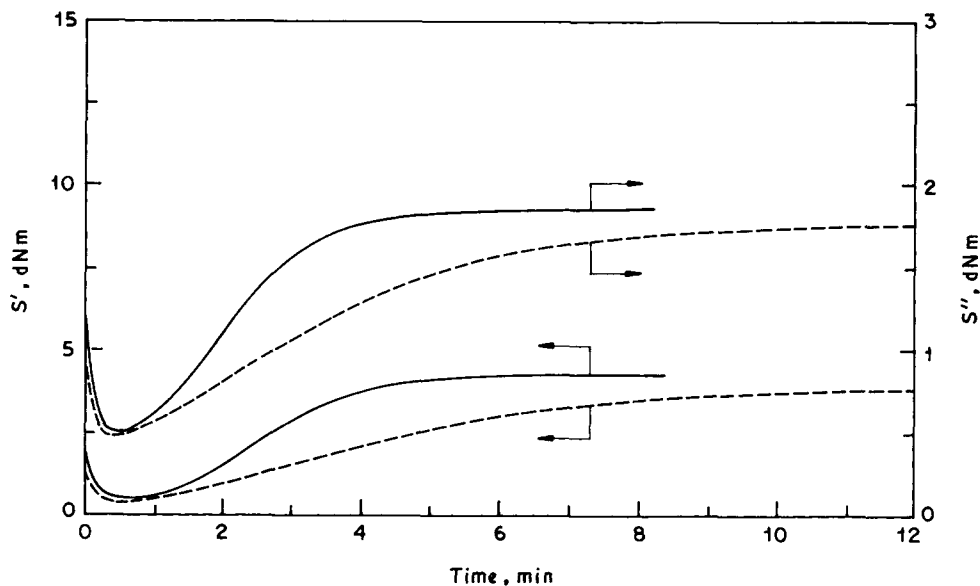


Figure 2 MDR traces (S' , S'') at 170°C of XNBR-ZnO: (-----) mix no. 3; (—) mix no. 4.

system is scorchy. As soon as a metal oxide is mixed with a carboxylated elastomer, reaction begins.^{5,6,8} Accordingly, the initial increase in S'' is attributed to the formation of ionic cross-links and the preceding decrease in S'' must be due to covalent sulfur cross-links. Furthermore, the in-between plateau region shows the completion of ionic cross-links and

the beginning of covalent sulfur cross-links. The S' vs. time plot also shows an expected increase in S' with cure time in two distinct stages: The first stage is presumably due to ionic cross-link formation, and the second stage, to covalent sulfur cross-linking.

Figure 4 shows similar rheographs at 140°C for three mixes (mix nos. 5-7) containing a fixed con-

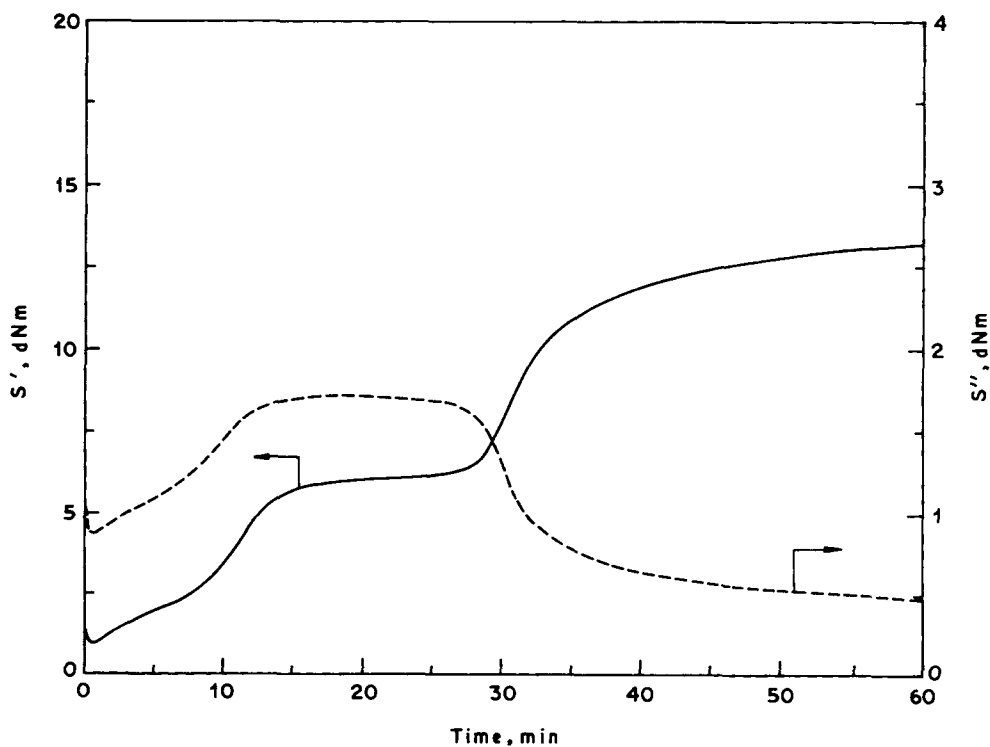


Figure 3 MDR traces (S' , S'') at 120°C of XNBR-ZnO/sulfur-accelerator (mix no. 6).

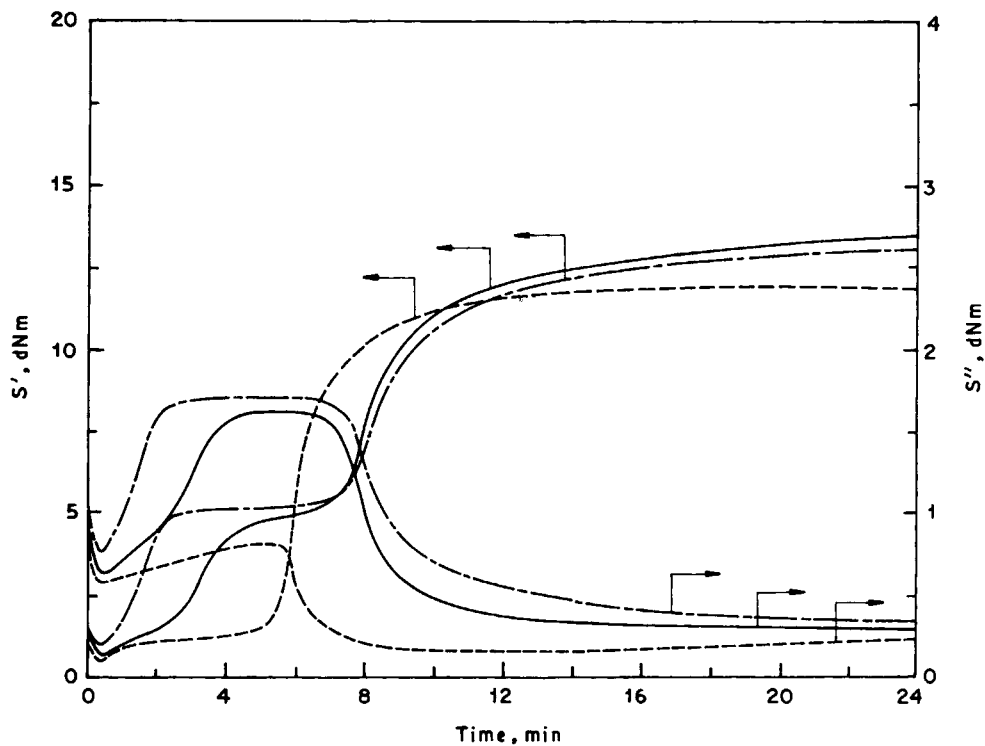


Figure 4 MDR traces (S' , S'') at 140°C of XNBR-ZnO/sulfur-accelerator: (-----) mix no. 5; (—) mix no. 6; (-·-·-) mix no. 7.

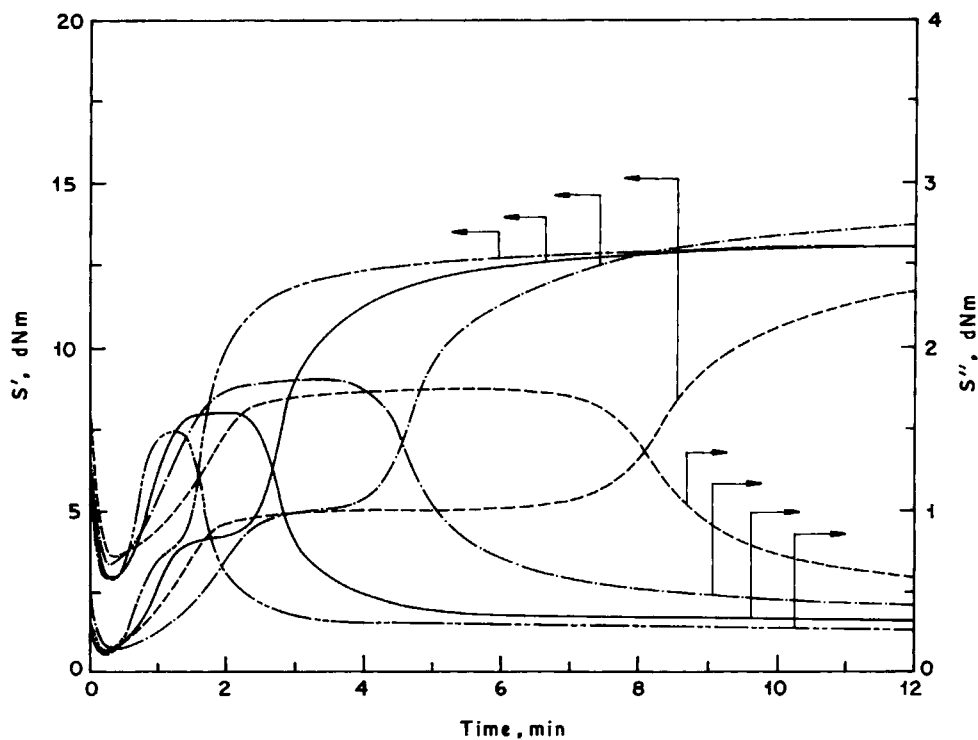


Figure 5 MDR traces (S' , S'') at different temperatures of XNBR-ZnO/sulfur-accelerator (mix no. 7): (-----) 140°C; (-·-·-) 150°C; (—) 160°C; (-·-·-) 170°C.

Table II MDR and DMA Data of XNBR Vulcanizate, Cured with Mixed Cross-linking System (Mix No. 7) at 140°C

Cure Time (min)	E' (MPa)	S' (dNm)	E'' (MPa)	S'' (dNm)
1.5	6.39	2.94	0.670	0.53
3.0	6.27	5.00	0.987	1.00
5.0	6.88	5.05	0.907	1.00
7.0	6.83	5.44	0.907	1.06
10.0	6.96	10.59	0.880	0.67
15.0	7.90	12.35	0.797	0.41

centration of sulfur curatives and three different concentrations of ZnO. It is apparent that the nature of the rheographs (both S' and S'') is similar to that of covalently cross-linked rubber system (see Fig. 1) when ZnO concentration is low (2 phr, mix no. 5). When the ZnO concentration is increased to 6 phr (mix no. 6), ionic cross-link formation starts, leading to a sharp initial increase in S'' , which is followed by covalent cross-link formation, leading to a plateau region followed by a decrease in S'' . S' vs. time plots also show an increase in S' in two distinct stages. When the ZnO concentration is increased further to 14 phr (mix no. 7), the rate of ionic cross-link formation increases, as is evident from the slope of the first part of both the S' and S'' vs. time plots. Figure 5 shows the rheographs at different temperatures of mix no. 7. In all cases, the clear demarcation between the two stages of vulcanization can be observed. The first stage is due to formation of ionic cross-links, the second stage is due to covalent sulfur cross-links, and the intermediate plateau region might consist of both types of cross-links. It is evident from Figure 5 that with increase in temperature the plateau region decreases, and at high temperature, it becomes difficult to distinguish between the two stages because sulfur cross-linking starts early and interferes with the metal oxide cross-linking process.

Earlier,⁹ it was found that rheometric S' and S'' correspond, respectively, to the storage modulus and loss modulus obtained by dynamic mechanical testing of vulcanizates. In the present studies, we step-cured the rubber compound according to the composition in mix no. 7 and measured the storage modulus and loss modulus of the rubber, cured for six different times, by rheovibron. Corresponding values of rheometric S' and S'' at the required times were obtained from the rheographs. Table II shows that S' and E' , and S'' and E'' , follow a similar trend with an increase in cross-linking.

It can be concluded, thus, that the moving die rheometer can be used to differentiate between the formation of ionic and covalent crosslinks in a rubber vulcanizate.

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REFERENCES

1. P. J. DiMauro, J. de Rudder, and J. P. Etienne, *Rubber World*, **201**(4), 25 (1990).
2. J. A. Sezna, Paper (No. 27) presented at the 139th meeting of the Rubber Division, American Chemical Society, Toronto, Canada, May 21–24, 1991.
3. P. J. DiMauro, Paper (No. 28) presented at the 139th meeting of the Rubber Division, American Chemical Society, Toronto, Canada, May 21–24, 1991.
4. A. Roychoudhury and S. K. De, Paper (No. 63) presented at a meeting of the Rubber Division, American Chemical Society, Nashville, TN, Nov. 3–6, 1992.
5. H. P. Brown and C. F. Gibbs, *Rubber Chem. Technol.*, **28**, 937 (1955).
6. H. P. Brown, *Rubber Chem. Technol.*, **36**, 931 (1963).
7. S. K. Chakraborty, A. K. Bhowmick, and S. K. De, *J. Appl. Polym. Sci.*, **26**, 4011 (1981).
8. N. D. Zakharov and T. A. Shadracheva, *Rubber Chem. Technol.*, **36**, 575 (1963).
9. J. A. Sezna, H. A. Pawlowski, and D. de Coninck, Paper (No. 78) presented at a meeting of the Rubber Division, American Chemical Society, Detroit, MI, Oct. 17–20, 1989.
10. S. K. Chakraborty, *Kautsch. Gummi Kunstst.*, **36**, 461 (1983).
11. S. K. Chakraborty and S. K. De, *Polymer*, **24**, 1055 (1983).

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