롤밀을 이용하여 동적가황된 NR과 EVA 블렌드의 기계적 성질

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Mechanical Properties of Dynamically Vulcanized NR and EVA Blends in a Roll Mill

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요 약 : 동적가황된 natural rubber(NR)과 ethylene/vinylacetate copolymer(EVA) 블렌드의 기계적 물성에 대해 연구하였다. 블렌드 조성, 과산화디큐밀(DCP) 함량 및 충진제인 zeosil 함량에 따른 인장물성, 인열강도 및 경도를 조사하였다. 동적가황된 NR/EVA블렌드는 NR/EVA 단순블렌드보다 모든 블렌드조성에서 높은 인장강도와 탄성율을 보였으나 DCP 함량의 증가에 따라 인장강도는 감소하였으며 탄성율은 증가하였다. 같은 DCP함량일 때는 인장강도와 인열강도 및 경도는 NR의 농도가 증가할수록 감소하였다. 블렌드 조성이 중량비로 10/90 및 30/70인 NR/EVA 블렌드에서 zeosil을 첨가할 경우 zeosil 함량에 따라 경도와 인열강도는 증가하였다. 동적가황된 10/90 조성의 NR과 EVA 블렌드는 zeosil을 50 phr 이상 함유할 경우 항복거동을 나타내었다.

Abstract : The mechanical properties of the dynamically vulcanized natural rubber(NR) and ethylene/vinylacetate copolymer(EVA) blends have been investigated in this study. The influences of the blend compositions, peroxide contents, and zeosil contents on the tensile properties, tear strength and hardness of the dynamically vulcanized NR/EVA blends were discussed. The tensile strength and modulus of the dynamically vulcanized NR and EVA blends were higher than those of the linear NR/EVA blends over the entire blend compositions. The tensile strength decreased but the modulus increased with DCP contents. The tensile strength, tear strength, and hardness decreased with NR compositions. The hardness and tear strength increased with zeosil contents at 10/90 as well as 30/70 blend compositions. The dynamically vulcanized NR/EAV(= 10/90) blends having zeosil contents above 50 phrs exhibited yield behavior.

INTRODUCTION

The dynamically vulcanized thermoplastic elastomer blends have attracted much interests in the plastic industry for years because of their important technical advantages in processing.[1~5] In the "dynamic vulcanization" process, blends of vulcanized rubber and plastic are prepared in an inten-

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sive mixer such as a roll mill or extruder where the rubber component is vulcanized under shear with a proper curing agent.[6~8] It was known that the technical advantages in processing of the dynamic vulcanization stem from the peculiar morphological features of the process ; i.e. the blend prepared by the dynamic vulcanization is known to be composed of a partly gelled elastomer and a physically crosslinked plastic, and flows at elevated temperature and yet behaves as a thermoset at use temperature.[9,10]

In this work, the dynamically vulcanized natural rubber(NR) and ethylene/vinylacetate copolymer (EVA) copolymer) blends have been prepared using dicumyl peroxide(DCP) as a curing agent in a roll mill. The effects of DCP contents and NR/EVA compositions on the tensile strength, hardness, and tear strength of the dynamically vulcanized NR and EVA blends were investigated. For the dynamically vulcanized NR and EVA blends having selected blend compositions, the effects of the addition of white carbon, zeosil, as a filler on those mechanical properties were also studied.

EXPERIMENTAL

Materials. EVA having 88 wt % of ethylene was obtained from Mitsui Polychemical Co.. The commercially available EVA(P1403 grade) has melt flow index of 1.4 and 34% of crystallinity. NR used in this work was a standard Malaysian NR(SMR 20 grade). The plasticity retention index of the NR was 80. DCP was purchased from Mitsui Chem. Co. and used as received. Zeosil(45 grade; specific area, $200 \, m^2/g$; average particle size, 18μm ; SiO_2 >88%) was kindly supplied from Hanbul Chem. Co. as a white carbon filler.

Preparation of Blends. Blends were prepared by the same method as decribed for the dynamically vulcanized ethylene-propylene-diene terpolymer (EPDM) and high density polyethylene blends[6] ; The $8'' \times 20''$ two-roll mill was used as an internal mixer. DCP contents ranged from 0 to 1.4 phr based on the amount of NR. The EVA was blended

with NR-DCP mixture in the molten state at 140℃ for 20 min. During the experimental runs, the rotating speed of the milling was given as 24 rpm. To some of these dynamically vulcanized blend samples with DCP contents of 0.6 phr zeosil was added as a filler. In this case, the blend compositions were fixed at 10/90 and 30/70(=NR/EVA) by weight. For the zeosil-filled NR/EVA blends, the amounts of zeosil ranged from 0 to 70 phr based on the total amount of the NR/EVA mixture. A detailed description of the dynamic vulcanization process was described elsewhere.[6,7] The blends prepared in this way were compression molded at 180℃ under the pressure of $200 \, kg/cm^2$ for 5 min for further measurements of thermal and mechanical properties using Differential Scanning Calorimeter(DSC) and universial testing machine (UTM), respectively.

Measurements. The tensile tests were carried out using an Ueshima UTM(TS-102-1 type) on the samples prepared according to KS M3006. The crosshead speed was 500 mm/min, and 5 measurements were averaged. Tear tests were also made using the same Ueshima UTM on the samples prepared according to KS M3001, and 5 measurements were averaged. Shore A hardness was measured using Shore A durometer, and ten measurements were averaged. The wt% crystallinity of EVA in the blend was evaluated from the ratio of the amount of heat of fusion of the blend to the heat of fusion of the perfectly crystalline polyethylene(H_{PE}=277.1 J/g in the literature.[11]) The thermal analysis was performed under nitrogen with a heating rate of 10℃/min using a Stanton DSC 700 Differential Scanning Calorimeter.

RESULTS AND DISCUSSION

The typical stress-strain curves of the linear NR/EVA blends having various blend compositions are illustrated in Fig. 1 and the tensile data are listed in Table 1. As expected, it is seen that the mechanical properties such as tensile strength, tear strength, modulus and hardness increase with
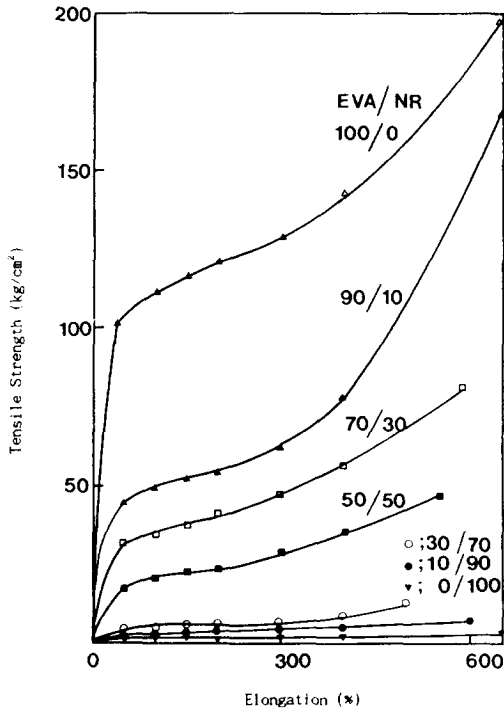
Fig. 1. Stress-Strain curves for NR/EVA blends having different blend compositions.

Table 1. Mechanical Properties of NR/EVA Blends

NR/EVA ratio (%)	Tensile strength (kg/cm²)	Modulus (kg/cm²)	Elongation at break (%)	Hardness (Shore A)	Tear strength (kg/cm²)
100/0	3	8	710	4	2
90/10	8	11	590	5	3
70/30	11	57	500	30	14
50/50	46	148	530	60	26
30/70	82	192	580	80	46
10/90	168	240	650	90	69
0/100	192	350	650	92	78

Fig. 2. Stress-Strain curves of the dynamically vulcanized NR/EVA(=50/50) blends with different DCP contents.(units of the numbers are phr)

increasing EVA compositions. Fig. 2 shows typical stress-strain curves of the dynamically vulcanized NR and EVA blends with different DCP contents. In this figure, the blend composition is 50/50(= NR/EVA) by weight. The figure shows that the tensile strengths of the dynamically vulcanized NR and EVA blends are higher than those of the linear NR/EVA blends regardless of DCP contents,
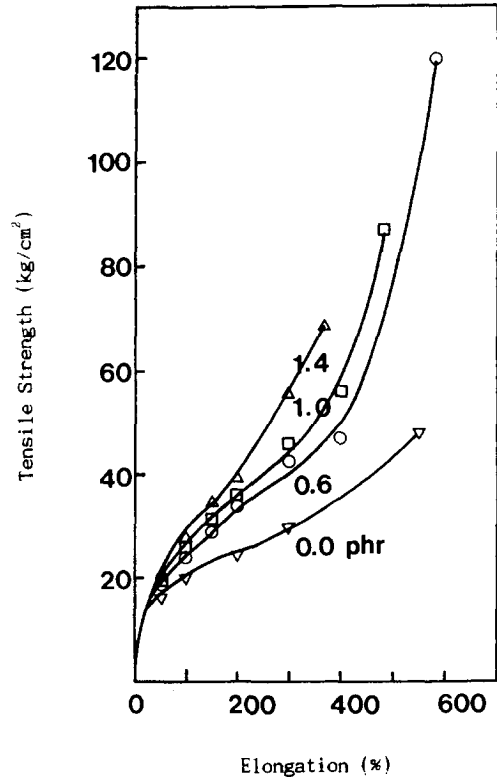
due to the chemical crosslinking of NR by DCP.

Meanwhile, the tensile strength and the elongation at break decreased with increasing DCP contents. The result may be attributed to the decreasing crystallinity of EVA phase in the blends, despite the increasing chemical crosslinking of NR phase by DCP. The chemical crosslinking enhances the mechanical properties of materials but at the same time prevents the crystallization of the crystalline phase acting as physical crosslinks.[11] In this case, therefore, it may be thought that the tensile properties of the dynamically vulcanized blends are affected more significantly by the decreasing crystallinity of EVA phase than the increasing chemical crosslinking by the peroxide.

Table 2 shows the wt% crystallinity of EVA phase in the blends along with other tensile data,

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Table 2. Tensile Properties of Dynamically Vulcanized NR-EVA Blends and wt. % Crystallinity of EVA in the Blends

NR/EVA ratio (%)	DCP* (Phr)	Tensile strength (kg/cm²)	Modulus (kg/cm²)	Elongation at break (%)	wt. %* Crystalli-nity
50/50	0.6	120	152	580	16.5
	1.0	87	160	490	15.2
	1.4	69	174	370	15.2
30/70	0.6	169	196	590	19.2
	1.0	137	200	490	18.7
	1.4	128	210	440	17.8
10/90	0.6	180	260	550	23.1
	1.0	169	278	520	22.7
	1.4	138	290	470	19.5

* DCP is in phr based on 100 gr of NR.
** The wt % crystallinity of EVA in the blend was evaluated from the ratio of the amount of heat of fusion of the blend to the heat of fusion of the perfectly crystalline polyethylene($\Delta H_{PE} = 277.1$ J/g(Ref. 11)).

in which the wt% crystallinity decreases with increasing DCP contents for the dynamically vulcanized NR and EVA blends having various NR/EVA compositions, even though the decrease of crystallinity with various DCP contents are not appreciably large.

The effects of DCP contents as well as blend compositions on the modulus are seen in Table 2. The modulus increased with increasing DCP contents, in contrast with the tensile strength. The result is likely to be ascribed to the balance of the increase in the chemical crosslinking of NR phase and the decrease in the degree of crystallinity of EVA phase with increasing DCP contents. In the intial stage of tensile experiments, the effect of chemical crosslinking of NR phase may be thought to be dominant over the effect of the decreasing crystallinity with increasing DCP contents, since the blends consisting of NR with higher crosslinking density(with higher DCP contents) have higher resistance to tensile deformation than those of NR with lower DCP contents. In the final stage of tensile experiments, however, it may be assumed that the tensile strength depends more on the decreasing crystallinity of EVA than on the increa-
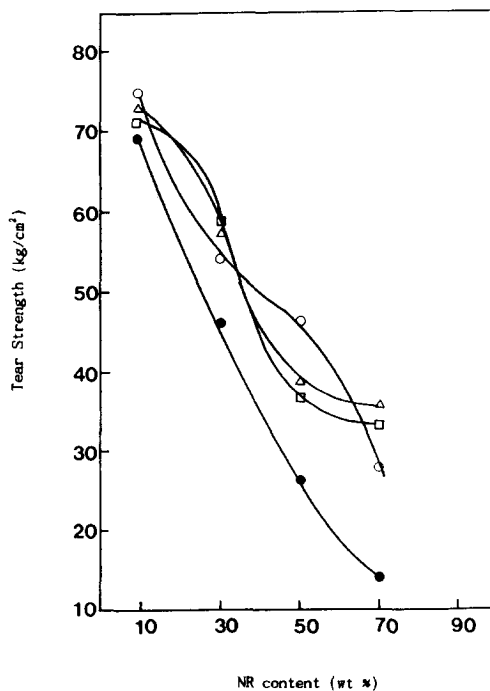

Fig. 3. Effect of DCP contents and blend compositions on the tear strength of the linear and dynamically vulcanized NR and EVA blends.(● : 0.0 phr, ○ : 0.6 phr, □ : 1.0 phr, △ : 1.4 phr)

sing chemical crosslinking of NR phase, since the tensile strength is a kind of ultimate property. In general, the tensile strength decreased with NR compositions at the same DCP contents.

Fig. 3 shows the effects of DCP contents and blend compositions on the tear strength of the linear and the dynamically vulcanized NR/EVA blends. The dynamically vulcanized blends showed higher tear strengths than the linear blends over the entire blend compositions but the effect of DCP contents on the tear strength was not clearly observed. The tear strengths of the blends increased with decreasing NR compositions.

The hardness of the linear and the dynamically vulcanized NR/EVA blend is shown in Fig. 4. In case of the linear NR/EVA blends, the hardness decreased with increasing NR composition. The dynamically vulcanized NR/EVA blends, however, showed maxima at the NR composition of 30 wt %

regardless of DCP contents. The result may be due to the balance of the increase in the chemical crosslinking of NR phase and the decrease in the degree of crystallinity of EVA phase with increasing DCP contents, as already mentioned in Table 2. The maximum hardness at the NR composition of 30 wt % implies that the effect of chemical crosslinking of NR phase by DCP may be maximum at the blend composition, which is more dominant than the effect of the decreasing crystallinity with increasing DCP contents. The dynamically vulcanized blends of higher DCP contents showed slightly higher hardness but the differences were not large.

In general, the properties and morphology of the dynamically vulcanized rubber/plastic blends are affected by a number of factors acting independently and simultaneously, including the decreasing crystallinity of the semicrystalline plastic component and the increasing crosslink density of the rubber component, the miscibility between the rubber and plastic components, and etc.[12] The results obtained in this work may be a combination of all the factors mentioned above. However, it is of no doubt that the dynamically vulcanized NR/EVA blends having DCP contents of 0.6 phr and 30/70 or 10/90(=NR/EVA) blend compositions showed relatively balanced mechanical properties than any other blends having different DCP contents and blend compositions. Thus, the investigation of the effect of the addition of zeosil as a filler on the mechanical properties of the blends was limited only to the dynamically vulcanized blends having DCP contents of 0.6 phr and 30/70 or 10/90(=NR /EVA) blend compositions.

Fig. 5 shows the effect of zeosil on the stress-strain curve of the dynamically vulcanized NR/EVA (=30/70) blends having DCP content of 0.6 phr. The tensile strength and elongation at break dec-
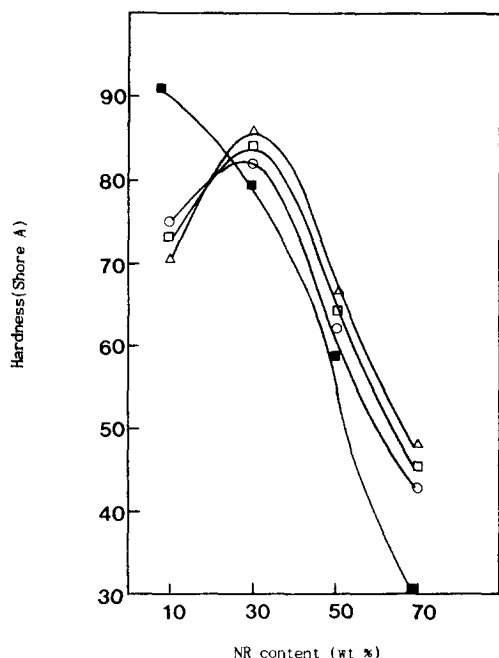

Fig. 4. Effect of DCP contents and blend concentrations on the hardness of the linear and dynamically vulcanized NR and EVA blends.(■ : 0.0 phr, ○ : 0.6 phr, □ : 1.0 phr, △ : 1.4 phr)
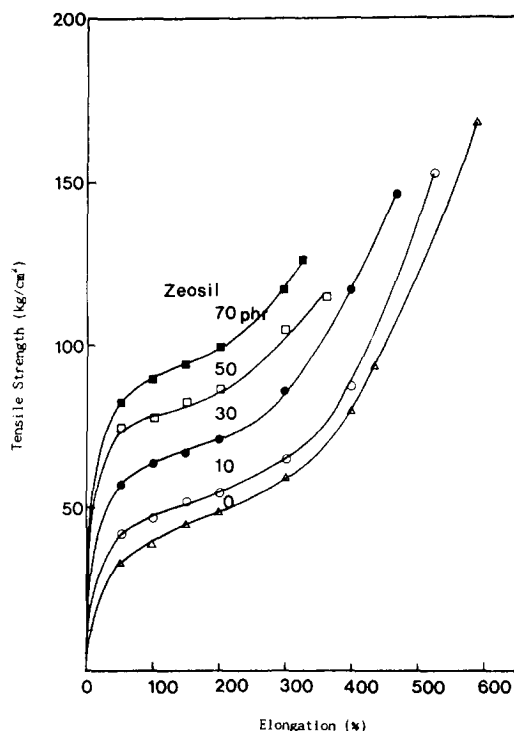

Fig. 5. Effects of zeosil content on the tensile strength of the dynamically vulcanized NR/EVA(=30/70) blends.

reased with increasing zeosil content up to 50 phr but increased again with zeosil content above 70 phr. The modulus, however, increased with increasing zeosil content. The initial decreases in ten-
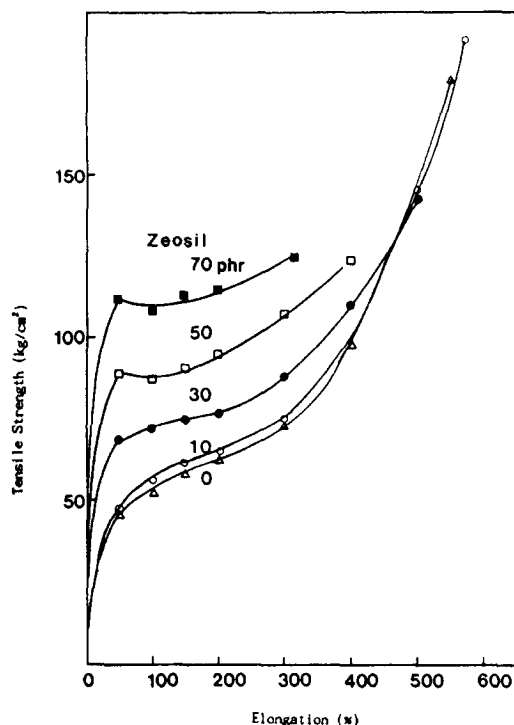

Fig. 6. Effects of zeosil content on the tensile strength of the dynamically vulcanized NR/EVA(=10/90) blends.

sile properties with increasing zeosil contents may be due to the poor adhesion between the zeosil particles and component polymers because of the complex morphology consisting of component polymers and filler particles. The role of zeosil as a reinforcing filler may be expected, however, to be functioned at higher zeosil loaded blends, even though the adhesions between the component polymers and the white carbon fillers are not good. Similar results for the dynamically vulcanized NR /EVA(=10/90) blends having DCP contents of 0.6 phr are shown in Fig. 6. The tensile strength and elongation at break of the dynamically vulcanized blends decreased but the modulus increased with increasing zeosil content.

Of interesting is, however, the fact that the yield point can be observed for the dynamically vulcanized NR/EVA(=10/90) blends having zeosil content above 50 phrs. The result implies that the dynamically vulcanized NR/EVA(=10/90) blends with DCP contents of 0.6 phr, showing yield points, exhibit hard plastic-like nature, even though the tensile strength is not large. The accurate interpretation is not easy at present for the reason why the blends exhibit yielding, and further studies should be made on this regards. The hardness and tear strength increased with the zeosil content at 10/90 as well as 30/70(=NR/EVA) blend compositions. Table 3 summarized the results.

Table 3. Effect of Zeosile Content on the Mechanical Properties of the Dynamically Vulcanized NR and EVA Blends

NR/EVA ratio (%)	DCP (phr)	Zeosile (phr)	Tensile strength (kg/cm²)	Modulus (kg/cm²)	Elongation at break (%)	Hardness (Shore A)	Tear strength (kg/cm²)
30/70	0.6	10	152	210	520	86	60
		30	147	230	460	92	72
		50	114	260	360	95	75
		70	126	290	320	97	82.5
10/90	0.6	10	191	270	570	91	80
		30	142	295	500	94	84
		50	124	320	400	96	83
		70	125	358	310	98	91

* Zeosile is in phr based on 100 gr of EVA-NR blend.

CONCLUDING REMARKS

This study revealed the influences of the blend compositions, peroxide contents, and zeosil content on the tensile properties, tear strength and hardness of the dynamically vulcanized NR/EVA blends. It was found that the tensile strength and modulus of the dynamically vulcanized NR and EVA blends were higher than those of the linear NR and EVA blends. The tensile strength decreased but the modulus increased with DCP contents. The tensile strength decreased with NR compositions. The tear strength and hardness also decreased with increasing NR compositions. The hardness and tear strength increased with the zeosil content at 10/90 and 30/70(= NR/EVA) blend compositions. The yield behavior was observed for the dynamically vulcanized NR/EVA(= 10/90) blends having zeosil content above 50 phrs. Exact interpretation of several results is not easy at the present moment but it is believed that the results given here are of practical importance in both plastic and rubber industries. More detailed studies on the crystallization kinetics and morphological changes during the dynamic vulcanization are now undertaken, in order to interpret more precisely our present experimental results.

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