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Epoxidized natural rubber–carboxylated nitrile rubber blend: a self-vulcanizable miscible blend system

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Epoxidized natural rubber and carboxylated nitrile rubber can be blended and vulcanized during moulding without addition of any curative. Such a blend system of self-vulcanizable rubber is completely miscible as is evident from differential scanning calorimetry and dynamic mechanical studies. Physical properties of the blends are comparable to those of conventional rubber vulcanizates. The blends are reinforced on addition of reinforcing carbon black filler.

(Keywords: epoxidized natural rubber; carboxylated nitrile rubber; self-vulcanizable rubber blend; miscible rubber blend)

INTRODUCTION

It has been reported earlier that carboxylated nitrile rubber (XNBR) is vulcanizable by epoxy resin[1] and epoxidized natural rubber (ENR) can be vulcanized by dibasic acids[2]. Accordingly the blend of carboxylated nitrile rubber and epoxidized natural rubber was studied to examine the vulcanizing ability of one rubber by the functional group of another rubber. In the present communication we report the results of our studies on XNBR–ENR blend. We designate such a system as a self-vulcanizable rubber blend. No curative was used.

EXPERIMENTAL

XNBR used was Krynac-221 (Polysar Limited, Ontario, Canada), containing high level of carboxylated monomer and medium high bound acrylonitrile level. ENR used was ENR-50 (Malaysian Rubber Producers' Research Association, UK), with 50 mol% epoxidation. Both ENR and XNBR were first masticated in the 14 × 6 in 2-roll mixing mill for 6 min each. Masticated samples were blended on the mill for a further period of 10 min. Rheographs were taken at 140°C on a Monsanto Rheometer R-100. The blends were vulcanized during moulding for 45 min at 140°C. The following physical properties of the vulcanizates were determined according to standard methods: stress–strain (Zwick UTM, ASTM D412-87); tear (Zwick UTM, ASTM D624-86); hardness (Shore A, ASTM D2240-86); resilience (Dunlop tripsometer, BS 903: Part A8: 1963, method A); compression set (ASTM D395-85, method A and method B); heat build-up (Goodrich flexometer, ASTM D623-78); abrasion resistance (Cryodon-Akron Dupont abrader, BS 903: Part A9: 1957, method C). For swelling studies the vulcanizates were swollen in chloroform for 48 h and the percent increase in weight due to solvent swelling was noted.

Dynamic mechanical properties (damping) were measured using a Rheovibron model DDV III-EP at a strain amplitude of 0.0025 cm and a frequency of 3.5 Hz. The procedure was to cool the sample to −100°C and record the measurements during the warm up. The temperature rise was 1°C min^{-1}.

D.s.c. measurements were run on a Dupont differential scanning calorimeter model 910 in nitrogen atmosphere. Glass–rubber transition temperatures (T_gs) of the samples were taken as the midpoint of the step in the scan, run at a heating rate of 10°C min^{-1}.

RESULTS AND DISCUSSION

Formulation of the two blends and the physical properties of the moulded blends are shown in *Table 1*. Blend A contains XNBR:ENR in the ratio 100:50. Blend A_c is similar to blend A, but contains 45 parts by weight of ISAF carbon black.

Rheographs of the two blends at 140°C are shown in *Figure 1*. Increase in rheometer torque with vulcanization time indicates progressive crosslinking of the system. As we shall discuss later, one blend constituent gets vulcanized at 140°C by the other component. The higher

Table 1 Composition and properties of ENR–XNBR blend moulded at 140°C for 45 min

	Blend designation	
	A	A_c
Composition (parts by weight)		
ENR	50	50
XNBR	100	100
ISAF carbon black	–	45
Properties		
100% modulus (MPa)	1.02	1.57
Tensile strength (MPa)	3.70	20.56
Elongation at break (%)	396	538
Tear strength (kN m^{-1})	14.40	38.00
Compression set at constant stress (%)	11	14
Compression set at constant strain (%)	20	32
Heat build up (ΔT) at 50°C (°C)	24	40
Resilience (%)	62	47
Hardness (Shore A)	43	55
Swelling in chloroform (percent increase in weight)	872	517

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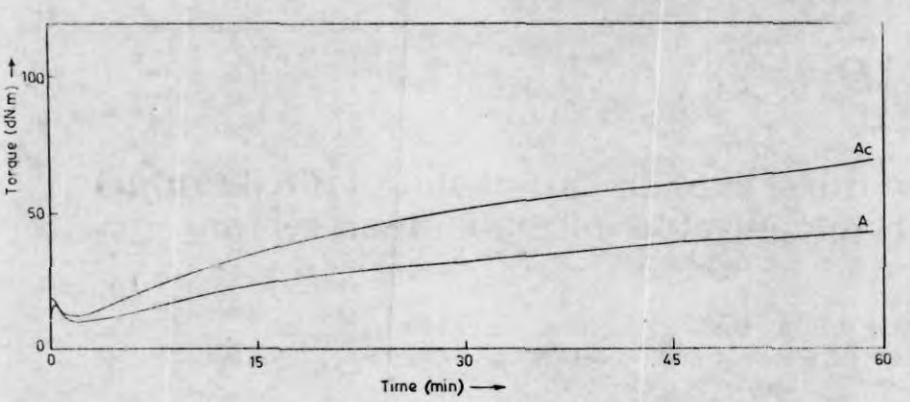

Figure 1 Rheographs of blends A and A_c at 140°C

Table 2 Effect of moulding/vulcanization time on physical properties of black-filled XNBR–ENR blend (A_c)

Physical property	Moulding/vulcanizing time (min)		
	30	45[a]	90
Modulus at 100% strain (MPa)	1.15	1.57	3.57
Tensile strength (MPa)	20.17	20.56	19.28
Elongation at break (%)	737	538	374
Tear resistance (kN m^{-1})	41.75	38.00	33.02
Heat build-up at 50°C (ΔT) (°C)	44	40	30
Dynamic set (%)	9.3	3.6	0.76
Resilience (%)	44	47	48
Swelling in chloroform (percent increase in weight)	652	517	426

[a] Values also reported in *Table 1*

torque value in the case of blend A_c is similar to that in a conventional rubber system in the sense that reinforcing carbon black increases the torque value due to high polymer–filler interaction. Results of physical properties and swelling studies, as discussed later in the paper, further substantiate these findings. Marching increase in modulus with cure time as shown in the rheographs implies that the cure reversion is absent and the vulcanizate network is thermally stable.

Physical properties of the blend vulcanizate, as summarized in *Table 1*, shows that gum blend vulcanizate shows poor physical properties. However, addition of reinforcing carbon black filler increases the tensile strength more than 5 times, tear resistance more than 2.5 times and abrasion resistance about 4 times. As expected, addition of reinforcing carbon black increases modulus and hardness and causes reduction in resilience. High hysteresis of the filled system causes an increase in heat build-up and compression set. Reduction in percent swelling in solvent (chloroform), from 872% for the gum system to 527% for the filled system, shows increased restriction to solvent swelling due to polymer–filler interaction.

The degree of crosslinking can be changed by varying the curing or moulding time. *Table 2* shows that with increase of cure time, percent swelling decreases due to the increase in crosslink density, which causes formation of a tighter network resulting in low dynamic set, low heat build-up in Goodrich flexometer test, lower elongation at break, higher modulus and higher resilience. However, tensile strength was not greatly affected. Tear strength decreased at higher curing time. It has been reported that undercuring results in higher tear resistance[3].

D.s.c. thermograms of ENR, XNBR and blends of ENR and XNBR are shown in *Figure 2*. Glass transition temperatures of the systems are summarized in *Table 3*. The T_gs of ENR and XNBR were detected at −14.5 and −25°C and the blends A and A_c showed T_g values at −19°C. The occurrence of single T_g in the blend and the transparent nature of the gum blend indicate complete miscibility of ENR and XNBR. This is also evident from the dynamic mechanical analysis. *Figure 3* shows the plot of damping (tan δ) at different temperatures. Both single

Table 3 Glass transition temperatures (T_gs) as obtained from differential scanning calorimetry studies

Rubber/blend	T_g (°C)
XNBR	−25
ENR	−15
Blend A	−19
Blend A_c	−19

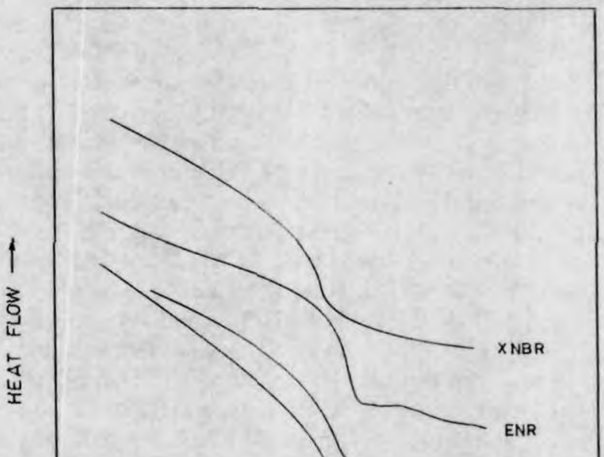

Figure 2 D.s.c. thermograms of XNBR, ENR and XNBR–ENR blends (A and A_c)

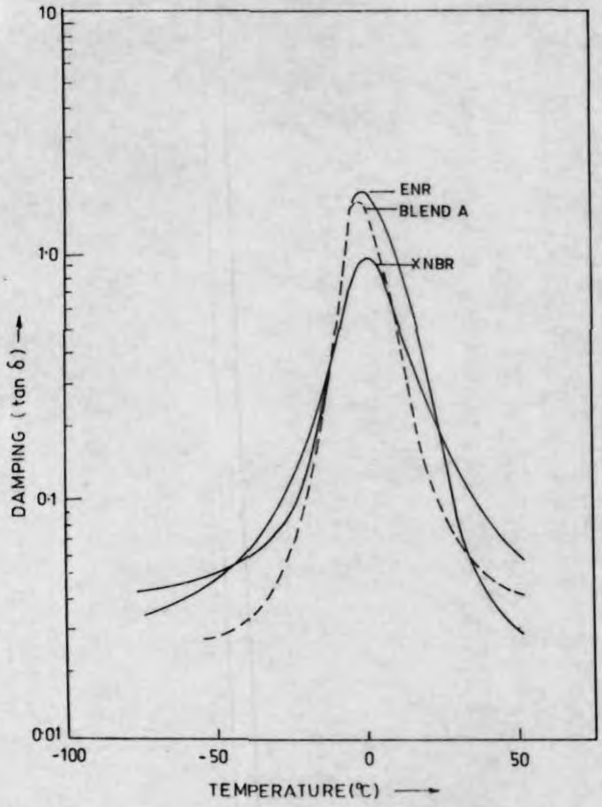

Figure 3 Damping (tan δ) plots for XNBR, ENR and ENR–XNBR blend

components and the blend A register maxima in the ta δ value almost at the same temperature varying betwee −1 and −2.5°C. However, the damping peak of th blend occurred in between the individual componen and the peak width or broadening is smaller in the ca of the blend as compared to XNBR and ENR. Th indicates that blends of XNBR and ENR form a miscibl system.

The present investigation shows that carboxylate nitrile rubber and epoxidized natural rubber form miscible blend system which is self-vulcanizable in th absence of curatives and the black-filled system exhibi reinforcement similar to conventional rubbers. Durin vulcanization, carboxyl groups of XNBR react wit epoxy groups of ENR to form ester crosslinks.

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