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Aramid 섬유보강 Chloroprene 고무복합재료 : 섬유 Loading과 Matrix 강도가 복합재료의 기계적 특성에 미치는 영향

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Short Aramid Fiber Reinforced Chloroprene Rubber Composite: Effects of Fiber Loading and Matrix Strength on Physical Properties of the Composite

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요 약 : 단섬유 충전이 고무의 물리적 특성에 미치는 영향을 검토하기 위하여, chloroprene 고무에 aramid 섬유(3mm)를 20wt%까지 충전하여 얻어진 복합재료의 물성을 검토하였다. 섬유함량이 10wt%에서 복합재료의 인장강도(L방향)는 최소로 나타났으며, 15~20 wt%에서 보강효과가 나타남을 알 수 있었다. 또한, 보다 강한 matrix를 사용했을 경우에는 섬유 보강효과가 다소 억제되었으며, 섬유함량 20wt%에서도 인장강도(L방향)의 증대는 나타나지 않았다.

Abstract : The effect of short fiber reinforcement on rubbery matrix has been studied for chloroprene / aramid system, up to 20 wt% fiber loading. The strength of composite in longitudinal direction showed minimem at 10 wt% loading, and the critical fiber loding was found at 15~20 wt%. When the matrix rubber was replaced by stronger one, the critical fiber loading was increased beyond 20 wt% with regard to tensile strength of the composite.

INTRODUCTION

Reinforcement of rubber with short fibers has gained widespread attention in rubber industry, especially in the production of hoses, V-belts and tires.[1,2]

A number of fibers, with or without surface treatment, have been applied to natural and synthetic rubbers, and valuable reviews on the topic have sometimes become available.[1~3] It is generally agreed that there is a critical fiber concentration for reinforcement regardless of fiber-matirx combination and bonding level.[2,4,6] However, studies on the effect of matrix strength on the fiber has not been considered to the knowledge of the present authors.

This report first considers the effect of short aramid fiber inclusion in chloroprene rubber(CR) as a function of fiber concentration. The effect of matirx strength was examined by employing

two types of CR rubber with significantly different viscosity. The results were interpreted in terms of hardness and wear, strength(tensile and tear), elongation, heat buildup, and compression set.

EXPERIMENTAL

Formulations of the rubber mixes are given in Tables 1 and 2. Two types of CR rubber with different viscosity(Table 3) were used.

Mixing was done using a conventional open mixing mill(150×330mm) at 50±5℃, with cooling water circulation, and roll speed ratio of 1:1.25. The plasticity of rubber was lowered by masticating the sample on a cold tight mill for 5 minutes, then the aramid fibers, chopped to 3mm and aspect ratio of 250, were evenly spreaded on the rubber sheet. Other ingredients were added following the conventional procedure employed in rubber indurstry, however, nip gap, time of mixing and the sequence of addition of the ingredients were kept same for all the mixes.

The mixes were vulcanized at 150℃, 150kg/cm^2 for 15 minutes. Cure times were determined from the rheometer(Monsanto R−100). Tensile and tear strengths of the vulcanizates were measured following ASTM D412−51T and D624−54. Specimens were prepared both in longitudinal(L) and transverse(T) directions of the fiber. Abrasion and Shore A hardness were measured following NBS method(KSM 6518) and ASTM D676−52T procedure, respectively. All of the above tests were done at room temperature, and average of five runs are reported here. Heat buildup was measured usig Goodrich Flexometer on 12.7mm(dia.)×25.4mm(height) rubber cylinders at 100℃, 8.75% stroke for 25minutes. The compression set was determined at 25% strain, 70℃, for 22 hours(ASTM D395−61).

Table 1. Rubber Mix Formulation of Series A

Sample Code	Content of Mix(parts by wt)				
	A_1	A_2	A_3	A_4	A_5
A−20[a]	100	100	100	100	100
MgO	4	4	4	4	4
Stearic acid	1	1	1	1	1
SRF[b]	29	29	29	29	29
ZnO	5	5	5	5	5
Na−22[c]	0.5	0.5	0.5	0.5	0.5
BHT[d]	1	1	1	1	1
Aramid fiber	0	5	10	15	20

[a]Chloroprene Rubber(Denka Co., Ltd., Japan)
[b]Semi Reinforcing Furnace(carbon black)
[c]2-mercaptoimidazolin(or ethylene thiourea)
[d]2,6-di-t-butyl-p-cresol

Table 2. Rubber Mix Formulation of Series B

Sample Code	Content of Mix(parts by wt)				
	B_1	B_2	B_3	B_4	B_5
A−120[a]	100	100	100	100	100
MgO	4	4	4	4	4
Stearic acid	1	1	1	1	1
SRF[b]	29	29	29	29	29
ZnO	5	5	5	5	5
Na−22[c]	0.5	0.5	0.5	0.5	0.5
BHT[d]	1	1	1	1	1
Aramid fiber	0	5	10	15	20

[a]Chloroprene Rubber(Denka Co., Ltd., Japan)

Table 3. Viscosities for Chloroprene Rubbers

Sample	A−30	A−120
Solution viscosity[a] (cps) (at 25℃)	110	810
Mooney viscosity[b]	20±3	67±5

[a]10% toluene solution viscosity measured by Brookfield viscometer
[b]$MS_{2+2.5}$(100℃)

RESULTS AND DISCUSSION

A basic problem in mixing CR stocks, especially the sulfur modified ones, is the prevention of scorch. typical rheographs of the CR rubber mixes are shown for mixes A_1−A_5(Fig. 1). As expected, the unreinforced mix(A_1) does not show maximum torque, and the torque value increases with fiber concentration. Increase in torque with fiber loading is generally observed, and increase

in scorch time up to 20 wt% fiber loadig was reported for silk fiber reinforced natural rubber composites.[2]

Physical properties of mixes A_1-A_5 are shown in Figs(Figs. 2~5). Hardness and wear strength (Fig. 2) increases and decreases as the fiber concentration increases. Hardness increases rapidly at lower concentration and slowly at higher concentration. Exactly the same decreasing tendency is true for wear strength.

Fig. 3 shows the tensile strength of the vulcaniz ates both in L and T directions. Tensile strength in L direction is minimum at 10 wt% loading and the critical fiber loding is found at 15~20 wt% fiber loading. The tensile strength in T direction drops with increase in fiber concetntration up to 10 wt% loading, and beyond that, the value remains almost constant. The results are similar to those of other fiber by other investigators.[2, 13, 14] Apparently at low fiber concentration, anisotropy in tensile property is not observable. Sometimes measurements of secant modulus provided clear distinction between the two directions.[2]

Notably, the difference in tensile strength between the two directions becomes apparent at high fiber loading. The results obtained in this experiment generally follow earlier findings[8,9] and theoretical predictions.[3,10,11] At lower concentration, there are not enough fibers to control matrix elongation, and fibers would be subjected to high strains with only small loads and break.[3] Therefore, the composite strengths could be lower than that of matrix. In literature[3], the fiber loading at which the composite strength are minimum and equal to matrix value are respectively referred to as minimum and critical concentrations. A value of critical fiber loading of 10 wt % was also reported,[9] and for fiber loading below the critical value, the composite strength is controlled by the matrix properties.

In T direction, fibers do not act as load carrier, and merely act as an hard inclusion.[11] Failure mode in T directon, in laminar form, was found to be brittle fracture.[12] This implies that the tensile properties of composites would be lowered by fiber addition, as our results indicate.

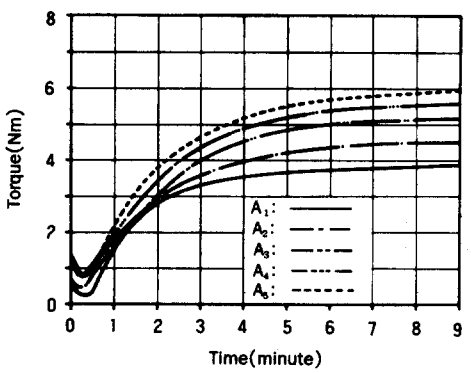

Fig. 1. Rheographs for series A.

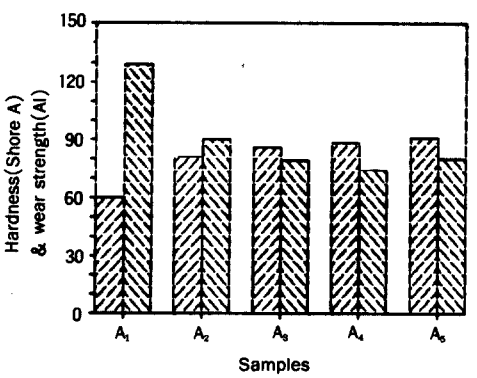

Fig. 2. Hardness(▨) and wear strength(▧) for series A.

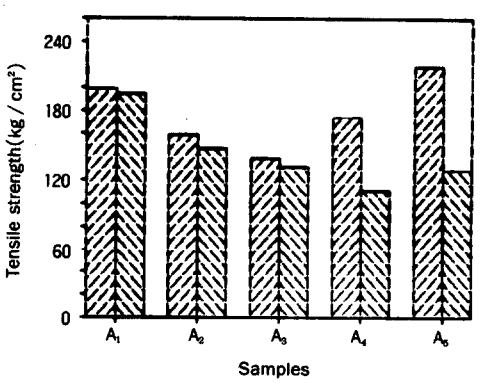

Fig. 3. Tensile strength for series A: L direction(▨); T direction(▧).

Fig. 4 shows the tear strength of the vulcaniz ates. Tear sterngth increases monotonically with fiber concentration in L direction. The tear strength in T direction increases rapidly up to 5 % loading, however, the value remains almost constant beyond this. Generally, the tear strength increases in the presence of fiber[3] and is also, more or less, affected by the addition of carbon black.[13] Fiber and carbon black increase the tear strength by obstructing the tear path and preventing it from proceeding in a straight path. It is generally agreed that the tear strength increases with fiber loading at low concentration, say up to 5 wt %. However, the effect at high concen tration is conflicting. Tear propagates along the fiber direction in transversely prepared sample, and perpendicular to the fiber direction in longitudinally oriented sample.[11] At high concentration, strain amplification between closely packed fibers can promote tearing parallel to the fiber direction in transversely oriented sample, and can reduce tear strength below the strength of matrix. The present results in T direction do not exactly confirm this. The reason is probably due to the imperfect orientation of the fiber, the case usually encountered in mixing to prevent serious fiber breakage.

Elongation at break is shown in Fig. 5. Elongation at break for the longitudinally oriented fibers drops almost linearly up to 15 wt % loading,

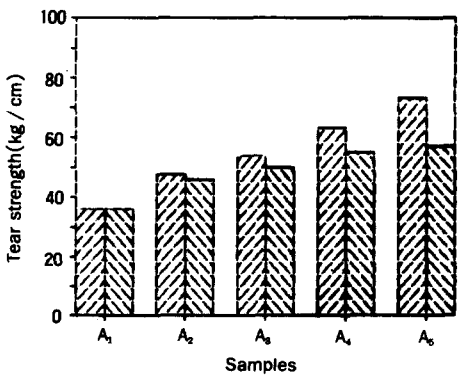

Fig. 4. Tear strength for series A:L direction(▨):T direction(▧).

followed by a drastic drop down to 60 %. Similar tendency is observed for transversely oriented fiber, however, the value is higher than that of longitudinally oriented fibers. When the variations of tensile strength and elongation at break are put together, it seems that the fiber can reinforce the rubber when the fiber concentration exceeds 15 wt %, for the particular systems considered in our experiments.

Heat buildup, cased by cyclic compression, is of a practical limit to use fiber reinforced rubber. Considerable heat buildup due to fiber addition over 10 wt % has been reported.[14] In the present experiments, heat buildup gradually increases with fiber loading both in L and T directions(Table 4). Though marginal, heat buildup in T direction is slightly higher than that of L direction, due probably to the flexible nature of armid. Essentially the same thermal anisotropy was reported for silk fiber reinforced natural rubber,[2] and for further details concerning the mechanism the reader is referred to ref. 2.

Compression set in both directions increases with the increase in fiber loading, rapidly at lower

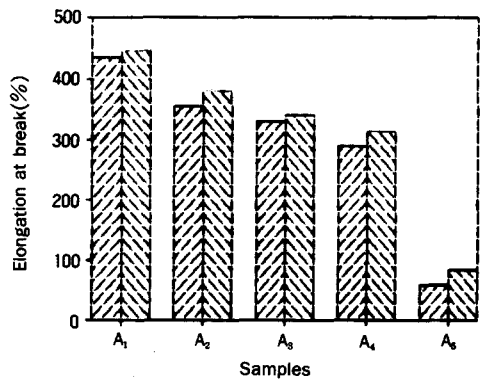

Fig. 5. Elongation at break for series A:L direction (▨):T direction(▧).

Table 4. Heat Bulidup* for Series A

Sample Code	A_1	A_2	A_3	A_4	A_5
L Direction	15.4	20.5	22.6	23.7	25.5
T Direction	16.1	21.2	23.1	24.3	26.4

* unit: ℃

concentration and asymptotically at higher concentration (Table 5). Following Setua and De,[2] compression set in T direction is less, in general, compared to that of L direction. The disagreement is probably due to the different experimental set up i. e., at constant stress by Setua and De, and at constant strain, presently.

The effect of matrix strength or viscosity on the physical property of short fiber reinforced rubber composite has been examined. For this, CR rubber in series A has been replaced by one having larger molecular weight(B_1-B_5) leading to higher viscosity and sterngth(Table 3).

Fig. 6 shows the hardness and wear strength of mixes, B_1-B_5. Hardness gradually increases with fiber concentration like in serires A. Tensile strength of mixes B(Fig. 7) in L direction shows minimum at 10 wt% loading like in mixes A. However, the critical fiber loding for mixes B should be higher than 20 wt%, and also higher than that of mixes A(15~20 wt%). Similar trend is observed for tensile strength in T direction. In mixes A, the minimum strength was found at 15 wt% loading, however for mixes B the tensile strength of mix B_1(unreinforced) is larger than that of mix A_1(unreiforced) by approximately 10%(Fig. 3 and 7) i. e., rubber matrix for mixes B is stronger than that of mixes A. Then, it seems true that fiber reinforcement is more effective with less stronger matrix, at least, for the particular composites considered here.

Elongation at break(Fig. 8) assures the above strength behavior. In mixes A, elongation at break showed monotonic decrease with fiber concentration up to 15 wt% loading followed by a sharp drop at 20 wt%. However, elongation at break for series B, in both directions, is almost constant up to 15 wt% fiber loading. At 20 wt% loading, elongation at break in L drection drops sharply down to 68% from 360%, indicative of certain reinforcement set up. Still almost constant

Table 5. Compression Set* for Series A

Sample Code	A_1	A_2	A_3	A_4	A_5
L Direction	48.2	63.0	74.3	72.5	75.7
T Direction	49.7	64.1	75.7	75.5	76.1

* unit: %

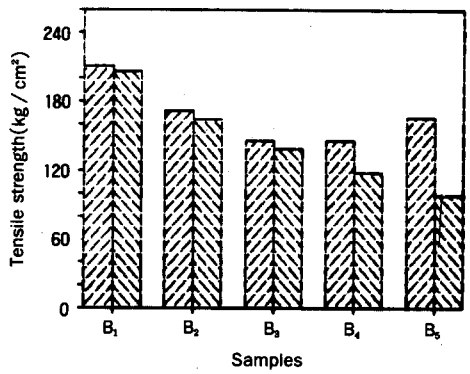

Fig. 7. Tensile strength for series B:L direction(▨): T direction(▧).

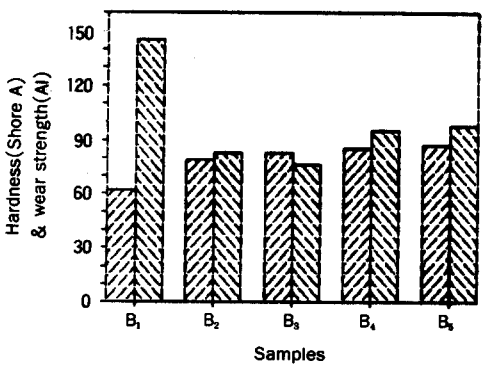

Fig. 6. Hardness(▨) and wear strength(▧) for series B.

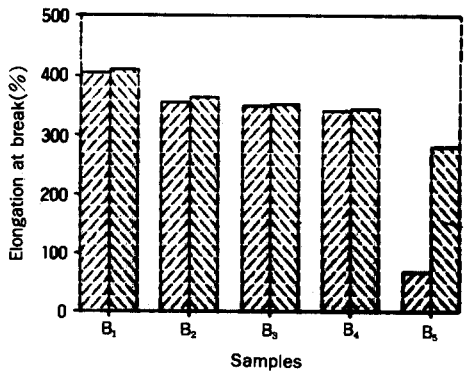

Fig. 8. Elongation at break for series B:L direction (▨):T direction(▧).

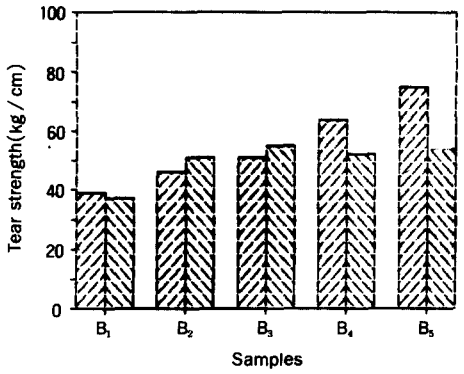

Fig. 9. Tear strength for series B: L direction(▨): T direction(▧).

value for T direction at this concentration is consistent with the continuous decrease in tensile strength.

Tear strength for mixes B is given in Fig. 9. Up to 10 wt % loading, tear strength in T direction is higher than in L direction, beyond that, the tendency is reversed. Alternatively, this means that the tear strength in T direction does not increase with fiber loading over 10 wt %. That is, the strain amplication of matrix leading to interfacial crack seems more feasible with more viscous matrix.[15]

The effect of aramid reinforcement on CR rubber was more pronounced with less viscous and less strong rubber matrix. That is, the critical fiber loading for reinforcement was lower for mixes A than for mixes B.

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