Effect of Silica Filler on Dynamic Mechanical Properties of Ionic Elastomer Based on Carboxylated Nitrile Rubber

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SYNOPSIS

Variation of dynamic mechanical properties like storage modulus (E') and loss tangent (tan δ) with temperature show the presence of two transitions in the carboxylated nitrile rubber (XNBR) molded in the presence of zinc oxide (ZnO). The low-temperature transition is due to the glass–rubber transition (T_g) of XNBR, and the high-temperature transition is due to formation of ionic clusters. Incorporation of reinforcing silica filler makes the high-temperature transition more prominent and high filler loading causes a shift of the transition temperature to the higher side. It is believed that the rubber–filler interaction in the cluster region causes striking changes in the variation of E' and tan δ with a double-strain amplitude (DSA). © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Ionomers contain a small amount of pendent ionic groups into polymer chains. Profound changes in physical properties of these modified polymers result due to the presence of the ionic groups, which at low concentration can exist as ionic aggregates, called multiplet, acting as physical cross-links.[1–4] At high concentration, the ionic aggregates can exist as a cluster consisting of both ion pairs and hydrocarbon chains, leading to microphase separation. Molding of the carboxylated nitrile rubber–zinc oxide (XNBR–ZnO) system is known to cause introduction of ionic cross-links in XNBR.[5–7] Dynamic mechanical studies showed the existence of the biphasic structure in the XNBR–ZnO system.[7] Apart from the low-temperature glass–rubber transition (T_g) of XNBR, there exists a high-temperature transition that is believed to be due to the presence of ionic aggregates in the cluster causing the phase separation and the effect becomes pronounced in presence of HAF black filler.[7] The present article reports the results of studies on the effect of silica filler on the dynamic mechanical properties of ionic elastomer based on the XNBR–ZnO system. For comparison,

XNBR cross-linked by a sulfur–accelerator system has been included in the study.

EXPERIMENTAL

Details of the materials and formulations used are given in Tables I and II, respectively. The compounding ingredients were mixed in a laboratory size two-roll mixing mill (325×150 mm) at a friction ratio of 1:1.9 according to ASTM D3182. The mixing schedule was 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. The temperature of the rolls was maintained around room temperature by circulating cold water through the rolls, and uniformity of mixing was maintained by adjusting the nip gap, time of mixing, and uniform cutting operation. Uniformity in degree of mixing was ensured by the Monsanto rheometric plots of the samples taken from different portions of the compounded sheet.

The rubber compounds were molded at 150°C in an electrically heated hydraulic press to the optimum cure time (i.e., 90% of the maximum cure) obtained from a Monsanto moving die rheometer, MDR 2000, with an arc of oscillation of ±0.5°. Test samples (8 cm $\times$ 6 mm $\times$ 2 mm) for the dynamic mechanical testing were cut from the molded sheets.

Table I   Details of Materials Used

Materials	Characteristics	Sources
Carboxylated acrylonitrile–butadiene rubber (XNBR)	KRYNACX 7.50 : Mooney viscosity (ML_{1+4} at 100°C) 57	Bayer Polysar, France
Zinc oxide (ZnO)	Rubber grade, specific gravity 5.4	Loba Chemicals, Bombay, India
Silica filler (SiO_2)	Vulcasil-S, BET surface area 120–160 m^2/g	Bayer, Germany
N-Cyclohexyl benzothiazyl sulfenamide (CBS)	Rubber grade, powder	I.C.I. Ltd., Rishra, India
Tetramethyl thiuram disulfide (TMTD)	Rubber grade, powder	I.C.I. Ltd., Rishra, India
Stearic acid	Rubber grade, crystalline	Loba Chemicals, Bombay, India
Sulfur (S)	Rubber grade, powder	Loba Chemicals, Bombay, India

Measurement of dynamic mechanical properties was carried out in the tension mode at a frequency of 3.5 Hz using a viscoelastometer, Rheovibron DDV-III-EP of Orientec Corp., Japan. Isothermal strain-dependent dynamic mechanical properties were measured at the same frequency at room temperature (28°C) at different double-strain amplitudes (DSA). DSA values were varied from 0.07 to 5% by changing the displacement amplitude and length of the test pieces. DSA is defined as

$$DSA = \frac{2 \times amplitude}{length \ of \ the \ test \ pieces}$$

RESULTS AND DISCUSSION

Figure 1 shows the effect of ZnO concentration on the variation of storage modulus (E') and loss tangent (tan δ) as a function of temperature of the XNBR–ZnO system. For comparison, the results of the XNBR–sulfur–accelerator system has also been shown in the same figure. The sulfur-curing system shows a single transition around −7°C, which is the glass–rubber transition (T_g) of XNBR. At the 2 phr ZnO level, the XNBR–ZnO system exhibits behavior similar to that of the XNBR–sulfur–accelerator system. But at the 4 phr ZnO level, the system ex-

**Table II   Formulations of the Mixes and Their Curing Times**

	Mix No.												
	S_0	S_{10}	S_{20}	S_{30}	S_{60}	$Z_0(2)$	$Z_0(4)$	$Z_0(6)$	Z_0	Z_{10}	Z_{20}	Z_{30}	Z_{60}
XNBR	100	100	100	100	100	100	100	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1	1	1	1	1	1	1	1
Silica	0	10	20	30	60	—	—	—	—	10	20	30	60
CBS	3	3	3	3	3	—	—	—	—	—	—	—	—
TMTD	1	1	1	1	1	—	—	—	—	—	—	—	—
S	1	1	1	1	1	—	—	—	—	—	—	—	—
ZnO	—	—	—	—	—	2	4	6	12	12	12	12	12
Curing time at 150°C (min)	46	42	40	38	35	8	7	6	5	5	5	7	8
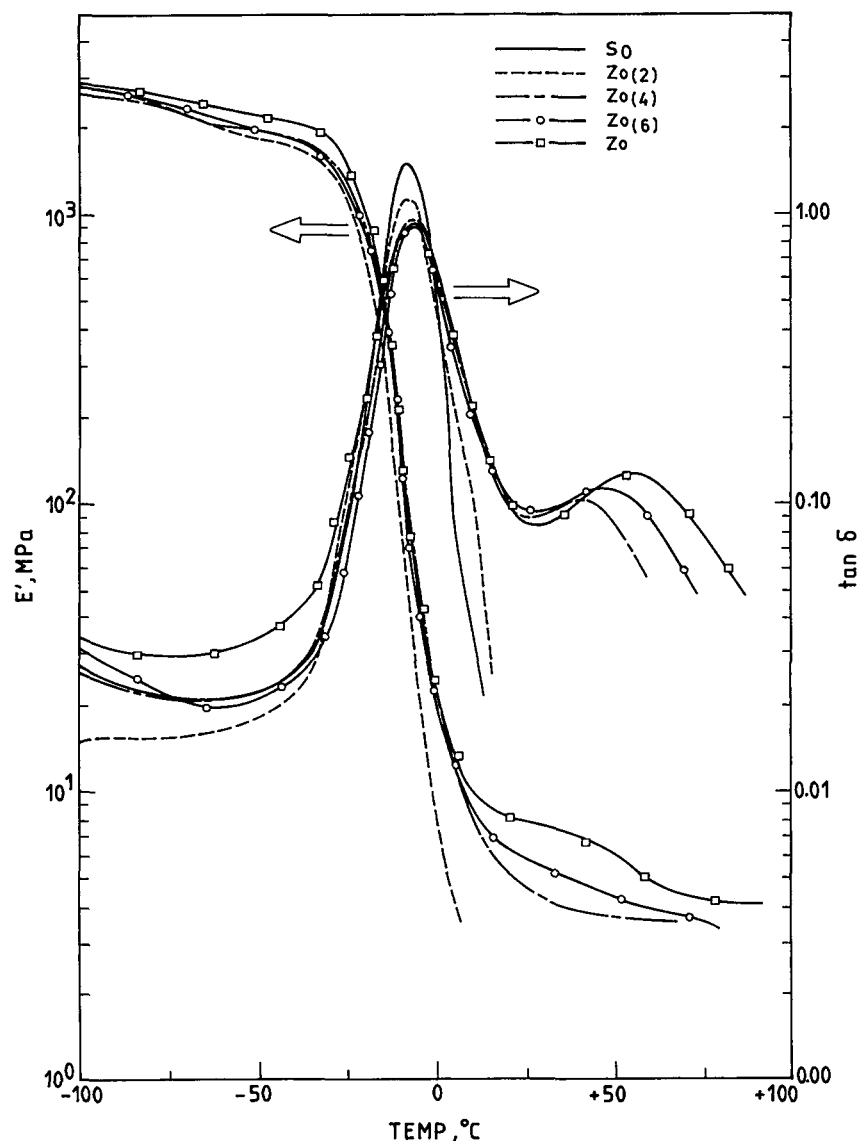
Figure 1 Plots of E' and tan δ as a function of temperature: effect of zinc oxide loading:
(————) S_0; (------) $Z_0(2)$; (— — —) $Z_0(4)$; (——O——) $Z_{(6)}$; (——□——) z_0.

hibits an additional transition (around 40°C) in the tan δ vs. temperature plot and a rubbery plateau in the E' vs. temperature plot. With further increase in ZnO loading, the tan δ peak height at the high-temperature transition increases and the peak shifts to higher temperature, along with increase in high-temperature E' values. The occurrence of the additional transition at high temperatures in the XNBR–ZnO system is believed to be due to formation of ionomers. The observation can be explained on the basis of multiplet cluster model.[8] At low ZnO loading, the ionic aggregates consist of several ion pairs constituting a multiplet and each mul-

tiplet is surrounded by a layer or "skin" of restricted chain mobility due to anchoring of the polymer chains by the ion pair at the point where it is attached. At a high ZnO level, the ion content increases and the average distance between the multiplets decreases, causing, thereby, some overlapping among regions of restricted chain mobility surrounding each multiplet. If a large continuous region of restricted mobility is formed due to a high degree of overlapping, the system constitutes a cluster and exhibits the characteristic behavior of a phase-separated region at a temperature higher than the T_g of the rubber. At the 12 phr ZnO level, the cluster formation
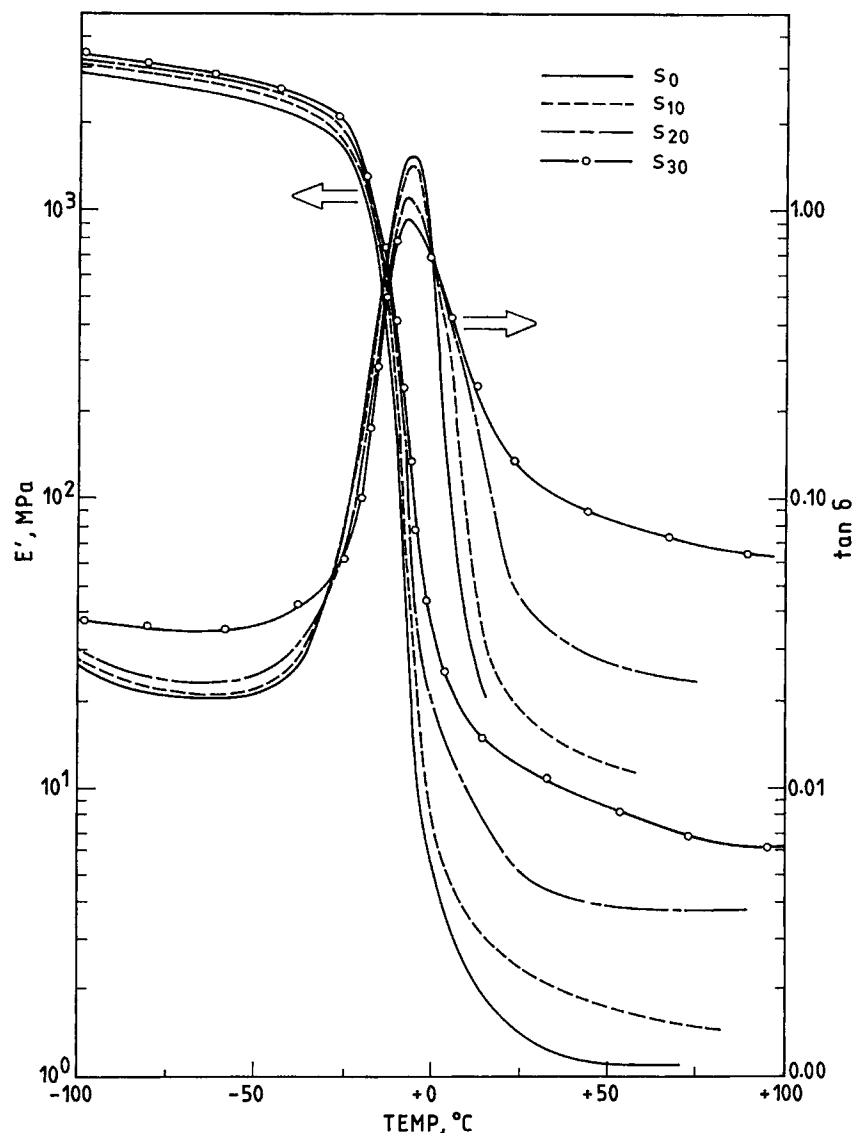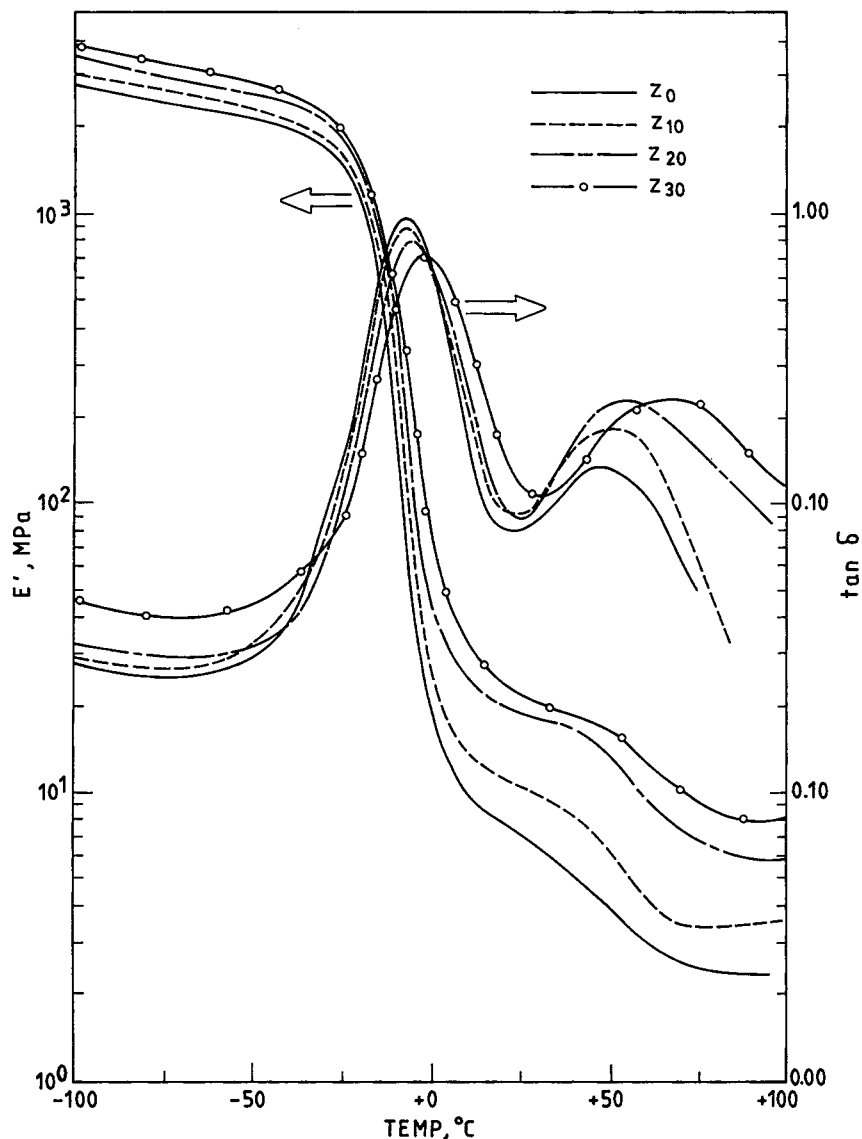
Figure 2 Plots of E' and tan δ as a function of temperature for the XNBR–sulfur–accelerator system: effect of silica filler loading: (———) S_0; (— — — —) S_{10}; (— - —) S_{20}; (——— O ———) S_{30}.

is so pronounced that both E' vs. temperature and tan δ vs. temperature plots registered the high-temperature transition.

Figures 2 and 3 show the effect of silica filler on the dynamic mechanical properties of the XNBR–sulfur–accelerator system and the XNBR–ZnO system, respectively. Figure 3 shows that an increase in filler loading does not cause a change in T_g, but that the tan δ peak value at T_g decreases and the E' value gradually increases. The results can be explained on the basis of the filler–rubber interaction.[9–10] Figure 3 shows that the incorporation of silica filler makes the high-temperature transition

due to ionic clusters more prominent and the peak temperature shifts to the higher side. Furthermore, at a high ZnO level (12 phr), the tan δ value at T_g decreases due to filler–rubber interaction and the T_g itself shows a minor shift to the higher-temperature side. It is believed that filler particles interact with the rubber chains both in the cluster region and in areas away from the cluster region. Rubber–filler interaction in areas away from the cluster region causes the expected changes in regard to variation of tan δ with temperature. But rubber–filler interaction in the cluster region is believed to enhance the overlapping of restricted chain mobility areas,

Figure 3 Plots of E' and tan δ as a function of temperature for the XNBR-ZnO system: effect of silica filler loading: (———) Z_0; (— — — —) Z_{10}; (— — —) Z_{20}; (——— O ———) Z_{30}.

thus shifting the second transition to higher temperature. It is believed that at a high ZnO level (12 phr), a higher concentration of multiplets may cause some degree of rigidity in the chains away from the cluster region, thereby shifting the T_g to the higher temperature side.

Figure 4 shows the effect of cross-linking systems and filler loadings on the variation of E' with double-strain amplitude (DSA). The results are summarized in Table III. E'_0 is the value of modulus at low DSA (0.07%) and E'_5 is the value at high DSA (5%). The difference between E'_0 and E'_5 is designated as $\Delta E'$, which is believed to be a measure of the struc-

ture breakdown of filler interaggregates.[11] The E'_0 value of the XNBR-ZnO system is higher than that of the XNBR-sulfur-accelerator system because of the occurrence of a rigid phase in the former due to ionic clusters. Furthermore, the rigid phase is stable and insensitive to the changes in DSA from 0.07 to 5%. This is contrary to the observation made in the case of the XNBR-sulfur-accelerator system, where E'_5 values are much less than are E'_0 values, indicating the sensitivity of this system to changes in the DSA. In the presence of silica filler, E'_0 values in both systems increase, but the increase is more prominent in the case of the XNBR-ZnO system,
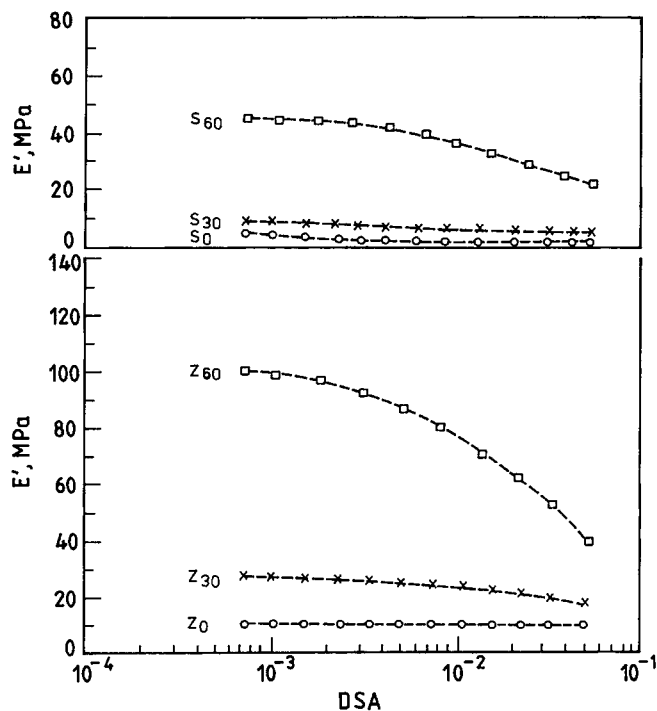
Figure 4   Plots of E' as a function of DSA: effect of cross-linking system and silica filler loading.

presumably due to stronger rubber–filler interaction in the cluster zone of ionic aggregates as compared to the rubber–filler interaction involving the polymer chains away from the cluster zone.

In the filled systems, E'_5 values are less as compared to the E'_0 values due to breakdown of filler interaggregates, but the phenomenon is striking in the case of the XNBR–ZnO system. Entrapped filler particles in the cluster region cause formation of additional filler interaggregates in addition to the interaggregates present within the main chain. These additional interaggregates undergo excessive breakdown with increasing DSA, resulting in high values of $\Delta E'$.

Table III   Values of E'_0, and E'_5, and $\Delta E'$ at 28°C

Mix No.	E'_0 (MPa)	E'_5 (MPa)	$\Delta E'$ (MPa)
S_0	6.45	2.55	3.90
Z_0	10.40	9.20	1.20
S_{30}	16.00	11.00	5.00
Z_{30}	28.00	20.00	8.00
S_{60}	46.10	21.80	24.30
Z_{60}	95.60	30.20	65.40

Figure 5 shows the effect of silica filler loading on the variation of loss tangent with DSA in both XNBR–ZnO and XNBR–sulfur–accelerator systems. In the unfilled systems, there is no change in tan δ with DSA. As the filler loading increases, tan δ values gradually increase with increase in DSA, whereas in the case of the XNBR–sulfur–accelerator system, tan δ attains a plateau at high DSA. This observation is similar to that observed in the conventional rubber vulcanizates.[9-11] The XNBR–ZnO system, however, does not show any plateau and the tan δ increases gradually with increase in DSA. It is believed that considerable slippage occurs between filler particles and the ionic aggregates in the cluster zone at high DSA in addition to normal breakdown and reformation of filler interaggregates. This causes high tan δ in the XNBR–ZnO system.

CONCLUSIONS

The variation of storage modulus (E') and loss tangent (tan δ) with temperature reveals the occurrence of a biphasic structure in the XNBR–ZnO system, particularly at a high ZnO level (12 phr). The low-temperature transition around −5°C is due to the T_g of XNBR and the high-temperature transition
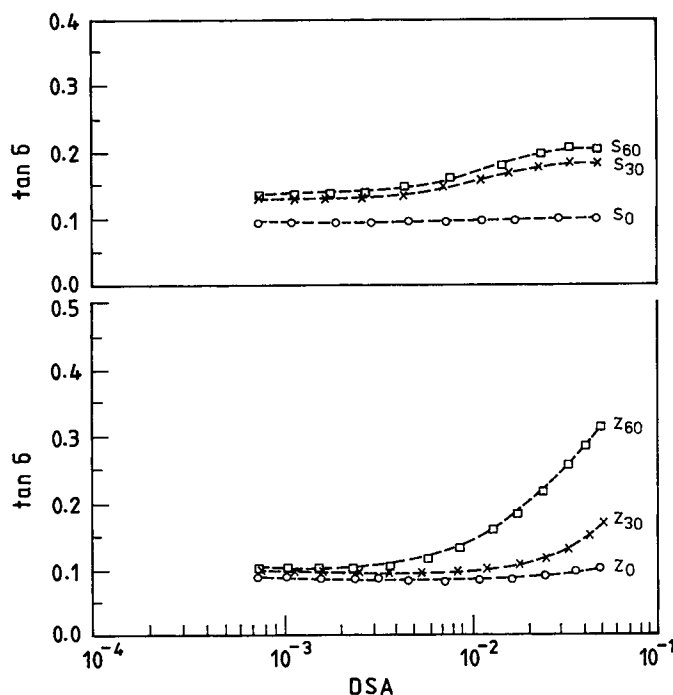
Figure 5 Plots of tan δ as a function of DSA: effect of cross-linking system and silica filler loading.

around +50°C is believed to be due to formation of ionic clusters.

The transition due to ionic clusters becomes prominent in presence of silica filler. The presence of silica filler in ionic clusters in the XNBR–ZnO system results in extensive breakdown and slippage of filler interaggregates in the region of ionic clusters with increasing DSA.

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