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

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Results of dynamic mechanical studies and measurements of physical properties of the ionic polymer based on carboxylated nitrile rubber (XNBR) and zinc oxide (ZnO) reveal that dioctylphthalate (DOP) plasticizes the backbone chain of the polymer, while dimethylsulfoxide (DMSO) plasticizes the hard phase arising from the ionic aggregates. Accordingly, the high-temperature ionic transition in the plot of tan δ *versus* temperature disappears at high DMSO loading, while the glass–rubber transition temperature (T_g) is little affected. Incorporation of DOP, on the other hand, causes shifting of T_g to lower temperature, without affecting the high-temperature transition. Both plasticizers cause a drop in physical properties, but the drop is greater in the case of the DMSO-plasticized system. Copyright © 1996 Elsevier Science Ltd.

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

Introduction

Moulding of carboxylated nitrile rubber (XNBR) in the presence of zinc oxide (ZnO) is known to cause the introduction of ionic crosslinks[1–4]. Dynamic mechanical studies showed the existence of a biphasic structure in the XNBR–ZnO system[5,6]. Apart from the low-temperature glass–rubber transition (T_g) of XNBR, there exists a high-temperature transition which is believed to be due to the occurrence of ionic clusters causing phase separation, the effect becoming more pronounced in the presence of reinforcing fillers[5,6]. The melt viscosity of the ionic polymer is too high for easy processing. The two-phase morphology and the large difference in the polarity of the hydrocarbon chain and the ionic phase offer two possibilities for the plasticization of ionomers, namely plasticization of the hydrocarbon phase and plasticization of the ionic clusters.

Bazuin and Eisenberg[7] studied the effects of polar (glycerol) and non-polar (ethyl benzene) plasticizers on the dynamic mechanical properties of styrene–methacrylic acid copolymer. Hara *et al.*[8] reported the role of dimethylformamide (DMF) as a dual plasticizer for sulfonated polystyrene ionomers. Navaratil and Eisenberg[9] reported the use of dimethylsulfoxide (DMSO) as an ionic plasticizer for sodium neutralized poly(styrene-*co*-methacrylic acid). Kurian *et al.*[10] have studied the plasticization by paraffinic oil and DMSO of the zinc salt of sulfonated ethylene–propylene–diene terpolymer rubber. Incorporation of zinc stearate causes remarkable improvement in processing due to plasticization of the ionic domains at elevated temperature[11,12].

The present communication reports the results of dynamic mechanical spectroscopic studies on the dioctylphthalate (DOP) and DMSO plasticization of ionic rubber based on the XNBR–ZnO system.

Experimental

Details of the materials used are given in *Table 1* and the formulations used are given in *Table 2*. Plasticized compounds were prepared in a two-roll mixing mill according to ASTM D3182 at a friction ratio of 1 : 1.6. The temperature of the rolls was maintained around room temperature by circulating cold water through the rolls. Plasticizer was added slowly, drop by drop, during mixing. In the case of unfilled compounds plasticizer was added before addition of zinc oxide and in the case of filled compounds plasticizer was added during the addition of filler. The compounds were moulded at 150°C in an electrically heated hydraulic press to the optimum cure time (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°.

Measurement of dynamic mechanical properties was carried out under tension mode at a frequency of 3.5 Hz using a Rheovibron DDV-III-EP viscoelastometer (M/S. Orientec Corporation, Japan). Rectangular samples (35 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 modulus, tensile strength and elongation at break was carried out at 25°C as per the ASTM D412-80 test method using dumb-bell shaped test-pieces and a Zwick model 1445 universal testing machine (UTM). Tear strength of the samples was determined as per ASTM D624-87 using unnicked 90° test-pieces at 25°C in the Zwick UTM. The tension set at 100% extension was measured at room temperature according to ASTM D412 (1987). The hardness of the samples was measured using a Wallace microhardness tester according to ASTM D1415.

Results and discussion

Figures 1 and *2* show the effect of DOP and DMSO on

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Table 1 Details of materials used

Materials	Characteristics	Source
Carboxylated acrylonitrile–butadiene rubber (XNBR)	% Acrylonitrile = 27[a]; % carboxyl = 7; KRYNAC X 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
Dioctylphthalate (DOP)	Liquid; b.p. 384°C	E. Mark (I) Ltd, Bombay, India
Dimethylsulfoxide (DMSO)	Liquid; b.p. 189°C	E. Mark (I) Ltd, Bombay, India
Stearic acid	Crystalline	E. Mark (I) Ltd, Bombay, India
High abrasion furnace carbon black (HAF)	N-330; surface area, 80 m^2 g^{-1}; pH, 7.6	Phillips Carbon Black Ltd, Durgapur, India

[a] In wt%

Table 2 Formulation of the mixes[a]

	Mix designation					
	X	X-P	X-S	X-F	X-FP	X-FS
XNBR	100	100	100	100	100	100
DOP	–	Variable[b]	–	–	20	–
DMSO	–	–	Variable[c]	–	–	10
HAF		–		40	40	40
ZnO	12	12	12	12	12	12
Stearic acid	1	1	1	1	1	1

[a] Figures in phr; i.e. parts per hundred parts of rubber
[b] DOP loading: 5, 10, 15 and 20 phr
[c] DMSO loading: 2, 5, 7 and 10 phr

the variation of tan δ with temperature; the results are summarized in *Tables 3* and *4*. In the absence of plasticizers, besides the low-temperature relaxation occurring around −5.2°C (which is the glass–rubber transition temperature (T_g) of XNBR), a high-temperature relaxation was observed around +54.7°C which is believed to be due to the formation of biphasic structure arising from the ionic multiplets and clusters formed in the XNBR–ZnO system[5]. The high-temperature ionic transition temperature is abbreviated as T_i. While incorporation of DOP causes lowering of T_g from −5.2°C (at 0 phr DOP) to −22.2°C (at 20 phr DOP) and increase in tan δ at T_g (that is, tan δ_{max}) from 0.920 (at 0 phr DOP) to 1.024 (at 20 phr DOP), its effects on T_i and tan δ at T_i are not significant. However, incorporation of DMSO causes dramatic changes of T_i and tan δ at T_i, so much so that T_i gradually decreases with increasing loading of DMSO and ultimately at 10 phr loading of DMSO the high-temperature relaxation disappears.

The effect of DMSO on the transition in the T_g region is not as pronounced as was observed in the case of DOP. Accordingly, it is inferred that DOP plasticizes primarily the main backbone chain, while DMSO plasticizes primarily the hard phase arising from the ionic aggregation. Results obtained in the case of the HAF carbon-black-filled system also show a similar trend (*Figure 3* and *Tables 3* and *4*). It has been shown earlier that the high-temperature transition (T_i) becomes pronounced in the presence of a reinforcing filler like HAF carbon black[5]. Although the effect of DOP on T_g in the filled system is not as pronounced as in the case of the unfilled system, its effect on T_i is more than expected. On the other hand, the effects of DMSO on both T_g and T_i are similar to those observed in the unfilled system.

Results of measurements of physical properties (*Table 5*) are in agreement with the behaviour observed in the case of dynamic mechanical properties. Both modulus and tensile strength decrease in the presence of plasticizers and the effect is more pronounced in the case of the DMSO-plasticized system. The role of ionic aggregates is to act both as physical crosslinks and as fillers providing strength and reinforcement to the matrix[13,14]. Plasticization by DMSO causes destruction of the ionic aggregates, which is responsible for the sharp fall in physical properties. In the case of DOP plasticization, ionic aggregates are not adversely affected. Accordingly, the matrix strength is maintained, although there is some drop in properties which is due to plasticization of the backbone chain.

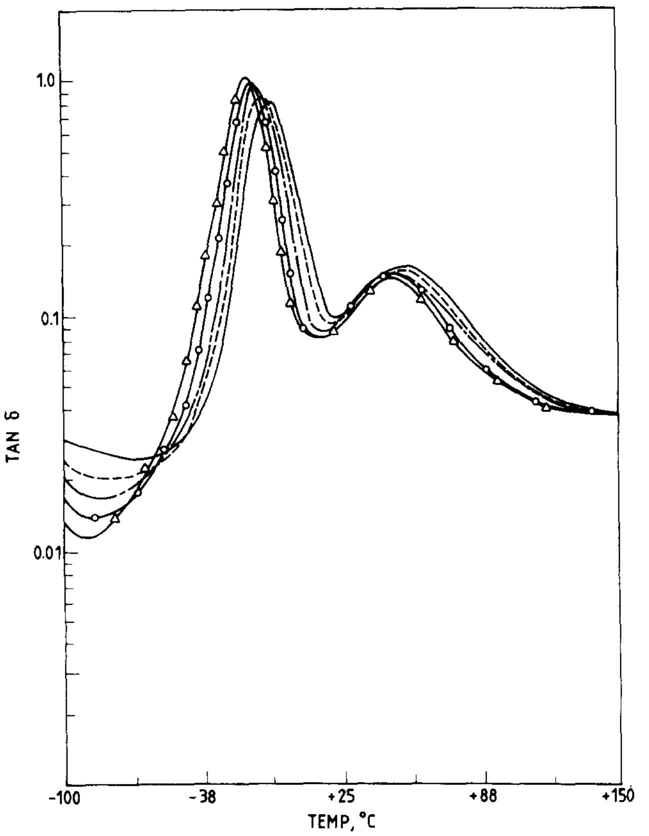

Figure 1 Effect of DOP on plots of loss tangent *versus* temperature in XNBR–ZnO system: ———, 0 phr; – – – –, 5 phr; — - — - —, 10 phr; —○—, 15 phr; —△—, 20 phr

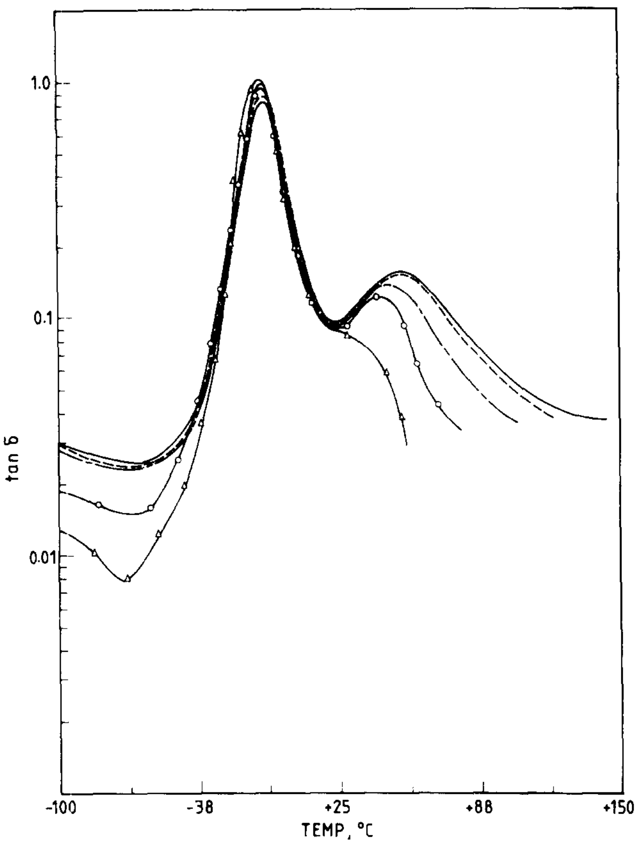

Figure 2 Effect of DMSO on plots of loss tangent *versus* temperature in XNBR–ZnO system: ———, 0 phr; – – – –, 2 phr; — - — - —, 5 phr; —○—, 7 phr; —△—, 10 phr

Table 3 Summary of results of the dynamic mechanical studies of DOP-plasticized ionomer[a,b]

DOP loading (phr)	Main chain transition temperature, T_g (°C)	Tan δ_{max} at T_g	Ionic transition temperature T_i (°C)	Tan δ_{max} at T_i
0	−5.2	0.920	+54.7	0.138
	(−5.2)	(0.623)	(+65.7)	(0.256)
5	−8.4	0.940	52.0	0.134
10	−11.2	0.970	+51.5	0.134
15	−16.5	0.988	+48.0	0.132
20	−21.2	1.024	+46.0	0.132
	(−10.2)	(0.737)	(+54.7)	(0.231)

[a] Mix designation: X-P

[b] Values in parentheses are the results of carbon-black-filled systems (i.e. mix numbers X-F and X-FP)

Table 4 Summary of the results of dynamic mechanical studies of DMSO-plasticized ionomer[a,b]

DOP loading (phr)	Main chain transition temperature, T_g (°C)	Tan δ_{max} at T_g	Ionic transition temperature T_i (°C)	Tan δ_{max} at T_i
0	−5.2	0.920	+54.7	0.138
	(−5.2)	(0.623)	(+65.7)	(0.256)
2	−7.0	0.938	+50.7	0.130
5	−7.2	0.945	+46.5	0.120
7	−7.4	0.950	+38.0	0.110
10	−9.2	1.034	[c]	[c]
	(−7.3)	(0.684)	[c]	[c]

[a] Mix designation: X-S

[b] Values in parentheses are the results of carbon-black-filled systems (mix numbers X-F and X-FS)

[c] Relaxation absent

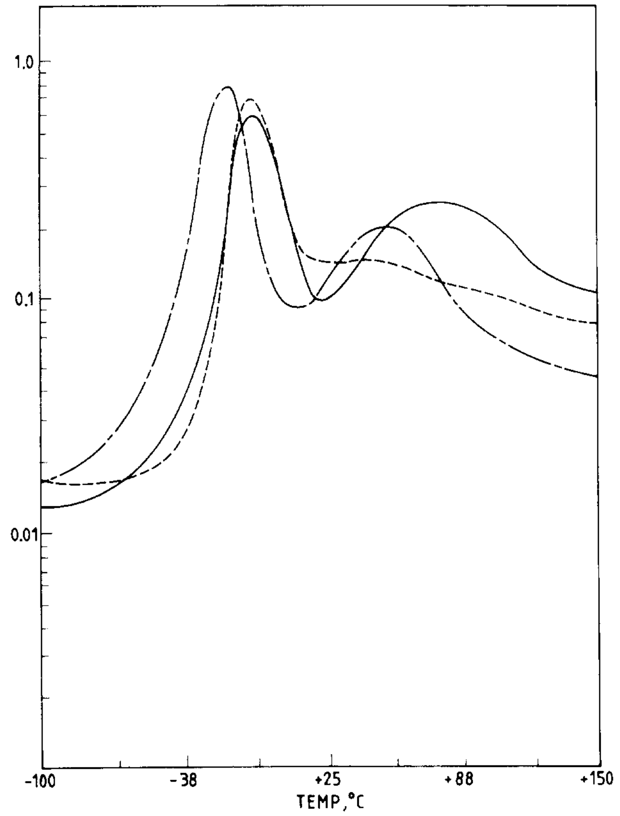

Figure 3 Effect of DOP on DMSO on plots of loss tangent *versus* temperature in carbon-black-filled XNBR–ZnO system: ———, X-F; — - — - —, X-FP; – – – – – –, X-FS

Table 5 . Physical properties[a]

	Mix designation[b]		
	X	X-P	X-S
100% Modulus (MPa)	1.85 (5.50)	1.23 (2.85)	1.42 (2.20)
300% Modulus (MPa)	3.70 (15.85)	2.36 (7.75)	1.90 (5.40)
Tensile strength (MPa)	24.5 (26.50)	21.40 (24.0)	7.90 (14.30)
Elongation at break (%)	950 (505)	1055 (720)	869 (750)
Hardness (IRHD)	58 (84)	52 (77)	50 (75)
Tension set (%)	9 (8)	15 (14)	23 (19)

[a] Values in parentheses are the results of carbon-black-filled systems
[b] X-P contains 20 phr DOP; X-S contains 10 phr DMSO

The morphological model (*Figure 4*) of ionic polymers is based on the formation of multiplets and clusters of ionic aggregates[15].

Conclusions

Dynamic mechanical studies reveal the formation of a biphasic structure in the XNBR–ZnO system, due to the formation of a hard phase arising from the ionic multiplets and clusters. DOP plasticizes the backbone chain or the soft phase and DMSO plasticizes the hard phase or the regions of the chains adjacent to the ionic aggregates.

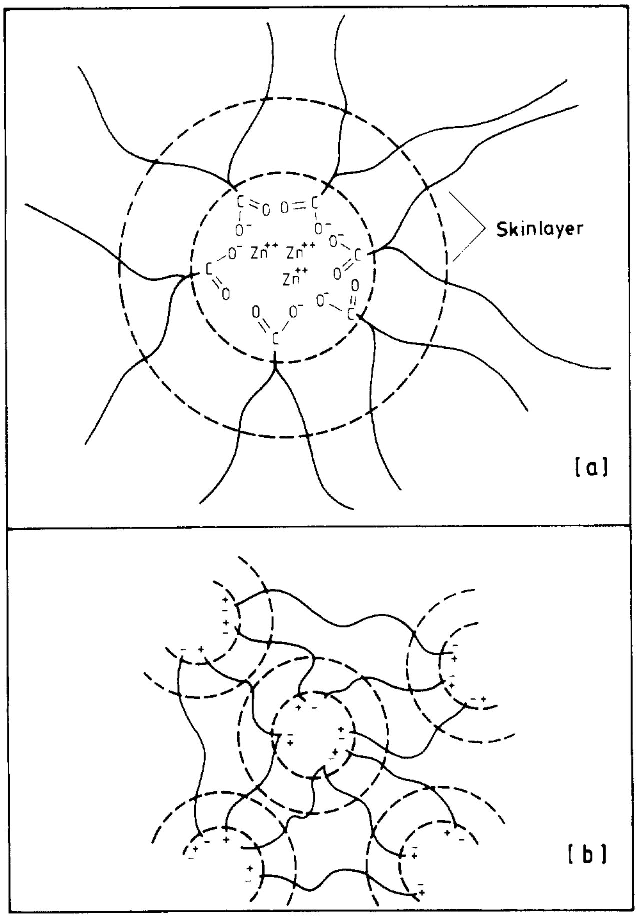

Figure 4 Schematic diagram of (a) the region of restricted chain mobility surrounding a multiplet; (b) clustered multiplets

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