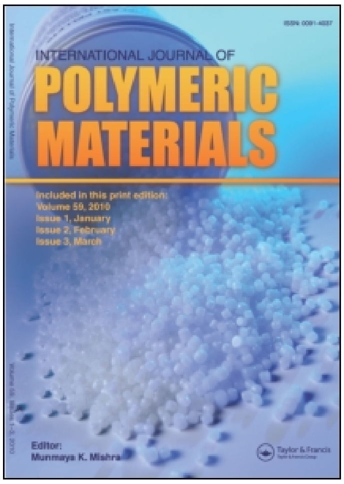

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Effect of Phthalic Anhydride on Thermo-Mechanical Properties of Ionic Elastomer Based on Carboxylated Nitrile Rubber

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The effect of phthalic anhydride (PhA) on the rheometric, viscoelastic, and mechanical properties and processability of an ionic elastomer based on carboxylated nitrile rubber (XNBR) cured with zinc oxide have been investigated. It has been found that the presence of this crystalline additive strongly affects the material properties and the ionic association. The rheometric results revealed new characteristics of rheographs with faster curing rates and a point of maximum torque values upon the addition of PhA. The values of elastic torque as well as loss torque depend on PhA loading and the maximum value have been found at the loading of 2.5 parts per hundred parts of rubber (phr). Dynamic mechanical thermal analysis also revealed that the viscoelastic properties, the storage modulus (E′) and the tan δ transition temperature are highly affected by the incorporation of PhA. Although the main chain glass transition temperature is unaffected by the addition of PhA, the high temperature transition temperature, due to ionic cluster formation, did shift to a higher temperature. The optimum valus of E′ and tan δ were at loading of 2.5 phr. The stress at break and elongation at break did not change significantly, whereas sharp rises in 300% modulus and hardness values were found at 2.5 phr loading of PhA. The plasticity results of 2.5 phr PhA loaded sample showed better proccssability characteristics with low scorch as compared to pure XNBR-ZnO vulcanizate.

Keywords: ionomer, phthalic anhydride, rheograph, viscoelastic, XNBR

INTRODUCTION

The presence of low concentration of ionic constituents in polymer chains is known to exert a profound effect on their physical and

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rheological properties attributed to the formation of ionic aggregates, which act as thermoreversible crosslinks and effectively retard the translational mobility of polymeric chains [1–4]. Ionomers or ionic elastomers combine both the ionic and non-ionic species in the same macromolecule, which brings about a change in their bulk properties. Despite the variety of chemical structures, ionomers exhibit certain common unique properties because of the possibility of microphase separation caused by the aggregation of the ionic groups called "ionic clusters." The presence of these clusters in ionomers has been discussed in depth by various researchers [5–6]. Eisenberg et al. [7] proposed a new morphological model for random ionomers based on the existence of multiplets, which reduce the mobility of the polymer chains in their vicinity. Isolated multiplets act as large crosslinks, thus increasing the glass-transition temperature of the materials. As the ion content is increased, the regions of restricted mobility surrounding each multiplet become large enough to exhibit phase separated behavior and are termed clusters. The model is in good agreement with a wide range of experimentally observed phenomena, especially those based on dynamic mechanical and X-ray scattering.

The acrylonitrile–butadiene-methacrylic acid terpolymer may be most concisely described as a speciality rubber [8]. XNBR is capable of providing harder and tougher vulcanizates with high modulus, tensile strength, and tear strength than the conventional nitrile rubbers [9]. Brown [10] has described a suitable process of neutralization of these materials with zinc oxide or other zinc salts and plasticizers to break up ionic association at elevated temperature. The simplest way to make ionic crosslinking of carboxylic rubber is by heating the acid copolymer in the presence of metal oxides like divalent zinc and magnesium oxides to give materials with the best physical properties [11]. It is reported that the crosslinking reaction does not involve a simple formation of $-\mathrm{COO}^{-}\mathrm{X}^{+}-$ but rather suggests the presence of physical crosslinking in the bulk of the polymers of carboxylic acid salts, which acts as thermoreversible crosslinks [12]. Due to the presence of ionic salts carboxylated nitrile rubbers generate a new type of elastomers called ionic elastomers, which are generally called ionomers [13–14].

The thermoreversible nature of ionic aggregation due to metal carboxylate salts in XNBR may address many disadvantages associated with covalently bonded high molecular weight polymers, such as poor melt processability, high melt viscosity, and low thermal stability at typical processing conditions such as high shear rate and temperature [14]. Metal oxide cure carboxylic elastomers are very scorch sensitive. Even zinc oxide stocks were scorched on the mill at room temperature [15]. Organic weak acids, anhydrides, amines, and similar reagents were found to be retarders and controllers of the reaction of metal oxides with carboxylic elastomers [15]. Phthalic anhydride (PhA) has been found to be a preferred organic acid controller for carboxylic elastomers containing acrylonitrile. But the mode of action of the controller and its mechanism, and viscoelastic properties of the weak acids modified carboxylic elastomers are not yet explored by the investigators.

The author's previous work [16–18] has reported the two-phase morphology of carboxylated nitrile rubber by the rheological and physical properties studies. Infrared spectroscopic analyses have also supported the proposed morphology of XNBR by dynamic mechanical studies [13]. The present article highlights the effect of phthalic anhydride on thermo-mechanical properties of ionic elastomers based on carboxylated nitrile rubber, by rheometric, dynamic mechanical, and physical properties measurements.

EXPERIMENTAL

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

The compounding ingredients were mixed with rubber in a laboratory size (325 mm × 150 mm) two-roll mixing mill at a friction ratio 1:1.19 according to ASTM D 3182, with careful control of temperature, nip gap, time of mixing and a uniform cutting operation. The rubber compounds were molded at 150°C in an electrically heated hydraulic press to optimum cure time (i.e., 90% of the optimum cure) obtained from a moving die rheometer MDR-2000 (Monsanto Company, USA) with an arc of oscillation ±0.5°.

Measurement of modulus, tensile strength, and elongation at break were measured at room temperature as per the ASTM D 412-80 test method using a Zwick Universal Testing Machine, model 1445.

Hardness measurements were carried out on a Wallace Indentation Microhardness Tester at room temperature according to ASTM D 1415. Hardness values quoted are an average of eight reading taken at random over the entire specimen surface.

TABLE 1 Details of Materials Used

Materials	Characteristics	Source
XNBR	KRYNAC X7.50 grade	Bayer Polyser, France
Zinc oxide (ZnO)	Specific gravity 5.4	Local made
Phthalic anhydride	Specific gravity 2.24	Local made
Stearic acid	Crystalline	Local made

TABLE 2 Formulation of the Mixture[a]

Mix Design	Z_0	Z_1	Z_2	Z_5	Z_{10}
XNBR	100	100	100	100	100
ZnO	12	12	12	12	12
PHA	—	1.25	2.50	5.00	10.00
Srearic acid	2	2	2	2	

[a] Values in phr (parts per hundred parts of rubber).

Dynamic mechanical analysis was carried out using a Rheovibron DDV-III EP viscoelastomer (Oriented Corporation, Japan) with a computer system for control and data analysis. Dynamic modulus measurements were made in the range of temperature −100°C to 150°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 $2°C\,min^{-1}$.

Plasticity measurement was made using Wallace Rapid Plastometer at the temperature of 100 ± 1°C as per ASTM D 926-03.

RESULTS AND DISCUSSION

Figure 1 depicts the rheograph of XNBR cured with zinc oxide and different loading of phthalic anhydride at 150°C. The results show that the storage torque (S′) increases as expected with the progress of curing, the loss torque (S″) unexpectedly increases with curing time, which has been reported in the case of the formation of networks consisting of ionic crosslinks [16]. In presence of phthalic anhydride the results show new types of rheographs as compare to the previously reported [16]. It is evident that in the presence of PhA the rate of curing action increases and PhA acts as strong accelerator activator. In presence of PhA both torque values reach a maximum and then fall to a certain value and then reach a plateau. Figure 2 indicates that the optimum values of both S′ and S″ increase with PhA loading and highly depend on the PhA loading concentration. Figure 2 also shows that at the loading of 2.5 phr the torques value reaches the maximum. The result has been tabulated in Table 3.

The effect of PhA on rheological properties of this ionic elastomer may involve the following actions: (i) devulcanization allowing more uniform distribution of the ionic clusters of zinc carboxylate salts, (ii) reaction with polymer and −COOZnOOC− group to give polymer −COOPhA salt, and (iii) salt formation of PhA with unreacted metal

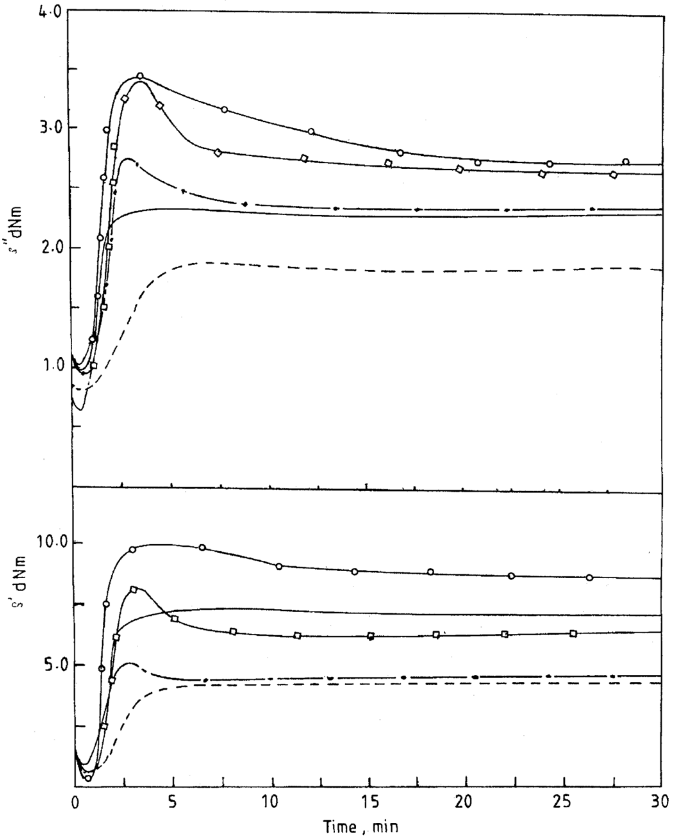

FIGURE 1 Rheographs at 150°C for the XNBR-ZnO systems with different loading of phthalic anhydride. ------- (Z_0); ——— (Z_1); —o— (Z_2); —□— (Z_5); —·— (Z_{10}).

oxide. The results could be explained based on the following mechanism of reactions: vulcanization accelerates in presence of PhA and excess ZnO, devulcanization of zinc-carboxylate acid salts by PhA acts as polar solvent and, lastly, permanent formation of zincarboxylate salts. As S′ value of all the samples in presence of PhA is higher than the XNBR-ZnO system, it indicates that stabilization of ionic association in presence of PhA has taken place.

Figures 3 and 4 show the dynamic storage (E′) modulus and loss (tan δ) as a function of temperature of XNBR-ZnO system with different loading of PhA. A sharp drop in storage modulus in the region of glass-rubber transition is found as expected. Incorporation of PhA in

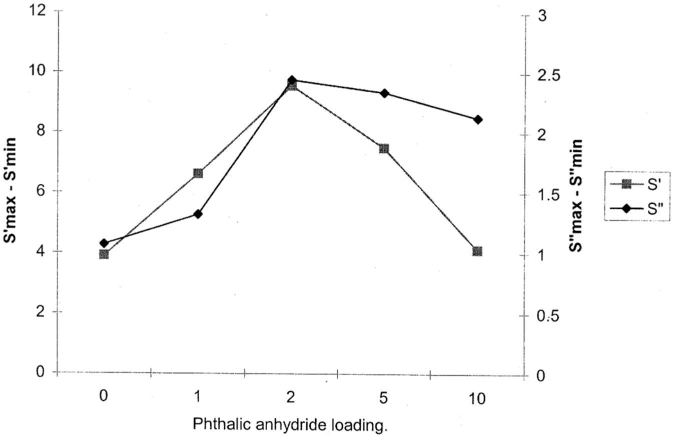

FIGURE 2 Rheometric results at 150°C: effect of phthalic anhydride.

this ionic elastomer affects significantly the modulus values in the high temperature transition T_i, that is, ionic transition region. It is also evident that PhA acts as a crosslinker and increases the modulus properties of the rubbery zone. The variation of dynamic storage modulus with PhA loading is shown in Figure **5**. The figure indicates that the modulus reaches a maximum at a loading of 2.5 phr PhA and then decreases. Analogous results have also been found in case of loss tangent plots. The results indicate two transition temperatures similar to the previous report [16], the main chain transition T_g around -9.2°C and ionic cluster transition T_i in the range of $+40$°C to $+50$°C. The position of the low-temperature or the high-temperature peak in the tanδ curves is a measure of the transition temperature. The T_g thus obtained from tanδ curves as a function of PhA loading is tabulated in Table **4**. It is clear that the incorporation of PhA does not affect the main chain glass transition temperature but it affects the ionic cluster transition, T_i. The T_i loss peaks due to ionic cluster

TABLE 3 Rheometric Resutls

Mix design	$\Delta S' = S'_{\max} - S'_{\min}$	$\Delta S'' = S''_{\max} - S''_{\min}$
Z_0	3.91	1.07
Z_1	6.618	1.318
Z_2	9.560	2.439
Z_5	7.500	2.335
Z_{10}	4.120	2.123

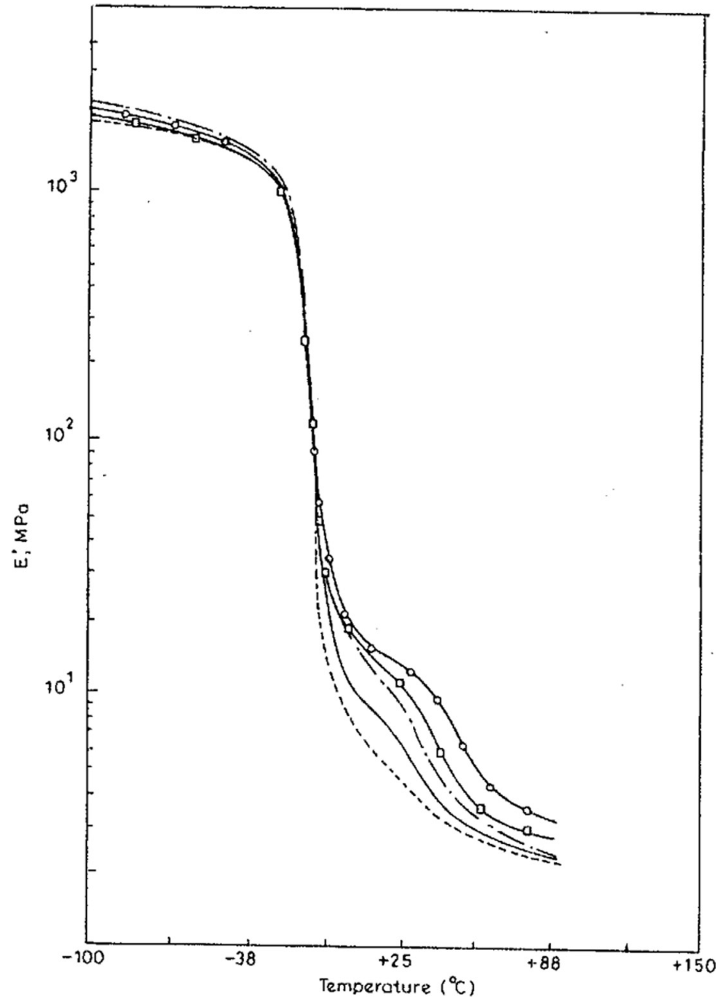

FIGURE 3 Plots of dynamic storage modulus (E′) versus temperature for XNBR-ZnO system with different loading of phthalic anhydride. ------ (Z_0); —— (Z_1); —○— (Z_2); —□— (Z_5); —·— (Z_{10}).

formation is broadened and shifted to the higher temperature to a certain loading around (2.5 phr) with increasing peaks height and decreases at higher loading but higher than the pure XNBR-ZnO system.

The aforementioned results could be explained as follows: At low loading of PhA the ionic cluster formation is distributed uniformly and stabilized through hexa-coordinated salt formation [19,13].

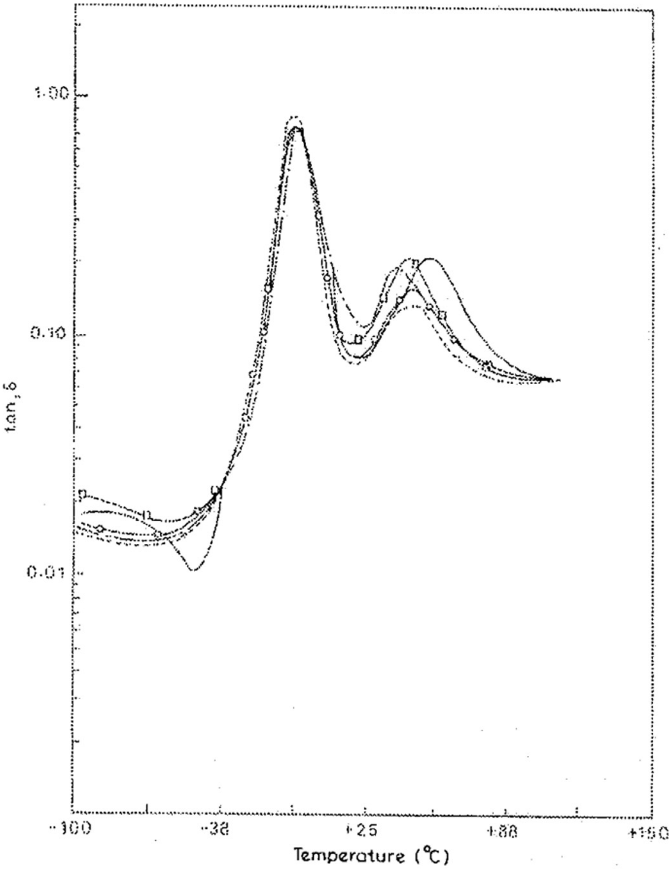

FIGURE 4 Plots of dynamic storage modulus (E') versus temperature for XNBR-ZnO system with different loading of phthalic anhydride. ------ (Z_0); —○— (Z_1); —— (Z_2); —□— (Z_5); —·— (Z_{10}).

The stabilization of ionic cluster formation restricts the mobility of the polymer chains in the vicinity of the ionic multiplets and gives rise to the hard phase, which is the cause for higher modulus at rubbery region and shifting of ionic cluster transition to higher temperatures. At higher loading the salt formation of PhA with zinc oxide is more stable and dilutes the ionic association.

The results are supported by physical properties measurement reported in Table 5. The tensile modulus shows similar trends, like storage modulus results at rubbery zone, which clearly indicate the

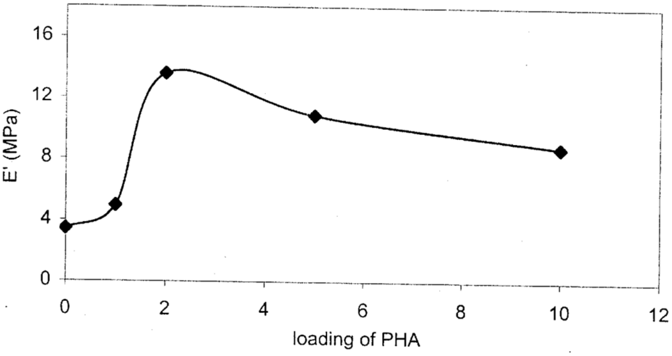

FIGURE 5 Effect of Phthalic anhydride on storage modulus at 25°C.

TABLE 4 Dynamic Mechanical Thermal Analysis Results

Mix design	T_g,°C	tanδ	T_i,°C	tanδ
Z_0	−9.2	0.912	40	0.148
Z_1	−9.2	0.889	43	0.163
Z_2	−9.2	0.712	49	0.262
Z_5	−9.2	0.717	41	0.227
Z_{10}	−9.3	0.632	28	0.186

TABLE 5 Physical Properties

Mix design	Z_0	Z_1	Z_2	Z_5	Z_{10}
Modulus, 100%	1.8	1.8	2.7	2.5	1.6
Modulus, 200%	2.6	2.9	3.1	3.4	2.0
Modulus, 300%	3.7	4.5	5.7	4.8	2.3
Tensile strength, MPa	33	32	36	28	18
Elongation to break, %	1150	1000	1000	1030	1240
Hardness, IRHD	58	62	74	72	60

TABLE 6 Plasticity Results

Time, hr.	0	6	18	20	40	Cured sample
Plasticity no. (sample Z_0)	19	42	71	86	90	92
Plasticity no. (sample Z_2)	21	32	60	73	81	96

formation of a denser network by ionic association in presence of PhA. The hardness measurement also supports the same.

Based on the present studies the plasticity results of XNBR-ZnO stock with 2.5 phr PhA and without PhA are reported in Table 6. The results predict that the PhA loaded stock is scorching less on the mill compared to the pure stock, add cured samples in presence of PhA show higher plasticity supporting the study results.

CONCLUSIONS

From the results presented here, it is evident that a weak organic acid, phthalic anhydride, acts as an accelerator for the curing reaction of XNBR with the metal oxide ZnO and also stabilizes the ionic cluster formation in the bulk of the polymer. It has also been reported that cluster formation is more favorable at low dosing of PhA.

Dynamic mechanical and physical properties measurements reveal that in presence of PhA, the reversible formation of ionic aggregation is more favorable and improves the physical properties. Plasticity measurement reveals that the scorch behavior of XNBR-ZnO stock is better in presence of PhA than the pure stock.

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