Self-Vulcanizable Rubber Blend System Based on Epoxidized Natural Rubber and Carboxylated Nitrile Rubber

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Although carboxylated nitrile rubber (XNBR) is vulcanizable by epoxy resin,[1] it has been reported that epoxidized natural rubber (ENR) can be vulcanized by dibasic acids.[2] Accordingly, it was thought that the carboxyl groups of XNBR could be made available for vulcanizing ENR and epoxy groups of ENR could be utilized for vulcanizing XNBR in a blend of XNBR and ENR. In the present communication we report the results of our studies on physical properties of XNBR/ENR blends which are vulcanizable by the blend constituent themselves in the absence of any curatives and additives. We designate the system as a "self-vulcanizable rubber blend system."

EXPERIMENTAL

XNBR used was Krynac-221 (Polysar Limited), containing high level of carboxylated monomer and medium high bound acrylonitrile level. ENR used was ENR-50 (Malaysian Rubber Producers' Research Association, U.K.), with 50 mol% epoxidation. Both ENR and XNBR was 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 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), and abrasion resistance (Cryodon-Akron Dupon abrader, BS:903:Part A9, method C). Ageing resistance was measured by studying retention of tear and stress-strain properties of the vulcanizate. For swelling studies the vulcanizates were swollen in chloroform for 48 h and the percent increase in weight owing to solvent

TABLE I
Formulation of the Mixes

Parts by weight	Blend no.				
	A	G	H	G_c	H_c
ENR-25	100	—	—	—	—
ENR-50	—	100	100	100	100
XNBR	50	100	50	100	50
Carbon black[a]	—	—	—	60	45

[a] ISAF-type, obtained from Phillips Carbon Black Ltd., Durgapur.

Journal of Polymer Science: Part C: Polymer Letters, Vol. 27, 361–367 (1989)

CCC 0887-6258/89/100361-07$04.00

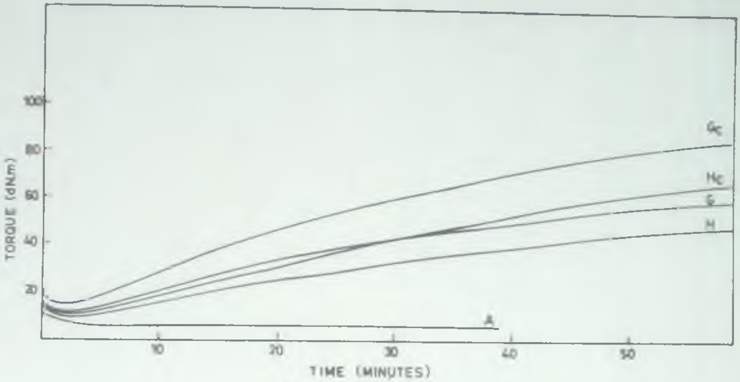

Fig. 1. Rheographs at 140°C.

swelling was noted. The hysteresis behavior of the blend vulcanizates was determined from the ratio of the retraction energy to the ratio of input energy of deformation up to the point of strain reversal, recorded by the electronic integrator attached to the Instron Universal Testing machine model 1193. The samples were pulled to the desired extension (200% or 400%) and retracted at a crosshead speed of 100 mm/min.

RESULTS AND DISCUSSION

Blend compositions are shown in Table I. Blends G and H contain two different proportions of ENR and XNBR and no other additives. Blends G_c and H_c are the corresponding blends containing the reinforcing ISAF carbon black filler. Rheographs of different blends are shown in Figure 1. Preliminary experiments with ENR-25 showed that an epoxidation level of 25 mol% is not sufficient to cause crosslinking of XNBR, as evident from the rheographs of XNBR/ENR-25 blend (Fig. 1). There is no increase in modulus with cure time. Chakraborty and De,[1] while studying vulcanization of XNBR by epoxy resins, observed dependence of crosslink density and the resultant rheometric torque on the loading of epoxy resin. However, where epoxidation level was increased to 50 mol%, as in ENR-50, crosslinking occurred and the rheographs show gradual increase in modulus with cure time. Teik[2] has also observed that vulcanization of epoxidized natural rubber by dibasic acids depends very much on epoxidation level. It is apparent that the extent of vulcanization in the XNBR/ENR-50

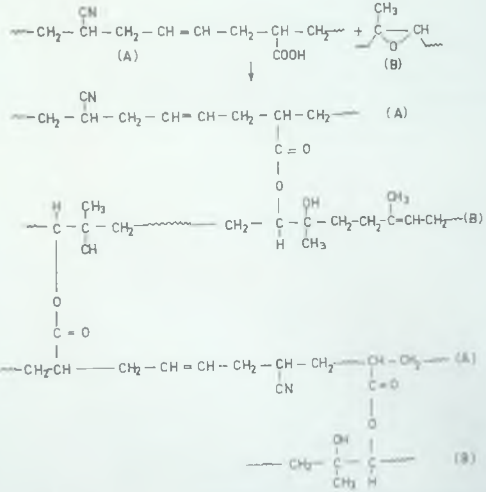

Fig. 2. Epoxidized natural rubber (B) crosslinked by carboxylated nitrile rubber (A) and vice versa in the self-vulcanizable rubber blend system.

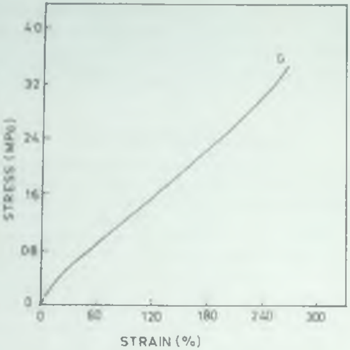

Fig. 3. Stress-strain plot for blend G.

system as measured by the maximum torque is higher in the case of formulation G(ENR/XNBR 100/100) as compared with H(ENR/XNBR 100/50). Mix G contains a higher quantity of XNBR, and the proportion of carboxyl groups available for crosslinking is also higher in case of mix G as compared with mix H. Accordingly, the extent of crosslinking and the resultant torque in the rheographs is higher in mix G. Teik,[7] while studying vulcanization of ENR by dibasic acids, observed that rheometric torque depends on the concentration of the acid. 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 (Fig. 2). Reinforcing carbon black owing to

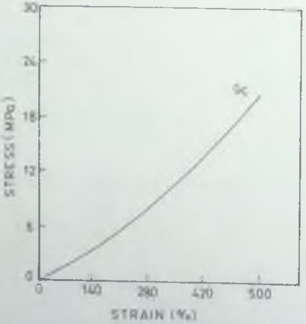

Fig. 4. Stress-strain plot for blend G_c.

TABLE II
Physical Properties of Self-Vulcanizable Rubber Blends

	Blend no.			
	G	H	G_c	H_c
100% Modulus (MPa)	1.38	1.18	2.40	1.25
Tensile strength (MPa)	3.02	3.01	19.46	22.30
Elongation at break (%)	273	327	535	634
Tear strength (kN/m)	12.6	11.1	41.9	38.5
Abrasion loss (cm^3/h)	2.88	24.23	0.48	2.65
Compression set, constant stress (%)	0.6	5.2	1.8	6.8
Compression set, constant strain (%)	8.5	9.9	8.6	22.0
Heat build-up, (°C) (ΔT), above 50°C	12.5	17.0	32.0	27.5
Resilience (%)	62	55	49	41
Hardness (Shore A)	40	32	54	54
Swelling in chloroform, increase in weight (%)	833	1192	532	581

strong polymer-filler interaction causes an increase in torque values in rheographs. Results of physical properties and swelling studies, as discussed below, further substantiates these observations. Typical stress-strain curves are shown in Figures 3 and 4, for blend G and blend G_c. Blends H and H_c also show similar behavior. Physical properties of different systems are summarized in Table II. It is evident that the gum systems show poor strength which, however, increases 6 to 7 times in the presence of reinforcing carbon black filler. Analysis of the results for mixes G and H (Table I) shows that blend G shows higher tensile value, tear resistance, hardness, and resilience and lower values of compression set. This is indicative of a greater extent of crosslinking in blend

TABLE III
Hysteresis Behavior of Different Blends

Blend no.	Cycle no.	Hysteresis loss (%)	Set (arbitrary units, Instron chart)
G	1	15	4.5
	2	7	1
	3	6.5	0.6
H	1	31	3
	2	9.5	0.9
	3	9	0.6
G_c^a	1	25.5 (43)	7 (16)
	2	18 (23)	1.5 (3)
	3	16 (18)	0.8 (2)
H_c	1	35	8
	2	19	2
	3	20	1

[a] Values in parentheses are the values where the extension was increased to 400%.

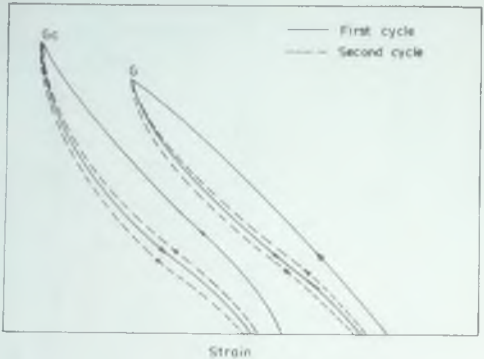

Fig. 5. Hysteresis curves for blend G and G_c at 200% extension.

G as compared with blend H. That heat build-up and abrasion loss for blend G is less than blend H also points out tighter crosslinking in the case of blend G. Solvent swelling studies show that blend G offers greater restriction to solvent penetration owing to higher crosslinking density. The proportion of carboxyl group available for crosslinking and for being crosslinked is more in blend G than blend H. This is true for both gum and filled systems. Rheographs also substantiate these observations. Blend G shows higher torque value than blend H. Similarly, blend G_c registers higher torque than blend H_c. Teik[2] has also observed that the tensile strength of ENR vulcanizates depends on the concentration of dibasic acid crosslinking agent.

Addition of carbon black reinforces both blend G and H. Both tensile and tear properties improve several fold owing to higher dissipation of energy in the filled system, which is manifested in higher heat build-up and set properties. Hysteresis studies (Fig. 5) showed that both energy dissipation and set are higher in blend G_c as compared with G owing to the additional energy dissipation mechanisms, such as motion of filler particles, chain slippage, and dewetting at high strains.[4] That abrasion loss, resilience, and solvent swelling decrease and hardness increases in filled systems also points out a high degree of polymer-filler interaction. When the hysteresis experiment was repeated after the first cycle is over, both hysteresis loss and set in the second and third cycles were less as compared with the first cycle. This is due to stress-softening or Mullin's effect. Where the extension was increased to 400% from

TABLE IV
Percent Retention of Properties after Ageing at 100°C for 48 h

	Blend no.			
	G	H	G_c	H_c
Tensile strength (MPa)	75	76	78	64
Tear resistance	73	70	49	60
Elongation at break (%)	51	62	33	30

200%, as was done in the case of G_c, higher energy input caused a higher dissipation of energy. This results in higher hysteresis and set.

Retention of properties after ageing for 48 h at 100°C (Table IV) indicates that the vulcanizates are quite stable under the ageing conditions owing to carbon-carbon and carbon-oxygen covalent bonds in the crosslinks (Fig. 2). Expectedly, carbon black catalyzes the degradation reactions during ageing, and the retention of properties worsens in filled systems, as is the case with normal rubber vulcanizates vulcanized by a sulfur curative system.[3]

In summary, we conclude that a novel self-vulcanizable rubber blend system has been studied wherein one constituent vulcanizes the other in the absence of any curatives. Further work on such systems is in progress.

Thanks are due to Sri S. Mushtaq, K. L. Saha, A. Talukdar, R. K. Banerjee, and J. Mitra of this center for assistance in experimental work.

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Received January 6, 1989
Accepted February 9, 1989