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# Dynamic mechanical spectroscopic studies on plasticization of an ionic elastomer based on carboxylated nitrile rubber by ammonia

**U. K. Mandal, D. K. Tripathy and S. K. De***
*Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721 302, India*
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Results of measurements of dynamic mechanical and physical properties of the ionic polymer, based on carboxylated nitrile rubber (XNBR) neutralized by zinc oxide (ZnO), reveal that ammonia works as an ionic plasticizer. Accordingly, the main chain transition is little affected but the high temperature transition due to ionic aggregates, as observed in dynamic mechanical measurements, disappeared after being exposed to ammonia for 24 h. Exposure to ammonia also caused a drop in physical properties of both unfulfilled and carbon black and silica filled XNBR–ZnO compositions. Copyright © 1996 Elsevier Science Ltd.

**(Keywords: carboxylated nitrile rubber; ionomer; dynamic mechanical studies)**

## *Introduction*

Formation of a caryboxylic acid salt, during moulding of carboxylated nitrile rubber (XNBR) in the presence of zinc oxide, is known to cause formation of an ionic elastomer or ionomer[1–3], which displays improved physical properties[4,5]. Measurement of dynamic mechanical properties of the moulded XNBR–ZnO composition show the occurrence of the biphasic transition. Apart from the low temperature glass–rubber transition of XNBR, there occurs a high temperature transition which is believed to be due to the occurrence of a hard phase arising out of the ionic clusters or aggregates, and the effect becomes more pronounced in the presence of reinforcing fillers[3,6].

In order to understand the nature of component phases in ionomers, several researchers have studied the effect of plasticizers on their physical properties[7–10]. Plasticizers can be grouped into two types: backbone plasticizers which, preferably plasticize the nonpolar hydrocarbon part of the chains, and ionic plasticizers, which preferentially affect the ionic clusters. A previous paper[11] reports the results of studies on the effect of dimethylsulfoxide, which is an ionic plasticizer, and dioctylphthalate, which functions as a backbone plasticizer, on the physical properties of the XNBR–ZnO system.

The present communication reports the results of studies on the effect of ammonia on the dynamic mechanical and physical properties of an ionic elastomer based on the XNBR–ZnO system.

## *Experimental*

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

*Preparation of the sample.* The compounding ingredients were mixed in a laboratory size-two roll mixing mill, according to ASTM D3182, at a friction ratio 1/1.6. The temperature of the rolls was maintained around room temperature by circulating cold water through them. The mixed compounds were moulded at 150°C in an electrically heated hydraulic press to the optimum cure times (i.e. 90% of the maximum cure) as obtained from the Monsanto moving die rheometer, MDR 2000, run at an arc of oscillation of ±0.5°. Ammonia treatment was done by exposing the moulded samples for 24 h in saturated ammonia vapour (i.e. 25% aqueous solution) in a dessicator.

*Dynamic mechanical testing.* Measurement of dynamic mechanical properties was carried out under tension mode at a frequency of 3.5 Hz using a viscoelastometer, Rheovibron DDV-III-EP, of M/S. Orientec Corporation, Japan. Rectangular samples (55 mm × 6.5 mm × 2 mm) were used. Testing was carried out at an amplitude of 0.025 mm and the linear temperature rise was $2°C\,min^{-1}$.

*Measurement of physical properties.* Measurement of modulus, tensile strength, and elongation at break was carried out at room temperature as per ASTM D412-80 test method, using dumb-bell shaped test pieces and a Zwick Universal Testing Machine (UTM), model 1445. Tear strength of the samples was determined as per ASTM D624-87 test method, using un-nicked 90° angle test pieces at room temperature in a Zwick UTM, Model 1445. The tension set at 100% extension was measured at room temperature according to ASTM D412 (1987).

## *Results and discussion*

The dynamic mechanical spectra of both untreated and ammonia-treated samples of the XNBR–ZnO system is shown in *Figure 1*. In this figure, the $\tan\delta$ vs temperature plot shows that in the untreated sample, besides the low temperature relaxation around −9°C, which is the glass–rubber transition temperature ($T_g$) of XNBR, a high temperature relaxation is observed around 40°C which is believed to be due to the formation of the biphasic structure arising out of the multiplets and

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* To whom correspondence should be addressed

**Table 1** Details of materials used

| Material name | Characteristics | Source |
|---|---|---|
| Carboxylated acrylonitrile butadiene rubber (XNBR) | %Acrylonitrile = 27[a]<br>%Carboxyl = 7[a]<br>KRYNAC × 7.50 grade; Mooney viscosity ($ML_{1+4}$ at 100°C), 57 | Bayer Polysar, France |
| Zinc oxide (ZnO) | Rubber grade; Specific gravity, 5.4 | E. Mark (I) Ltd., Bombay, India |
| High abrasion furnace (HAF) carbon black | Grade, N-330; surface area, 80 $m^2 g^{-1}$; pH, 7.6 | Phillips Carbon Black Ltd., Durgapur, India |
| Silica filler ($SiO_2$) | Grade, Vulcasil-S; BET surface area 120–160 $m^2 g^{-1}$ | Bayer, Germany |
| N-cyclohexyl benzothiazyl sulfenamide (CBS) | Rubber grade; powder | ICI (I) Ltd., Rishra, Howrah, India |
| Tetramethyl thiuram disulfide (TMTD) | Rubber grade; powder | ICI (I) Ltd., Rishra, Howrah, India |
| Sulfur | Precipitated; powder | Loba Chemical, Bombay, India |
| Stearic acid | Crystalline | E. Mark (I) Ltd., Bombay, India |
| Ammonia | 25% aq. solution | E. Mark (I) Ltd., Bombay, India |

[a] In wt %

**Table 2** Formulation of the mixes[a]

| Mix designation | Z[b] | S[b] | ZF[b] | ZSi[b] |
|---|---|---|---|---|
| XNBR | 100 | 100 | 100 | 100 |
| ZnO | 12 | | 12 | 12 |
| TMTD | | 1 | | |
| CBS | | 3 | | |
| Sulfur | | 1 | | |
| Carbon black | | | 20 | |
| Silica | | | | 20 |
| Stearic acid | 1 | 1 | 1 | 1 |

[a] Figures in phr (parts per hundred parts of rubber)
[b] Moulded at 150°C for: Z, 10 min; S, 45 min; ZF, 10 min; ZSi, 10 min

clusters in the XNBR–ZnO system[3]. The high temperature ionic transition is abbreviated as $T_i$. In the case of the ammonia-treated sample, however, the low temperature glass–rubber transition occurs with only little shift to the low temperature side, but the high temperature ionic transition almost disappeared. The shoulder observed above $T_g$ in the ammonia-treated sample indicates traces of the hard phase in the high temperature transition still remaining after ammonia treatment. Similar result was observed in the variation of storage modulus with temperature. The storage modulus in the high temperature region decreased on ammonia treatment. The measurements could not be made at temperatures higher than that shown in the figure because the machine stopped at the point when the sample became soft and the tanδ registered negative values. As shown in *Figures 2* and *3*, dynamic mechanical spectra of the XNBR–ZnO system in the presence of carbon black and silica fillers also register similar changes on ammonia treatment in the variation of tanδ and storage modulus with temperature. The results are summarized in *Table 3*. For comparison, *Figure 4* shows the effect of ammonia on the dynamic mechanical spectra of a sulfur crosslinked sample of XNBR. It is seen that both tanδ and modulus remain unaffected at all temperatures on ammonia treatment. Accordingly, it can be argued that ammonia attacks the ionic aggregates in the XNBR–ZnO system. Results of measurements of physical properties (*Table 4*) are in conformity with those of dynamic mechanical properties. Ammonia treatment caused reduction in both modulus and tensile strength and an increase in tension set due to dissolution of the physical crosslinks arising out of the ionic aggregates in the presence of ammonia.

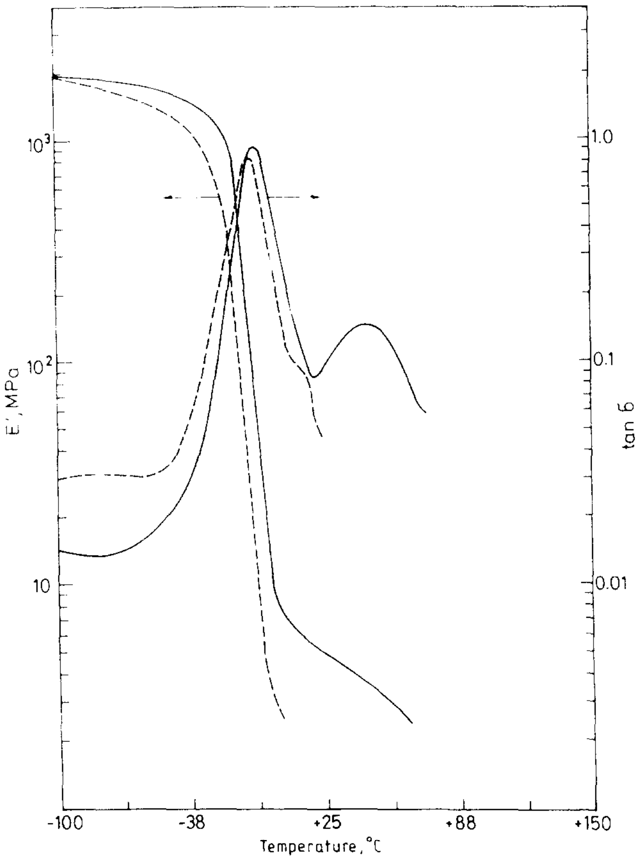

**Figure 1** Effect of ammonia on dynamic mechanical spectra of gum XNBR–ZnO composition: —— untreated; - - - - ammonia-treated.

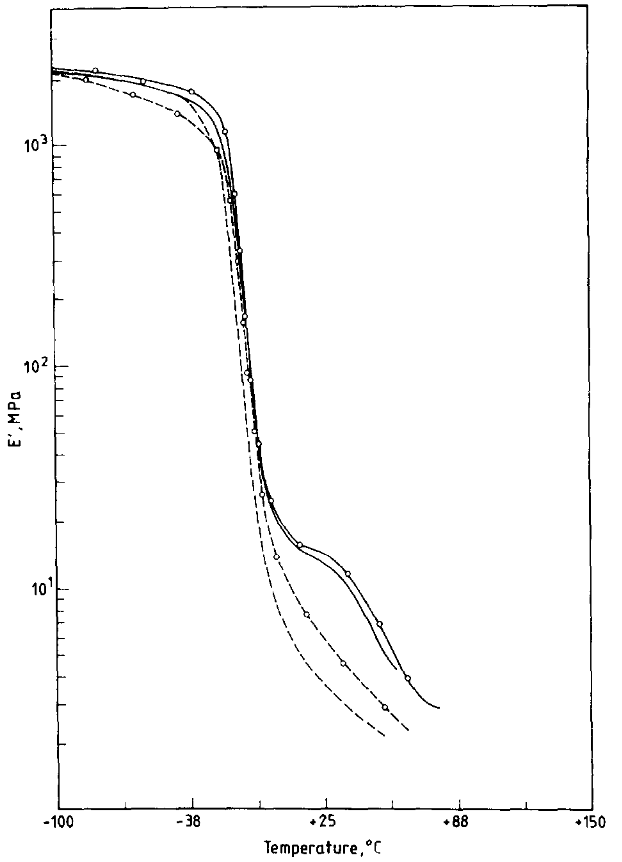

**Figure 2** Effect of ammonia on dynamic mechanical spectra of filled XNBR–ZnO composition: plots of $E'$ vs temperature. —— untreated, ZF; —o— untreated, ZSi; - - - ammonia-treated, ZF; - - o - - ammonia-treated, ZSi

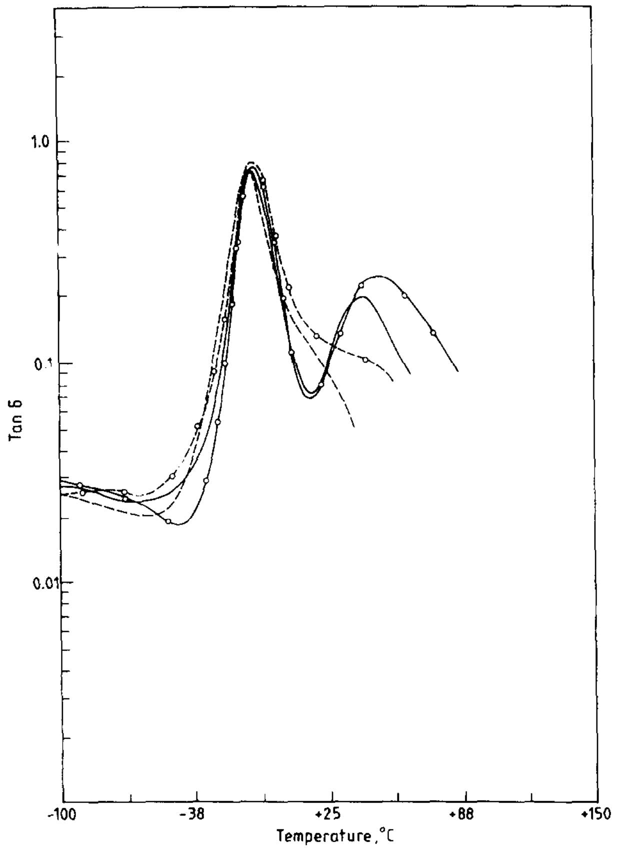

**Figure 3** Effect of ammonia on dynamic mechanical spectra of filled XNBR–ZnO composition: plots of tan$\delta$ vs temperature. Key as in *Figure 2*

**Table 3** Summary of the results of the dynamic mechanical spectroscopic studies. Figures in parentheses are the results of ammonia-treated samples

| Mix name | Main chain transition temperature ($T_g$, °C) | Tan$\delta_{max}$ at $T_g$ | Ionic transition temperature ($T_i$, °C) | Tan$\delta_{max}$ at $T_i$ |
|---|---|---|---|---|
| Z | −7.2 | 0.92 | +40.5 | 0.15 |
|  | (−11.7) | (0.84) | $^a$ | $^a$ |
| S | −7.0 | 1.48 | – | – |
|  | (−7.2) | (1.47) | – | – |
| ZF | −7.2 | 0.77 | +46.0 | 0.19 |
|  | (−11.3) | (0.74) | $^a$ | $^a$ |
| ZSi | −7.2 | 0.80 | +51.0 | 0.26 |
|  | (−9.2) | (0.76) | $^a$ | $^a$ |

$^a$ Not detectable

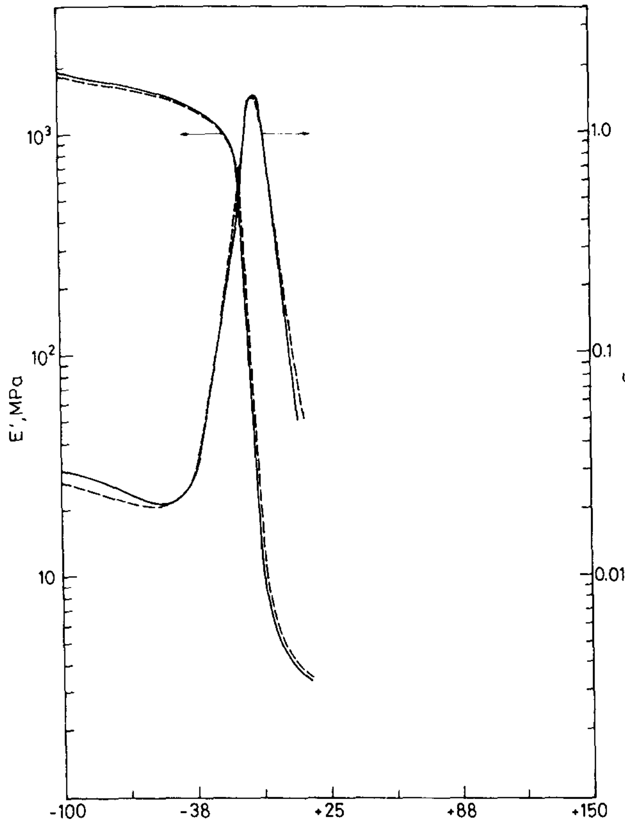

**Figure 4** Effect of ammonia on dynamic mechanical spectra of XNBR–sulfur composition. ——, untreated; - - - ammonia-treated

Eisenberg and King have proposed spatial arrangement of ionic groups in ionomers[12]. The morphological structure of ionomers is based on the multiplet-cluster model[13] in which the restricted chain mobility of the polymer chains in the vicinity of ionic salt aggregates gives rise to the hard phase. Clusters may be formed by the association of multiplets. This association is favoured by electrostatic interaction between multiplets and opposed by the retractive elastic forces of the backbone chains. It is believed that ammonia may form a coordinating linkage with the zinc ions of zinc carboxylate slats[14,15] or may solvate the carboxyl ions[16,17] (*Figure 5*), as a result of which the electrostatic interaction between the multiplets decreases, inhibiting the formation of clusters. Accordingly, the high temperature transition in the dynamic mechanical spectra disappears and the physical properties decrease on

**Table 4** Physical properties. Figures in parentheses are the results of ammonia-treated samples

| Mix designation | Z | S | ZF | ZSi |
|---|---|---|---|---|
| 100% modulus (MPa) | 1.82<br>(0.64) | 0.94<br>(0.96) | 4.75<br>(1.18) | 4.00<br>(1.35) |
| 200% modulus (MPa) | 2.56<br>(0.92) | 1.34<br>(1.37) | 7.24<br>(1.75) | 9.54<br>(2.23) |
| 300% modulus (MPa) | 3.70<br>(1.18) | 1.80<br>(1.95) | 10.00<br>(2.45) | 11.65<br>(3.28) |
| Elongation at break (%) | 1150<br>(1040) | 580<br>(550) | 1000<br>(650) | 1050<br>(770) |
| Tensile strength (MPa) | 33.00<br>(7.50) | 4.50<br>(5.00) | 31.00<br>(8.00) | 32.00<br>(8.50) |
| Tear strength ($N\,cm^{-1}$) | 48<br>(16) | 32<br>(34) | 58<br>(18) | 62<br>(20) |
| Tension set (%) | 9<br>(24) | 2<br>(2) | 11<br>(28) | 12<br>(29) |

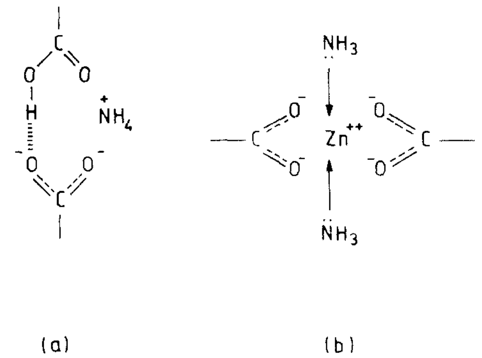

**Figure 5** Schematic diagram of (a) solvation of carboxylic acid by ammonia, (b) co-ordination of ammonia with zinc ion of carboxylic acid salt

ammonia treatment. A minor shift in the glass transition temperature towards the low temperature side may be due to dissolution of the hard phase in the presence of ammonia.

## *Conclusions*

Dynamic mechanical spectroscopic studies reveal the formation of a biphasic structure in the ionomer based on XNBR–ZnO composition, due to the formation of a hard phase arising out of the ionic aggregates. Ammonia acts as a plasticizer for the ionic aggregates, thus causing disappearance of the hard phase in the high temperature region of the dynamic mechanical spectra and a consequent drop in physical properties.

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