Chloroprene 고무개질 에폭시화 천연고무 : 1. 가류거동, 동적, 굴곡/오존 균열저항특성

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Chloroprene Rubber Modified Epoxidized Natural Rubber : 1. Cure Behavior, Dynamic, Flex/Ozone Crack Resistance Properties

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요 약 : Master batch법으로 ENR(epoxidized natural rubber)/CR(chloroprene rubber) 블렌드를 제조, 이들의 점성 및 가류특성, resilience, 굴곡저항 및 내오존 특성들을 검토하였다. 동적특성 측정(rheovibron)으로부터 ENR/CR 블렌드는 단일 tan δ peak를 나타냄을 확인하였고, peak의 위치는 CR의 함량증가와 더불어 저온쪽으로 이동함을 볼 수 있었다. 아울러 ENR의 내오존성은 소량의 CR (10%) 첨가로 크게 개선되었다.

Abstract : The ENR(epoxidized natural rubber) blends with CR(chloroprene rubber) were prepared by master batch process. Viscosity, cure characteristics, resilience, flex and ozone crack resistance were subsequently determined. Dynamic measurement(rheovibron) showed a single tan δ peak for the blend, and the peak monotonically moved toward the lower temperature with the increasing content of CR. It was also found that the ozone crack resistance was significantly improved upon blending a small amount(10%) of CR.

INTRODUCTION

During the last couple of decades there have been many advances in the modifications of natural rubber(NR). These include the epoxidation of NR to give a new polymer with properties different from those of NR.[1] Epoxidized natural rubber (ENR) has oil resistance, gas permeability and damping performance more like some of the speciality rubbers.[2] For example 50 mole % epoxidized NR is comparable in oil resistance to a medium nitrile rubber(NBR), and has higher tensile strength since, like NR, it is strain crystallizable. Also, ENR of 50 mole % epoxidation has similar air permeation properties to butyl rubber. In addition the high damping characteristics of ENR make

it suitable for many engineering applications.

The improved technical properties of ENR mainly comes from the polar modification of NR, which on the other hand gives troubles for certain specific applications. For example T_g(glass transition temperature) of ENR is increased by approximately 1℃ per mole % epoxidation.[1] This reduces the room temperature resilience as well as low temperature properties. ENR is also subjected to epoxy ring-opening under sulfur cure system, and this would leads to undue crosslinking.[3] These problems can in part be resolved by blending with other elastomers.

The ENR blends with chloroprene rubber(CR) are studied in this paper. The two elastomers are polar with similar solubility parameters, and hence a certain level of compatibility is expected. Viscosity, cure characteristics, dynamic properties, resilience, flex and ozone crack resistance are reported in this paper.

EXPERIMENTAL

Formulations of the rubber mix are given in Table 1. ENR of 50 mole % epoxidation(Epoxyprene 50) was used in this experiment. Blends were prepared as follows. First rubber stocks, S/A(see the footnote of Table 1), SRF, ZnO(MgO), and processing oil were mixed in a laboratory banbury at 120± 5℃, followed by maturing for the next 12 hr. The master batch compounds were then fed to an 8″ open mill with crosslinking agents. Crosslin-

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

king was done at 165℃ for 5 min but 100% CR was done for 10 min, as determined by a rheometer (Monsanto to MRD 2000).

Test specimens were prepared by compression molding at 165℃, 150 kg/cm². Flex cracking tests (JIS K6301) were done using De Mattia flex cracking tester at 50℃. Dynamic properties were determined using a Rheovibron(DDV II, Toyo Baldwin). Measurements were done at 11 hz from −80 to 40℃, with liquid N_2 purging. The ozone crack test was done at 500 pphm for 50 hr.

RESULTS AND DISCUSSION

Fig. 1 shows the variation of Mooney viscosity, $ML_{1+4}(100)$ with blend composition. It seems that the curve is composed of two discrete ones, i. e. an arc type one showing positive deviation from the simple additivity(dotted line) in ENR-rich($\geq$ 60) and linear variation in CR-rich blends. Positive deviation of viscosity in blends often occurs when there are strong interactions between the dispersed phases.[4] In this regard, CR having higher viscosity than ENR would have stronger interparticle interactions when it forms dispersed phase.

Fig. 2 shows scorch and optimum cure times for the blends. The optimum cure time(T_{90}) of CR is much longer than that of ENR, and this is due to the cure characteristic of CR. A basic problem in mixing CR stocks, especially the sulfur modified

ones, is the prevention of scorch.[5] In blends, T_{90} shows a strong negative deviation from the additivity(dotted line), i. e. T_{90} of the ENR-rich blends is essentially the same as ENR, a tendency also seen for scroch time. It seems that the increased rate of cure in blends gives an increase in viscosity over the simple additivity(Fig. 1). However, no unique relationship between the rate of cure and viscosity seems to exist.

The reduced optimum cure time to the level of ENR in ENR-rich blends may in part be due to the lower viscosity of ENR. In incompatible blends, lower viscosity component tends to form continuous phase,[6,7] which more or less governs the curing process. In addition, curative should also preferentially migrate into the lower viscosity component, unless the chemical affinity of curatives is significantly different between ENR and CR.

Fig. 3 shows the storage modulus(E') of the blends determined by a rheovibron. NR gives a single transition followed by a long rubbery plateau. On the other hand, ENR defines double transitions and consequently the plateau between the two transitions becomes short. Rubbery plateau is the response of nearly reversible process of entanglement and disentanglement of the chains, and of crosslinking in vulcanized rubber. Since part of the double bonds in NR is epoxidized in ENR, it may
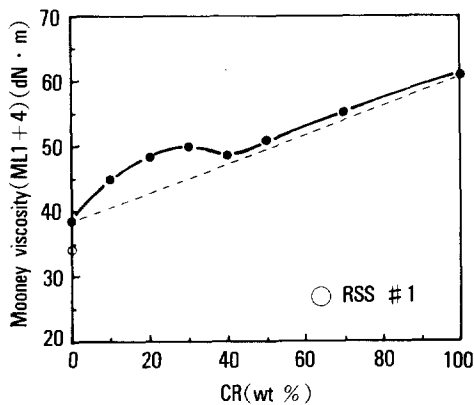

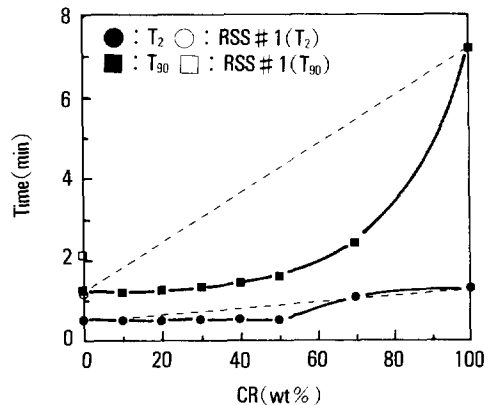**Fig. 1.** Mooney viscosities of ENR/CR blends.

Fig. 2. Scorch and optimum cure time(Rheometer) (165℃ × 12 min) : T_2 ; scorch time, T_{90} ; optimum cure time.
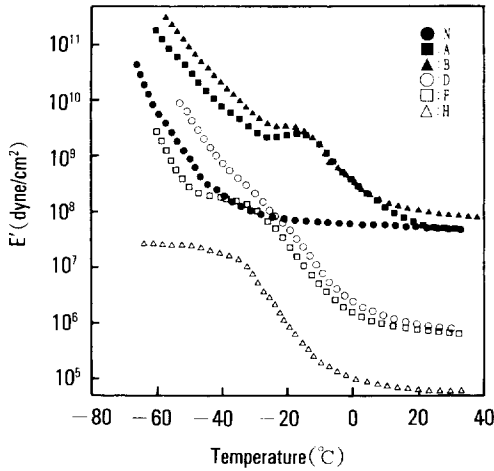
Fig. 3. Storage modulus vs. temperature of ENR/CR blends(11 Hz).

Fig. 4. Tan δ vs. temperature of ENR/CR blends(11 Hz).

be inferred that the higher transition appeared in ENR should be related to the epoxy groups. It is seen that CR shows tendency similar to NR, however the curve is moved toward the higher temperature due probably to the strong interchain interactions between hydrogen bondings.

The temperature dependence of E′ becomes more complicated in blends. It seems that two transitions are defined in the blends. At 90/10(ENR /CR) composition, the shape of the curve generally follows ENR, however the plateau between the two transitions becomes shorter. At 50/50 blends the shape of the curve resembles CR at higher temperature, and ENR at lower temperature, respectively.

Fig. 4 shows that the tan δ peak of NR(−50℃) is increased in ENR(−15℃) by approx. 35℃. It is of interest to see that a well defined single tan δ peak appeared in blends. Moreover, the peak temperature monotonically decreases with the increase in CR. Single and monotonic decrease of tan δ peak with CR would imply that the blends are interactive and at least partially compatible.[8]

The partial compatibility should in part be due to the hydrogen bondings between CR and epoxy group of ENR. However, the possibility of crosslinking between the two rubbers should also be con-
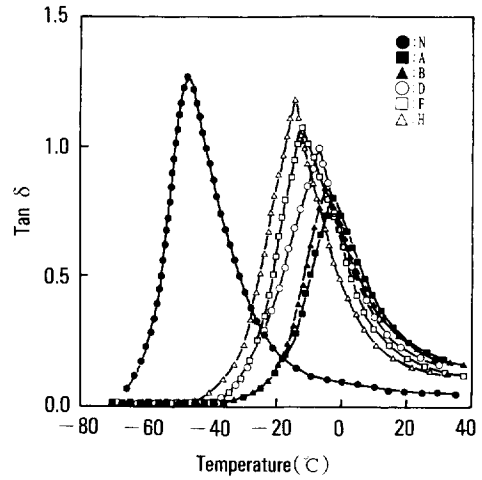
sidered. In general interphase crosslink gives broadening in NMR spectrum[9] and develops an intermediate dynamic peak.[8]

With regard to the compatibility criterion, the ones applied for plastic blends do not always hold for elastomer blends. For example, a single T_g of blends generally indicates compatibility in plastics, and gives homogeneous morphology.[10] In elastomer blends, however, single T_g which can be measured from dilatometric,[11,12] thermal[13,14] and dynamic[15,16] methods does not necessarily mean compatibility. In fact, compatibilization at the phase boundary, viz. interface crosslink is in many systems the cause of single T_g of elastomer blends.[16] For example, the gum blend of NR(natural rubber)/BR(butadiene rubber)(50/50 by weight) showed two distinct loss peaks at about −88℃ (BR) and −35℃(NR). However, when the same blends were vulcanized, a single loss peak at around −55℃ was observed, due presumably to the interface crosslinking.[17]

The resilience of ENR decreases with extent to oxidation in line with the increase in tan δ peak. It is seen that the rebound resilience of the blend (Fig. 5) monotonically increases with CR content, a result consistent with the decrease in tan δ peak position with CR(Fig. 4). Maximum mechanical

damping occurs at T_g, and hence at temperature higher than the T_g of blend, higher rebound resilience is obtained with lower T_g.[3]

Flex crack growth is shown in Fig. 6, where the growth rate increases with the increase of CR content in blends. In ENR-rich blends($\geq 80\%$), however, the growth rate remains at the level of ENR, and it increases rapidly with CR at blend compositions $\geq 30\%$ CR. The fatigue crack resistance of CR is improved upon blending with ENR. It seems that flex cracks propagate through the bulk of the blends, neither along the continuous phase nor along the interface. At blend compositions $\geq 80\%$ ENR, ENR forms continuum and CR of insignifi-

cant crack resistance does not contribute to the resistance, whereas in 20/80 blends. ENR of significant resistance does contribute.

A prime objective of this work was to improve the ozone resistance of ENR upon blending with CR. Fig. 7 shows ozone crack at various temperatures, and the measured number and size of the cracks are given in Table 2. It is seen that the ozone resistance of ENR is effectively improved upon adding a small amount(10%) of CR at 40℃. At 0 and 20℃, the number of crack is reduced, however, the depth and length of the crack is increased upon adding 10~20 wt % CR to ENR.
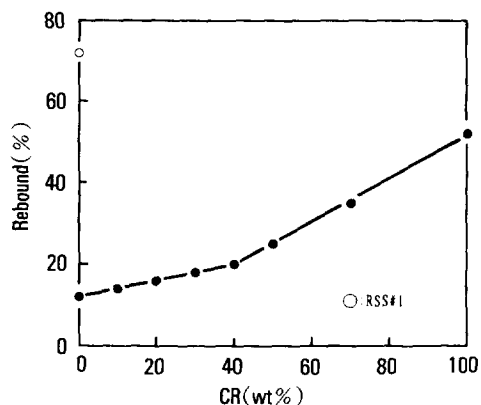

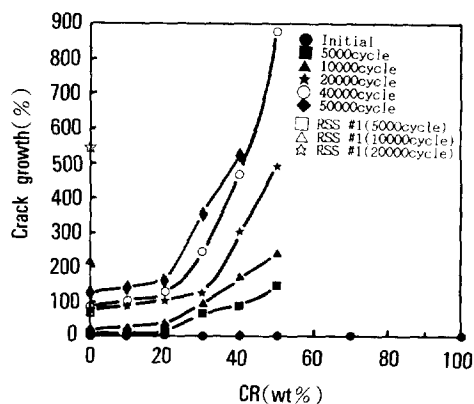**Fig. 5.** % rebound of ENR/CR blends(room temperature).

Fig. 6. Flex crack growth of unaged blends upon cyclic loading(50℃).

Table 2. Resistance to Ozone Crack*

Item \ Blend	N	A	B	C	D	E	F	G	H
40℃	C-4	eB-4	N.C	N.C	N.C	N.C	N.C	N.C	N.C
20℃	C-4	C-3	B-4	B-4	B-3	A-2	A-2	A-1	N.C
0℃	C-4	C-3	B-5	B-5	A-1	N.C	N.C	N.C	N.C
−10℃	N.C	eA-1	eA-1	eA-1	N.C	N.C	N.C	N.C	N.C

* A ⟶ B ⟶ C

Number of crack increasing

1 ⟶ 2 ⟶ 3 ⟶ 4 ⟶ 5

Depth and Length of crack increasing

e : Cracks at edge

N.C : No crack

Ozone crack test results
50 PPHM 50 HRS

−10℃		0℃		20℃		40℃	
	NR(100)		NR(100)		NR(100)		NR(100)
	ENR/CR (100/0)		ENR/CR (100/0)		ENR/CR (100/0)		ENR/CR (100/0)
	ENR/CR (90/10)		ENR/CR (90/10)		ENR/CR (90/10)		ENR/CR (90/10)
	ENR/CR (80/20)		ENR/CR (80/20)		ENR/CR (80/20)		ENR/CR (80/20)
	ENR/CR (70/30)		ENR/CR (70/30)		ENR/CR (70/30)		ENR/CR (70/30)
	ENR/CR (60/40)		ENR/CR (60/40)		ENR/CR (60/40)		ENR/CR (60/40)
	ENR/CR (50/50)		ENR/CR (50/50)		ENR/CR (50/50)		ENR/CR (50/50)
	ENR/CR (30/70)		ENR/CR (30/70)		ENR/CR (30/70)		ENR/CR (30/70)
	ENR/CR (0/100)		ENR/CR (0/100)		ENR/CR (0/100)		ENR/CR (0/100)

Fig. 7. Photographs of ozone crack.

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