

ENR/CSM Blend의 자기가류

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Self-Vulcanization of ENR/CSM Blends

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요 약 : ENR(epoxidized natural rubber)과 CSM(chlorosulfonated polyethylene)의 자기 공가류를 검토하기 위하여 open roll에서 다양한 조성의 블렌드를 제조하였다. Rheometer 측정(최고 torque, $\tan \delta$ 및 최적 가류시간)결과 70/30(ENR/CSM) 중량조성에서 공가류가 가장 효과적으로 일어남을 확인할 수 있었다. 또한 가류물의 Rheovibron 측정결과 블렌드는 -20°C 및 40°C 부근에서 두개의 전이를 보였으며 이를 각각 비가류고무 및 가류고무의 T_g 로 해석하였다. 또한 70/30 블렌드는 35°C 부근에서 가류고무전이에 해당하는 단일 T_g 를 보인다.

Abstract : The self-vulcanization, defined as a vulcanization which occurs without any curative, between ENR(epoxidized natural rubber) and CSM(chlorosulfonated polyethylene) was tested for a wide range of the blend(ENR/CSM) composition. Results from Rheometer(maximum torque, $\tan \delta$, and optimum cure time) showed that 70/30(ENR/CSM by weight) blend is subject to a most effective crosscure. Viscoelastic properties determined from a Rheovibron generally showed two glass transitions(T_g) for the blends, each indicating T_g of the uncured(lower one) and cured rubber(higher one). In 70/30 blend, a single T_g corresponding to that of cured rubber was observed.

INTRODUCTION

It has been known for many years that chemical modification of natural rubber(NR) can alter their physical properties quite significantly.¹ ENR(epoxidized natural rubber) is derived from the partial epoxidation of the natural rubber molecule resulting in a randomly distributed epoxy groups along the natural rubber backbone. The incorporation of

epoxy group in NR gives substantial changes. For example, a linear relationship is obtained between the degree of epoxidation and glass transition temperature, i. e., with every 1 mole % epoxidation approximately 1°C rise in T_g occurs, the oil resistance increases, and gas permeability decreases.² ENR of 50 mole % epoxidation(hereafter called ENR-50) has similar oil resistance to medium nitrile rubber and the gas permeation property of

ENR-50 is equivalent to that of butyl rubber.

Polyethylene(PE), being as a commodity polymer, is a hard crystalline material at room temperature. PE can be converted into an elastomer if crystallization is prevented by suitable substitution. As a means of introducing structural irregularities, random chlorosulfonation onto PE molecules is employed. CSM(chlorosulfonated polyethylene) was first applied in the rubber industry, and was introduced in 1952 under the name of Hypalon. The chlorosulfonic groups attached to the PE are reactive and facilitate vulcanization.

A prime objective of this work is to examine the curing ability of one rubber by the functional group of another rubber in ENR/CSM blends. With crosscure between ENR and CSM, a block or graft copolymer will be obtained in situ, and this should act as an effective compatibilizer. In addition, the polar nature of the two types of rubbers would contribute to the enhanced compatibility to some extent.³ In this paper, the viscosity, cure behavior, dynamic mechanical characteristics and mechanical properties of the blend are studied.

EXPERIMENTAL

Formulations of the rubber mix are given in Table 1. ENR-50 with 50 mol % epoxidation(Epoxy-pyrene) of natural rubber was used. CSM, Hypalon-610(du Pont), was employed in this experiment. Blends were prepared as follows. First ENR-50 was masticated in a two-roll open mill(14×6 in.) for 6 min, followed by adding Hypalon-610 and mixed for another 10 min.

Rheographs were determined at 160 and 180°C by a Monsanto Rheometer MRD 2000. Vulcanization was done during molding at 160°C for 60 min. Tests were made using specimens prepared by compression molding at 160°C, 150 kg/cm². Dynamic characteristics were determined using a Rheovibron(DDV II, Toyo Baldwin). Measurements were done at 11 hz from -100 to 60°C, with liquid nitrogen purging. Tensile tests were done using a Quick Reader MX(Ueshima) following ASTM D 412. The above tests were done at room temperature, and at least five runs were made to report.

RESULTS AND DISCUSSION

The cure characteristics of ENR/CSM blend are shown in Table 2. The blend contains ENR/CSM in the ratio of 10/90, 30/70, 50/50, 70/30 and 90/10 parts by weight. Rheographs of the blend are given in Fig. 1. It is generally seen that the torque value increases with time, except 90/10 blend. Since tor-

Table 1. Formulation of ENR/CSM Rubber Mix

Materials	Composition(wt %)				
	A	B	C	D	E
ENR-50	90	70	50	30	10
CSM-610	10	30	50	70	90
Total	100	100	100	100	100

Table 2. Cure Characteristics of ENR/CSM Blends

Stocks	Condition	A	B	C	D	E
Tan δ MH	160°C×1 hr	0.667	0.007	0.064	0.113	0.245
ts ₁ ^{a)} (min : sec)		—	2 : 18	3 : 03	3 : 44	24 : 40
t ₉₀ ^{b)} (min : sec)		19 : 25	39 : 02	46 : 41	47 : 48	47 : 40
MH ^{c)} (lb · in)		0.42	7.14	6.35	4.98	3.30
Tan δ MH	180°C×1 hr	—	0.017	0.076	0.136	0.360
ts ₁ (min : sec)		—	1 : 15	1 : 11	2 : 33	16 : 54
t ₉₀ (min : sec)		—	22 : 10	33 : 12	38 : 07	40 : 57
MH(lb · in)		—	7.09	6.16	4.74	2.29

^{a)} Scorch time

^{b)} Optimum cure time

^{c)} The highest Mooney torque value

que is directly proportional to the viscosity, which on the other hand is proportional to the molecular weight of the rubber, the increase of torque with time clearly indicates that self-vulcanizations do occur. Torque of 90/10 blend does not vary with time, i. e., self-vulcanization is insufficient, due presumably to the lack of SO_2Cl group. When the torque of ENR-rich blends is compared with that of CSM-rich ones, ENR-rich blends show asymptotic behavior with time, whereas, almost a linear increase of torque with time is obtained for CSM-rich blends. This implies that the ENR-rich blends are subject to fast vulcanization, as will be seen in

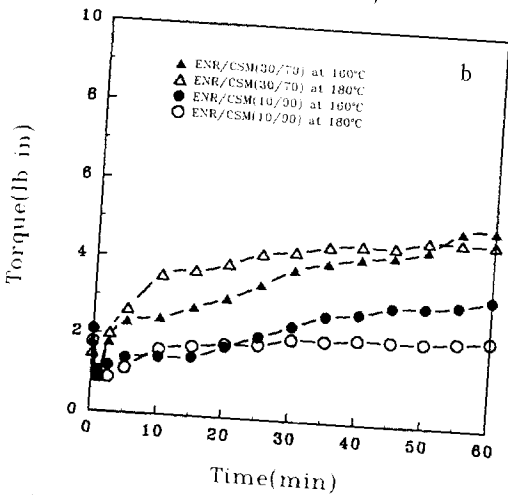
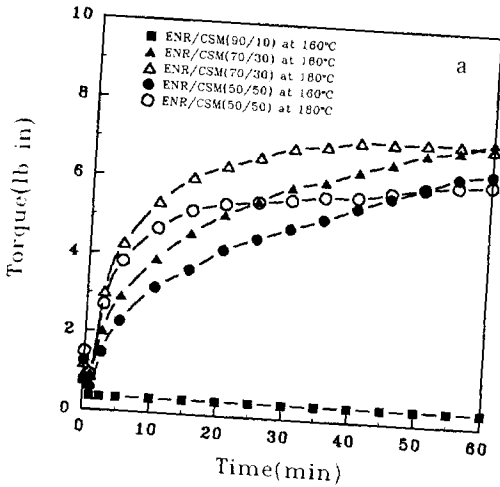


Fig. 1. Rheographs of ENR/CSM blend : (a) 90/10, 70/30 and 50/50 blends. (b) 30/70 and 10/90 blends.

Fig. 5. From the figure, it is seen that torques at 180°C is generally higher than that of 160°C . This is probably due to the rapid rate of cure at higher temperature.

Fig. 2 shows the variation of maximum torque values with blend composition. The highest level of maximum torques is seen at the CSM content of 30 wt % and this should indicate most extensive crosslink at this blend composition. In fact, the self-vulcanization between ENR and CSM has physically been verified by De et al.^{4,5} These authors prepared the blend at a fixed composition (50/50) and found that both ENR and CSM were soluble in chloroform, however, molded ENR/CSM blend was insoluble in the same solvent. This clearly indicates in situ crosscure between ENR and CSM.

Fig. 3 shows the $\tan \delta$ of maximum torque determined from the Monsanto Rheometer. The $\tan \delta$ during compounding corresponds to the ratio of out-of-phase shear stress to the in-phase shear stress. Therefore, it is expected to decrease with the progress of curing due to the increased elasticity via crosslinking. $\tan \delta$ shows a drastic drop at 30% CSM, beyond which it increases with CSM. The minimum $\tan \delta$ obtained at 30% CSM indicates that the most effective crosslinking is obtained at this composition, a result consistent with the maximum torque obtained at this composition.

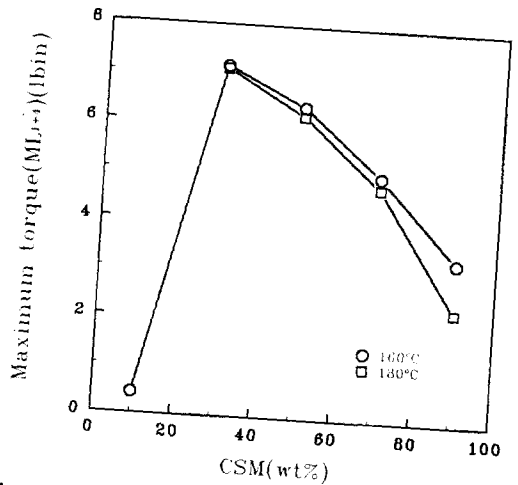
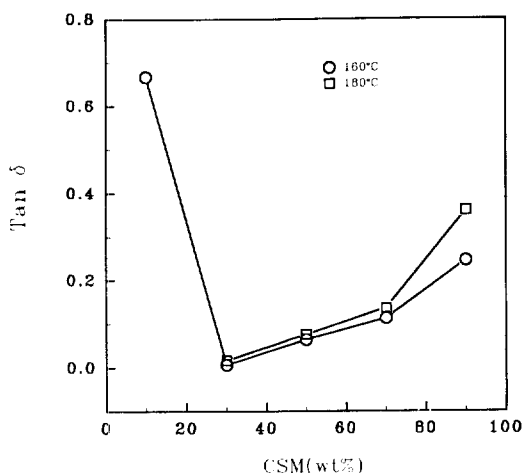


Fig. 2. Maximum torques of ENR/CSM blends.

Fig. 3. Tan δ of ENR/CSM blends.

Figs. 4 and 5 show scorch and optimum cure times for the blends. The scorch time slowly increases with CSM up to 70% CSM in the blend. However, scorch time increases abruptly at 90% CSM. The abrupt increase in scorch time is due to the delayed cure which is caused by significant unbalance between epoxy and SO_2Cl group in the blend. On the other hand, the optimum cure time (Fig. 5) asymptotically increases with CSM contents. As is often the case with rubber vulcanization process, scorch as well as optimum cure time is reduced when the temperature rises.

Figs. 6 to 8 show the viscoelastic properties of the blends determined using a Rheovibron. The amorphous nature of rubber blends clearly defines glass-rubber transition (T_g) with a significant drop in modulus. At and above room temperature, the storage modulus (E') generally increases with the decrease of CSM content in the blends. It is also noted that most of the blends show double transitions (Figs. 7 and 8), lower one at about -20°C , and higher one at about 40°C . However, in 70/30 blend only a single transition about 35°C is observed. In rubber, T_g increases significantly with the increase of crosslinking density.² The lower T_g obtained for 50/50, 30/70, and 10/90 blends should correspond to the T_g of uncured rubber, and the higher one correspond to the crosslinked rubbers.

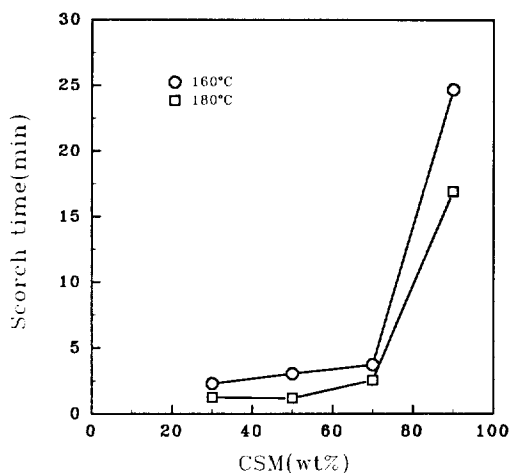


Fig. 4. Scorch time of ENR/CSM blends.

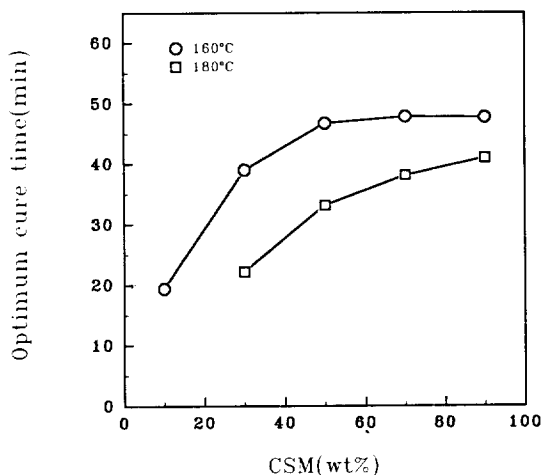
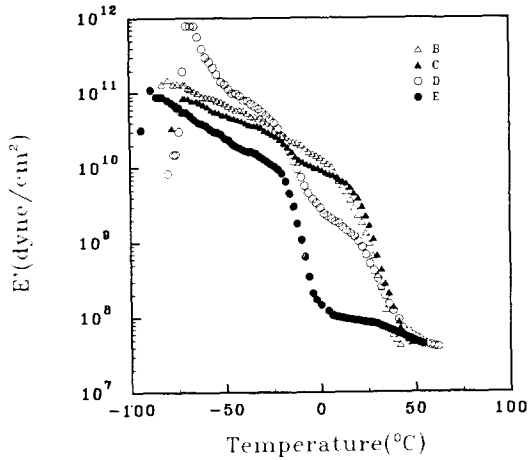
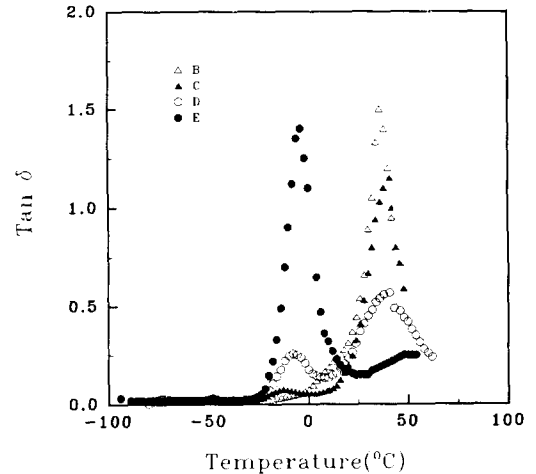
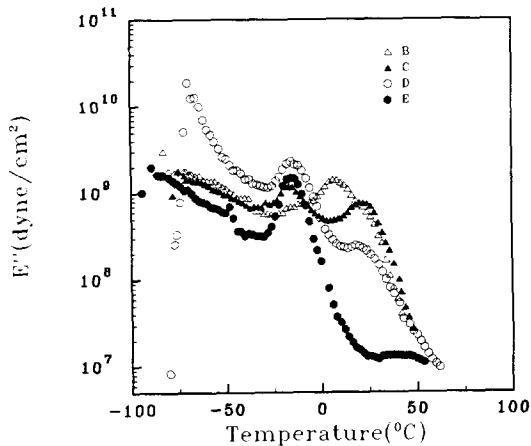


Fig. 5. Optimum cure time of ENR/CSM blends.

In incompatible rubber blends, double T_g is generally observed.^{6,7} However, when crosscure, i. e., cure between unlike components of the blend, occurs a single T_g is often reported.^{3,8,9} It should be mentioned that the T_g of uncured rubber is also increased in the blend. This is most likely due to the restricted motion of the uncured rubbers by the crosslinked rubbers around. In this regard, the single T_g of 70/30 blend is understood. As discussed earlier, most extensive crosslinking is obtained at this blend composition, and due to the insignificant fraction of the uncured rubber, the T_g of un-

Table 3. Mechanical Properties of ENR/CSM Blends

Stocks	Condition	A	B	C	D	E
Tensile strength(kgf/cm ²)	160°C × 1 hr	—	67.5	74	96.5	—
100% Modulus(kgf/cm ²)		—	29.9	35.7	37.7	—
Elongation(%)		—	213.0	222.0	317.2	—
Tear strength(kgf/cm)		—	30.8	33.8	44.5	—

**Fig. 6.** Storage modulus vs. temperature of ENR/CSM blends(11 Hz) : B=70/30, C=50/50, D=30/70, E=10/90(ENR/CSM).**Fig. 8.** Tan δ vs. temperature of ENR/CSM blends(11 Hz) : B=70/30, C=50/50, D=30/70, E=10/90(ENR/CSM).**Fig. 7.** Loss modulus vs. temperature of ENR/CSM blends(11 Hz) : B=70/30, C=50/50, D=30/70, E=10/90(ENR/CSM).

cured rubber is not observed.

The mechanical properties of the blends were

measured for a limited compositions(30/70, 50/50, and 70/30)(Table 3). For 10/90 and 90/10 blends, the crosslinking was insufficient and hence the tensile specimens were not successfully prepared since they were unable to carry a measurable load. It is seen that tensile and tear strength, modulus and elongation at break monotonically increase with the CSM content in the blends. This regular behavior may arise from the significantly improved compatibility of the blends via crosscures.¹⁰

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