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CR/NBR 블렌드의 단섬유 강화 복합재료 : 2. 복합재료의 물리적 성질, 열노화 및 내유특성

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Short Fiber Reinforced CR/NBR Blends : 2. Physical Properties, Aging and Oil Resistance of the Composite

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요 약 : roll mill을 사용하여 CR/NBR(25/75 wt%) 블렌드에 aramid 단섬유(3 mm)를 25 wt%까지 충전하면서 섬유함량에 따른 복합재료의 물성을 측정하였다. scorch 시간, 최적가류시간, 탄성율 및 강도의 이방성은 섬유 함량과 더불어 증가하였다. 마모저항, compression set 및 발열 역시 섬유함량과 더불어 증가하는 경향을 보였으나 고농도에서는 거의 일정하게 유지되었다. 노화 실험후에는 섬유첨가 효과와 이방성이 감소되었으며, 용매 팽윤은 섬유함량 증가와 더불어 전반적으로 감소하는 경향을 보였다.

Abstract : CR(chloroprene rubber)/NBR(nitrile rubber)(25/75 by weight) blend was reinforced with surface treated short aramid fibers(3 mm) using an open mill, and effects of fiber loading were examined. Scorch and optimum cure times were increased with increasing fiber loading. Anisotropy in tensile modulus and strength was pronounced as the fiber loading increased, indicative of effective fiber alignment at high concentration. Abrasion resistance, compression set, and heat buildup were increased rapidly at low loading, and were kept almost constant at high loading. Upon aging, effect of fiber loading and modulus anisotropy became less pronounced due presumably to the post cure during aging test. Solvent swelling was reduced with fiber loading, especially at > 15%.

INTRODUCTION

Reinforcement of rubber with short fiber combines the rigidity of fiber with the elasticity of rubber,[1] and the composites are of great interest in many industrial applications. Notably, such applications include the production of hose, V-belt, tire, and complex shaped mechanical parts.[2~4]

Though it is not possible to attain the strengthening level of continuous fibers, short fiber reinfor-

cement takes the advantage of processing, i.e., fibers can be incorporated, as one of the ingredients of rubber formulation, with rubber during the mixing process. The orientation of fibers is achieved along the direction of cylinder rotation in roll mill operation.[1]

In order to obtain adequate reinforcement, uniform distribution/orientation of fibers in rubber matrix, adequate interfacial bonding, and preservation of an appropriate aspect ratio were of the major concerns.[3~7] Various fibers have in the past been incorporated with natural and synthetic rubbers. However, studies on aramid fiber reinforced rubbers, especially for rubber blends, are rare in the open literature.

This paper considers the short aramid fiber(3 mm in length) reinforced CR/NBR(25/75) blend. Fiber loadings up to 25 wt% were prepared in a laboratory roll mill. Mechanical properties, both in longitudinal(L) and transverse(T) directions, and heat buildup of the vulcanized composites were measured. Aging and oil resistance properties of the composites were also determined.

EXPERIMENTAL

Formulations of the rubber mix used in the experiment are given in Table 1. CR(Toyosoda R-10, NBR(Nipol P-70), and first grade of other ingredients were used without further treatments.

Compounding was done using a roll mill(150×330 mm) following the polymer blending technology.[8] Namely, the component rubbers were first blended, followed by adding the ingredients to the blend. CR latex treated short aramid fiber(Du Pont, 6F517) were incorporated at the last stage of compounding to minimize the breakage. It was observed that the fiber orientation was mostly obtained during the first several passages in roll mill operation. Oil resistance test was done in ASTM # 3 oil for 70 hrs at 100℃, whereas aging was done at 70℃ for 96 hrs. Other tests including tensile, tear, abrasion, hardness, heat buildup etc. were made following the procedures described in our earlier report.[9]

Table 1. Formulations of Rubber Mixes

Sample Code	A	B	C	D	E	F
CR/NBR[a] (25/75 by weight)	100	100	100	100	100	100
Kevlar[b]	0	5	10	15	20	25
Stearic Acid	1	1	1	1	1	1
PA[c]	2	2	2	2	2	2
MgO[d]	1	1	1	1	1	1
SRF[e]	75	75	75	75	75	75
A#2[f]	15	15	15	15	15	15
ZnO	5	5	5	5	5	5
Na_{22}[g]	0.25	0.25	0.25	0.25	0.25	0.25
DM[h]	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	1.0	1.0	1.0	1.0	1.0	1.0

[a] chloroprene rubber(CR), Toyosoda, R-10
nitrile rubber(NBR), Nipol, P-70
[b] surface treated short aramid fiber(3 mm)
[c] antioxidant
[d] vulcanizing agent
[e] semi reinforcing furnace carbon
[f] aromatic oil, processing agent
[g] accelerator
[h] dibenzothiazyl disulfide accelerator

RESULTS AND DISCUSSION

Cure Behavior

Cure behavior of the blend composite, determined from Curastometer and Rheometer, is given in Tables 2 and 3. Viscosity and maximum torque of the composites at low fiber loadings($\leq 10\%$) are slightly lower as compared to fiber-free control, and higher at high fiber loadings. Reduction of viscosity at low concentration probably indicates relatively poor interfacial adhesion at elevated temperature leading to interfacial slippage.[10] However, as the fiber loading is increased, viscosity would increase as a bulk property.[11]

Scorch time(T_{s1}) of the composite, regardless of concentration, is longer than that of fiber-free control, and the optimum cure time(T_c) increases with the increase of fiber loading. The retarded

Table 2. Cure Characteristics of the Blend Composite (Curastometer Data)

	A	B	C	D	E	F
MV[a](dN · m)	8	6	6	10	8	8
MT[b](dN · m)	48	46	46	56	54	60
T_{10}[c](min : sec)	1 : 10	1 : 30	1 : 30	1 : 30	1 : 40	1 : 30
T_{90}[e](min : sec)	2 : 00	2 : 20	2 : 20	2 : 20	2 : 30	2 : 20
CR[e](min : sec)	0 : 50	0 : 50	0 : 50	0 : 50	0 : 50	0 : 50
ML_{1+4}(100℃)[f] (dN · m)	98	91	92	107	112	119

[a] minimum viscosity
[b] maximum torque
[c] time for torque = 0.1 × maximum torque
[d] time for torque = 0.9 × maximum torque
[e] cure rate
[f] Mooney viscosity

Table 3. Cure Characteristics of the Blend Composite (Rheometer Data)

	A	B	C	D	E	F
ML[a](dN · m)	10.5	9.5	9.5	11.0	11.5	12.5
T_{s1}[b](min : sec)	1 : 36	2 : 10	2 : 30	2 : 20	2 : 30	2 : 23
$T_c(90)$[c] (min : sec)	3 : 07	4 : 25	4 : 50	5 : 25	5 : 35	5 : 35
MH[d](dN · m)	44	43.5	43.5	47.5	47.5	51.5

[a] Mooney viscosity low
[b] scorch time
[c] optimum cure time
[d] Mooney viscosity high

rate of cure is perhaps due to the increased viscosity at high concentrations.

Physical Properties

Hardness(Fig. 1) and modulus(Table 4) of the composites increase with increasing fiber concentration. Modulus in L-direction, except 5% loading, is approximately one order of magnitude higher than that of T-direction. A significant anisotropy of modulus is achieved, indicating sufficient fiber orientation.

Tensile strength in L-direction(Fig. 2) increases with fiber loading, and slightly decreases in T-direction(Fig. 3). Dilution effect often observed in hybrid composite and fiber reinforced rubber is

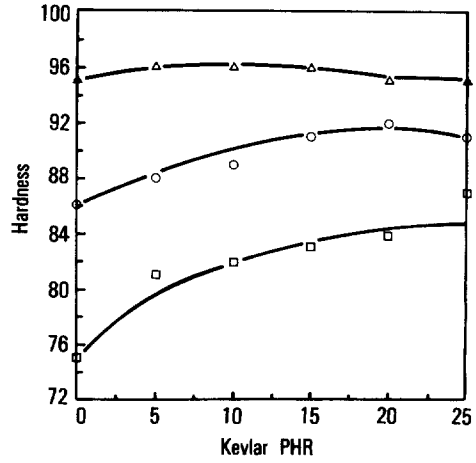

Fig. 1. Hardness vs. fiber loading for virgin(○), after aging(△), and immersion in oil(□).

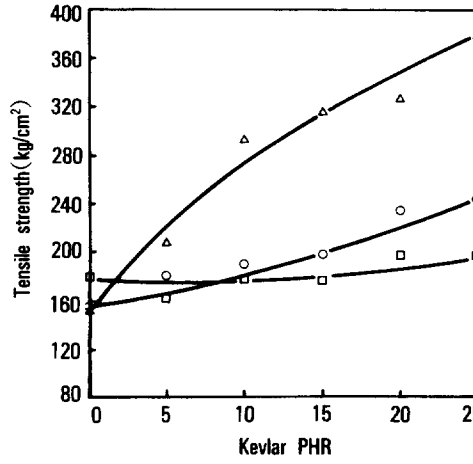

Fig. 2. Longitudinal tensile strength vs. fiber loading : same symbol with Fig. 1.

not seen.[12,13] It is obvious that the anisotropy in tensile properties becomes significant as the fiber loading increases. This clearly indicates that the fiber orientation is more feasible at high concentration, as observed by earlier investigators.[10]

Elongation at break of the composites(Figs. 4 and 5) drops drastically with the addition of fibers at 5% loading in T-direction, and up to 10% in L-direction, beyond which the drops are not sharp in both directions. At low fiber loading, anisotropy in elongation at break is not significant, like in modu-

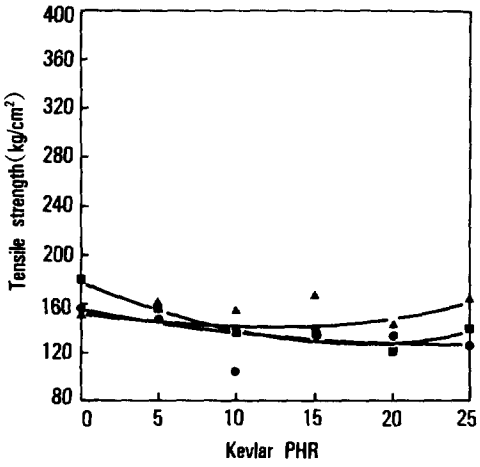

Fig. 3. Transverse tensile strength vs. fiber loading for virgin(●), after aging(▲), and immersion in oil (■).

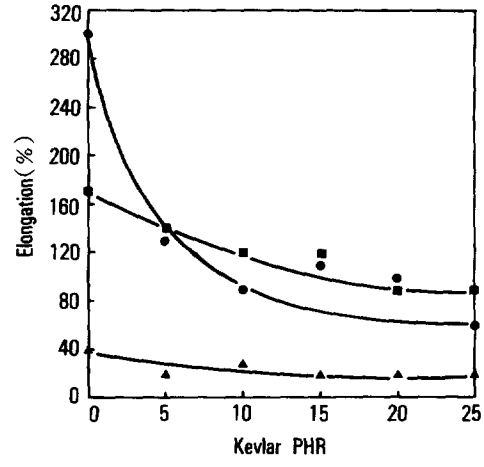

Fig. 5. Transverse elongation at break vs. fiber loading : same symbol with Fig. 3.

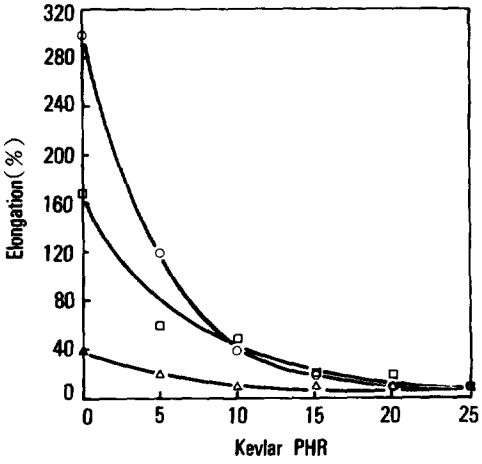

Fig. 4. Longitudinal elongation at break vs. fiber loading : same symbol with Fig. 1.

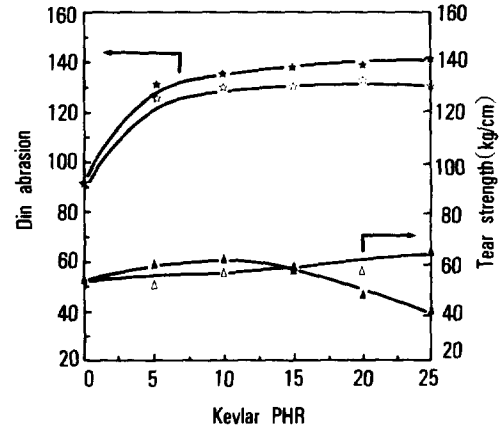

Fig. 6. Abrasion and tear strength vs. fiber loading in longitudinal(☆ and △) and transverse(★ and ▲) directions.

lus and strength. However, at high fiber loadings, the anisotropy becomes also significant, i.e., elongation at break in T-direction is approx. 4 times of L-direction.

Tear strength(Fig. 6) gradually increases with fiber addition. Up to 15% loading, tear strength in L-direction increases to a less extent compared to that in T-direction.[10] Beyond 15% loading, tear strength in T-direction decreases, and the anisotropy effect is produced. Following the literatures,[3,4,7] tear strength increases with fiber loading by obstracting the tear path and preventing it from proceeding in a straight path. However, at high fiber loading, strain amplification between closely packed fibers can promote tearing parallel to the fiber directon. Tear path is parallel to the transversely oriented fiber, and perpendicular to the longitudinally oriented fiber, and hence the observed results would occur.

Din abrasion resistance(Fig. 6) shows a rapid in-

creases with 5% fiber loading and is kept almost constant beyond that concentration with no significant anisotropy. Qualitatively, the result is in agreement with short silk fiber reinforced natural rubber, reported by Setua and DE.[10]

Compression set(Fig. 7) in both directions increases with the increase in fiber loading up to 10 %, beyond which it remains almost constant, and the compression set in L-direction is higher than in T-direction due probably to the buckling in L-direction.[14]

Heat buildup(Fig. 8) increases with the increase of fiber loading, rapidly at low($\leq$ 10%), and slowly at high concentration. The extent of heat generated by cyclic compression in the Goodrich Flexometer depends on the interactions between rubber and fibers, but the fiber length has no significant effect.[7,10] In general, heat buildup becomes significant above 10 phr loading.[10]

Hardness(Fig. 9) and compression set(Fig. 10), respectively increases and decreases upon cyclic compression in the Flexometer, and the property change increases with the increase of fiber loading, more in L-direction and less in T-direction. With fibers oriented perpendicular to the compression stroke, fibers would subject to recoil and buckling leading to breakage and debonding from the matrix.[14,15] The result is to lose the elasticity of the composite.

Aging and Oil Resistance

Hardness of the fiber-free blend increases upon aging and decreases after immersion in oil(Fig. 1). With fiber loading, hardening is retarded during the aging test, keeping essentially the same value with fiber-free blend, and increases in oil with the increase of fiber concentration. These results imply that the reinforcement is more pronounced

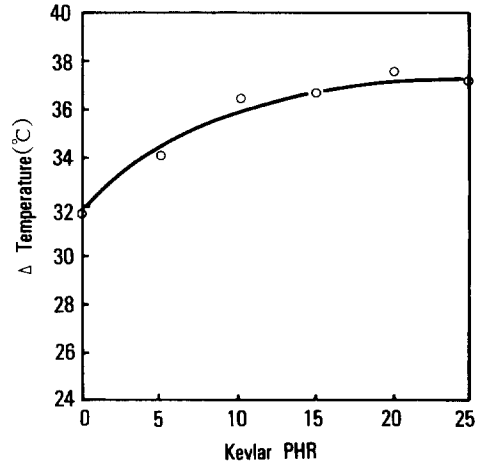

Fig. 8. Heat buildup vs. fiber loading in longitudinal direction.

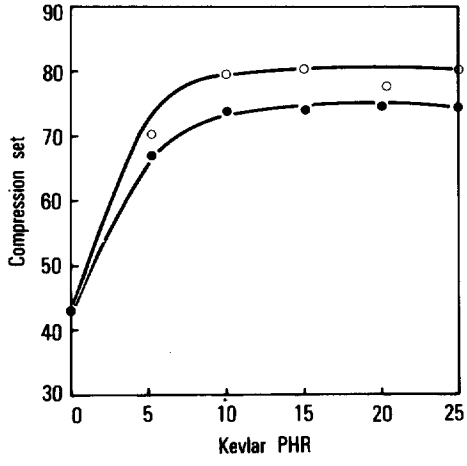

Fig. 7. Compression set vs. fiber loading in longitudinal(○) and transverse(●) directions.

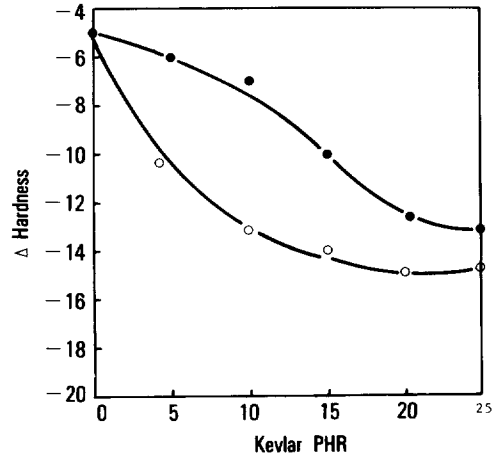

Fig. 9. Hardness change upon heat buildup test : longitudinal(○) and transverse(●) directions.

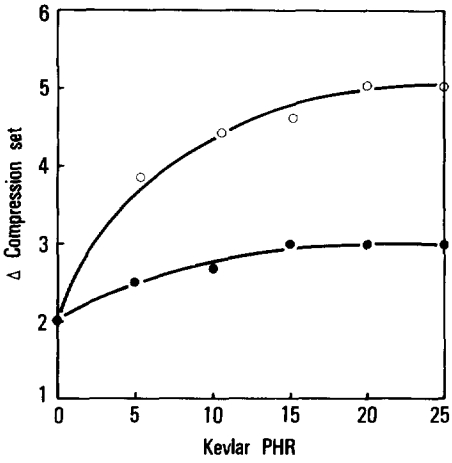

Fig. 10. Compression set change upon heat buildup test : longitudinal(○) and transverse(●) directions.

with week matrix.

Modulus(Table 4), both in L- and T-directions, is increased upon aging, however, is almost independent of the level of fiber loading. Upon immersion in oil, modulus in L-direction increases at 5% loading, and decreases below the virgin composite level as the fiber loading increases. In T-direction, the modulus increases with fiber loading, however, is lower than that of virgin composite when compared at the same fiber loading.

The longitudinal tensile strength(Fig. 2) increases upon aging, and decreases upon immersing in oil, as compared to the virgin composites at the same fiber loading. However, the transverse tensile strength(Fig. 3) is almost independent of fiber loading, and slightly higher than that of the virgin composite. Maximum anisotropy is noted from the aged sample at the highest concentration(25%).

Elongation at break(Figs. 4 and 5) of the fiber-free control is significantly reduced upon aging treatment, and is almost independent of the level of fiber loading. Upon immersion in oil, elongation at break of the fiber-free control is reduced to about half, and decreases as the fiber loading increases.

When the above aging properties are combined together, it seems that cure proceeds during the aging test. With post cure, rubber matrix becomes

Table 4. Modulus of the Blend Composite(kg/cm^2) : (a) Longitudinal

		A	B	C	D	E	F
	5%		27	153	125	170	226
Before	10%		47	170	165	228	–
Aging	20%		104	185	–	–	–
	100%	128	176	–	–	–	–
After Aging	5%		–	280	281	285	297
After	5%		109	102	70	95	82
Oil	10%		132	129	119	157	–
Resist.	20%		–	156	–	–	–

(b) Transverse

		A	B	C	D	E	F
	5%		17.5	21	26	30	40
Before	10%		18.3	27	34	38	53
Aging	20%		38	39	52	51	73
	100%	128	130	–	125	–	–
After	5%		115	89	105	93	110
Aging	10%		147	114	127	112	132
	20%		–	149	–	–	–
After	5%		13	13	17	17	20
Oil	10%		19	17	27	30	30
Resist.	20%		31	30	41	39	40
	100%		123	115	128	–	–

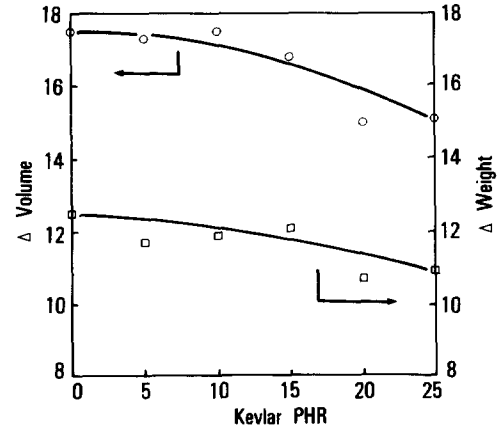

Fig. 11. Volume(Δ V) and weight(Δ W) increase upon immersion in oil (ASTM #3 oil, 100℃, 70 hrs).

hard and rigid. As the matrix becomes rigid, fiber reinforcement becomes less effective, i.e., the effect of fiber loading and anisotropy become less pronounced compared to the virgin composite.

Reduced hardness, modulus in general, and strength in L-direction upon immersing in oil directly come from the penetration of oil into matrix. In swelled composite, interfacial stress acting perpendicular to the fiber surface should increase,[16] and this would give slightly higher tensile strength in T-direction over the virgin composite. The compression effect would also give plausible explanation on the effect of fiber loading on transverse modulus. That is, as the fiber loading is increased, the effect should pronounced.

Volume and weight increase upon immersing in oil(Fig. 11). However the degree of increase is reduced with the increase of fiber loading.

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REFERENCES

1. L. Ibarra and C. Chamorro, *J. Appl. Polym. Sci.*, **37**, 1197 (1989).
2. S. Yamamoto, *J. Jap. Inst. Rubber Tech.*, **60**, 12 (1987).
3. D. K. Setua and S. K. DE, *J. Mat'l. Sci.*, **19**, 983 (1984).
4. L. A. Goettler, R. I. Lieb, and A. J. Lambright, *Rubber Chem. Tech.*, **52**, 838 (1979).
5. A. Y. Coran, K. Boustany, and P. Hamed, *ibid*, **45**, 396 (1974).
6. G. C. Derringer, *J. Elastoplast.*, **3**, 230 (1971).
7. A. P. Foldi, *Rubber Chem. Tech.*, **49**, 379 (1976).
8. Denka Technical Report #66, Denka, 1969.
9. C. K. Kang and B. K. Kim, *Polymer(Korea)*, **15**, 459 (1991).
10. D. K. Setua and S. K. DE, *Rubber Chem. Tech.*, **56**, 808 (1983).
11. "Rubber Technology and Manufacture"(C. M. Blow and C. Hepburn eds.) Chaps 7 and 8, Butterworth Scientific, London, 1982.
12. S. K. Chakraborty, D. K. Setua, and S. K. DE, *Rubber Chem. Tech.*, **55**, 1286 (1982).
13. D. C. Blackley, "Synthetic Rubbers", Applied Science, New York, 1983.
14. P. K. Mallick, "Fiber Reinforced Composites", Marcel Dekker, New York, 1988.
15. V. M. Murty, S. K. DE, S. S. Bhagawan, R. Sivaramakrishnan, and S. K. Athithan, *J. Appl. Polym. Sci.*, **28**, 3485 (1983).
16. R. M. Jonse, "Mechanics of Composite Materials", McGraw Hill, New York, 1975.