Chloroprene 고무개질 에폭시화 천연고무 : 2. 압축 Set성 및 노화특성

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(1992년 6월 24일 접수)

Chloroprene Rubber Modified Epoxidized Natural Rubber : 2. Compression Set and Aging Properties

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(Received June 24, 1992)

요 약 : ENR/CR 블렌드 가류물에 대한 기계물성을 측정하였다. 열노화에 따라 경도는 증가하였으나 탄성율(300%), 인장강도 및 파단신율은 현저히 감소하였다. 기름노화에 따라 인장강도 및 파단신율과 아울러 경도도 감소하였으며, 경도감소는 체적팽창으로 설명하였다.

Abstract : The mechanical properties of ENR(epoxidized natural rubber) blends with CR(chloroprene rubber) were measured for both unaged and aged vulcanizates. Upon heat aging, hardness increased, and tensile strength, modulus, and elongation at break decreased. Tensile strength and elongation at break also decreased upon aging in oil, hardness decreased due to the oil swell into the rubber.

INTRODUCTION

In our earlier report,[1] cure characteristics, dynamic properties, resilience, flex and ozone crack resistance were reported for the ENR(epoxidized natural rubber) blends with CR(chloroprene rubber). The blends showed a single tan δ peak, which monotonically moved toward the lower temperature as the content of CR increased, and consequently an increase in room temperature resilience resulted. It was found that the ozone crack resistance of ENR was significantly improved upon blending with a small amount(10%) of CR. In this paper, we report the tensile properties and compression set of the blends, together with the air and oil aging properties.

EXPERIMENTAL

Experimental details with rubber formulation are decribed in our earlier report.[1] Basic formulations are given in Table 1. ENR of 50 mole% epoxidation was used in this experiment. Blends were prepared in a laboratory banbury at 120± 5℃, followed by maturing for the next 12 hr. The master batch compounds were then fed to an open mill

Table 1. Formulation of ENR/CR Rubber Mix

Materials	PHR								
	N	A	B	C	D	E	F	G	H
RSS#1[1]	100								
ENR-50[2]		100	90	80	70	60	50	30	
M-41(CR)[3]			10	20	30	40	50	70	100
S/A[4]	2	2	2	2	2	2	2	2	2
SRF[5]	50	50	50	50	50	50	50	50	50
ZnO[6]	5	5	5	5	5	5	5	5	5
MgO[7]			0.5	1.0	1.5	2.0	2.5	3.5	5
P#3 Oil[8]	10	10	10	10	10	10	10	10	10
TT[9]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
CZ[10]	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Na$_{22}$[11]	0	0	0.1	0.2	0.3	0.4	0.5	0.7	1.0
Sulfur	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Total	169	169	169.6	170.2	170.8	171.4	172	173.2	175

1) Natural Rubber

2) Epoxidized NR(Epoxy cont. 50 mole%)

3) Chloroprene Rubber(Denka Japan)

4) Stearic Acid

5) Semi Reinforcing Furnace Carbon(Lucky)

6) Zinc Oxide

7) Magnesium Oxide

8) Paraffinic oil, Processing Agent

9) Tetramethyl Thiuram Disulfide

10) N-Cyclohexyl-2-2-Benzothiazyl Sulfenamide

11) (Ethylene thiourea) 2-Mercapto-imidazoline-EU

with crosslinking agents. Crosslinking was done at 165℃ for 5 min, as determined by a rheometer (Monsanto MRD 2000). Air aging and oil resistance tests were done at 100℃ for 50 hr following ASTM D573-81 and D471-79(in ASTM #3 oil), respectively.

Tests were made using specimens, compression molded at 165℃, 150 kg/cm². Tensile tests were done using a Quick Reader MX(Ueshima) following ASTM D412. Hardness(Shore A) was measured accroding to ASTM D2240. The above tests were done at room temperature, and at least five runs were made to report. The compression set was measured at 70, 100, and 120℃ following ASTM D359-85, method B. The compression set (C_B) was obtained as the percentage of original

deflection by the following formula :

$$C_B = \frac{t_0 - t_i}{t_0 - t_n} \times 100$$

where t_0 and t_i are respectively the original and final thickness of specimen, and t_n is the thickness of the spacer bar.

RESULTS AND DISCUSSION

Fig. 1 shows the hardness of the blends. The hardness of ENR is much higher than that of NR due primarily to the higher T_g of ENR.[2,3] In blends, hardness shows a negative deviation from the additivity rule with minimum in ENR-rich blends. Modulus at 300% elongation(Fig. 2) is smaller in

ENR than in NR. This probably is due to the retarded strain crystallization of ENR.[2] In blends, modulus increases with CR. Tensile strength(Fig. 3) of ENR is again smaller than that of NR, as expected. NR undergoes low-temperature crystallization, with the maximum rate occuring at $-26°C$.[2] However, epoxidation even at low levels significantly retards the rate of crystallization, and crystallization of ENR is not expected in most practical situation at temperatures around and above room temperature. In fact, higher hardness, but lower modulus and lower tensile strength of ENR than NR is expected. In blends, it shows a smooth synergism with a maximum. With the reduction of hardness, elongation is increased in ENR-rich blends(Fig. 4). It is generally observed that the mechanical response of the blend is closely related to

its compatibility, and synergistic effect is often obtained with miscible or partially compatible blends.[4,5] In compatible blends, especially when the morphology is sensitive to the composition, larger scatter of data is often reported. The mechanical properties of ENR/CR generally vary smoothly with composition, and this would imply certain level of compatibility.[6,7]

Upon aging in air, hardness(Fig. 1) increases, in proportion to the aging temperature. Epoxidation provides NR with increased T_g in simple terms, by 1°C for every mole % epoxidation,[2] which augments the hardness. ENR is crosslinked by any cure system used for unsaturated polymer, but a sulfur based system is preferred. During heat aging, sul-
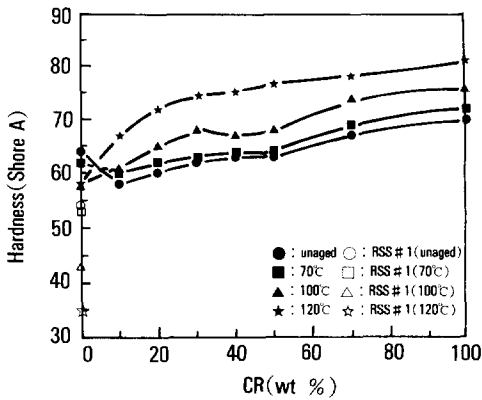

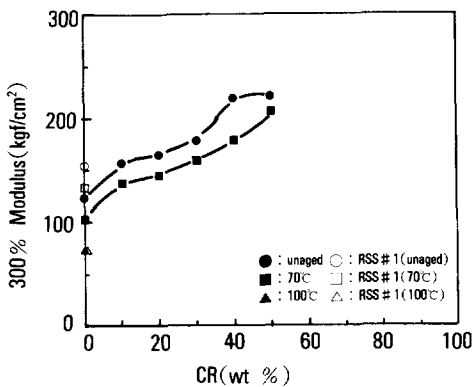**Fig. 1.** Hardness of unaged and air aged blends.

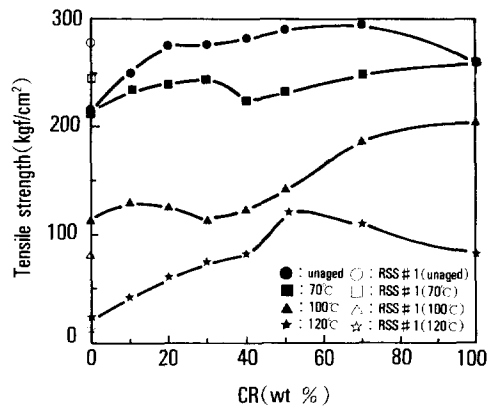**Fig. 2.** Modulus of unaged and air aged blends.

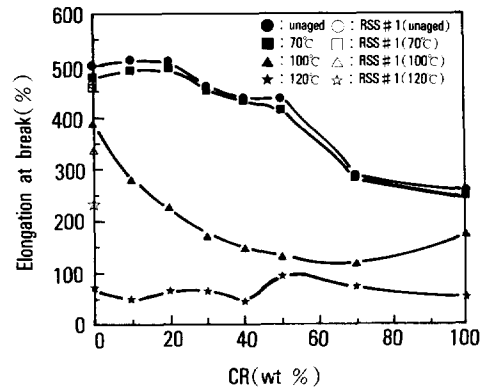**Fig. 3.** Tensile strength of unaged and air aged blends.

Fig. 4. Elongation at break of unaged and air aged blends.

furic acid attack of the epoxy group can lead to ring opening and crosslinking whick leads to undue stiffening of the elastomer.[2,8,9] CR has longer cure time than ENR, and in fact curing in CR proceeds infinitely. Therefore hardening of CR during aging is a natural consequence. In blends hardness increases regardless of its composition due to the reason described above.

It is seen that tensile properties(modulus(Fig. 2), strength(Fig. 3), and elongation(Fig. 4)) are significantly reduced upon aging in air, especially at 100 and 120℃. Modulus at 300% elongation decreased upon aging, however, the initial modulus (not measured) would show similar tendency with hardness(Fig. 1). The property-composition curve at different temperatures give no trend in common, and this would come from fact that the samples are blends of elastomers with different heat resistance characteristics.

The compression set measured at three different temperatures shows very consistent trend with composition(Fig. 5). The compression set is reduced below the additivity rule with exception at 90/10(ENR/CR). The reduction in compression set is an indication of improved rebound resilence, the result qualitatively agreed upon with our earlier report.[1]

Fig. 6 shows the increase of specimen volume upon immersion in oil. The epoxidation of NR results in a considerable increase in oil resistance

and reduction in gas permeability.[2] It is seen from the figure that oil resistance of ENR is favorably compared with CR. Compositional variation of swell at different temperatures is also smooth. This relatively smooth variation may imply the similar solvent interaction of ENR and CR.[10] However, partial miscibility implemented by interfacial crosslinking would contribute more. Though not directly verified, the sign of interfacial crosslinking was verified from a single tan δ peak of the blends located between the two peaks of ENR and CR.[1]

With solvent swell, the elastomer blends become softened(Fig. 7), however, the variation with composition is again smooth.
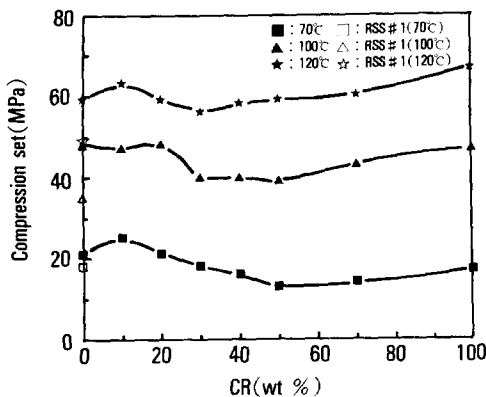
Tensile strength(Fig. 8) and elongation at break

Fig. 6. Volume change during oil aging test.
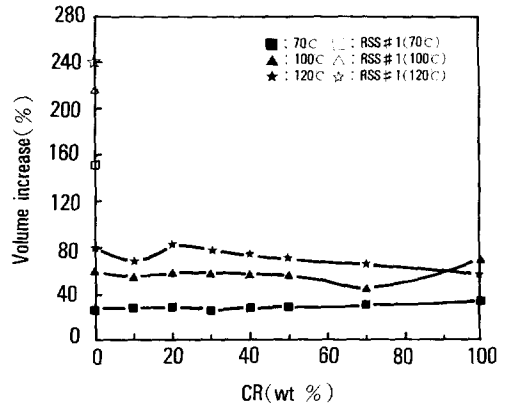

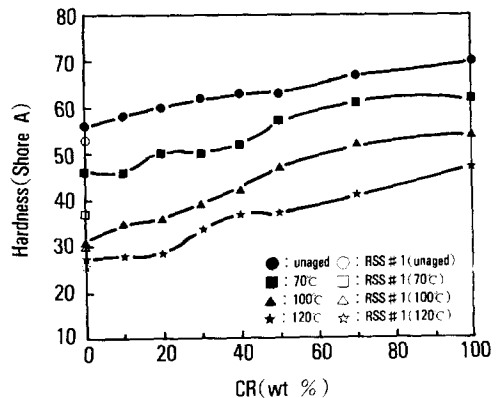Fig. 5. Compression set of unaged blends.
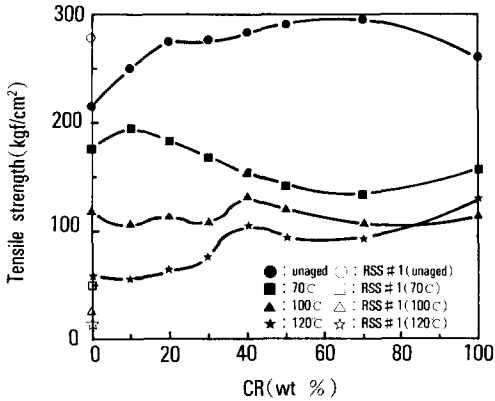

Fig. 7. Hardness of oil aged blends.

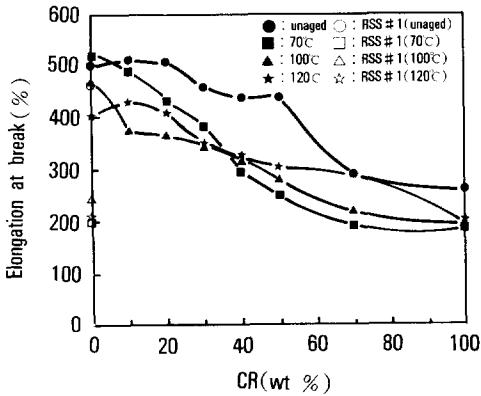**Fig. 8.** Tensile strength of oil aged blends.

Fig. 9. Elongation at break of oil aged blends.

(Fig. 9) decrease upon immersion in oil. The variation of mechanical properties with composition, however, is not smooth.

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