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나일론 단섬유 강화 스티렌-부타디엔 고무

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Short Nylon Fiber Reinforced Styrene-Butadiene Rubber

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요 약 : V-Belt제조에 이용할 목적으로 나일론 단섬유 강화(16wt%) styrene-butadiene고무(SBR) 복합재료를 제조, 이들의 가황특성 및 복합재료의 형태학적, 기계적 특성을 측정하였다. 아울러 복합재료를 70C에서 96시간 노화시켜, 복합재료의 노화로 인한 물성변화를 검토하였다. 본 실험에서 얻어진 결과는 대체로 섬유표면처리효과로 설명할 수 있었으며, nylon/SBR계의 경우 resorcinol-formaldehyde-latex(RFL)계 표면처리가 효과적임을 알 수 있었다.

Abstract : Short nylon fiber reinforced(16wt%) styrene-butadiene rubber composites were prepared for V-Belt application. Cure characteristic, morphological and mechanical properties of the composites were subsequently measured both in longitudinal and transverse directions. In addition, the retention of the mechanical properties after ageing for 96 hrs at 70C, was also determined. The results obtained in these experiments were interpreted in terms of fiber surface treatment, and it was found that resorcinol-formaldehyde-latex(RFL) was effective adhesion system for nylon/SBR composites.

INTRODUCTION

Short fiber reinforced rubber composites have become very popular due mainly to their processing advantages and technical properties such as strength, stiffness, modulus and damping.[1] Works in this area of study up to 1981 were extensively reviewed by Goettler and Shen,[2] and most recently by Yamamoto.[3] The major applications of short fiber reinforced rubber find in the production of hoses and V-Belts.[4~6] Depending on the specific purpose of fiber reinforcement, fiber would or would not reinforce the matrix strength, and simply gives improved power transmission, stiffness and abrasion resistance.[3] This paper considers short nylon(nylon-6) fiber reinforced styrene-butadiene rubber (SBR) with a specific application for V-Belt production. Therefore, a brief description and function of short fiber reinforced element in V-Belt should be given here to relate the purpose of this paper.

The conventional V-Belt is shown in Fig. 1(a), where the polyester cable cords act as tension layer and carry most of the load. The body of V-

belt is wrapped with cotton to protect the tension member as well as the compression rubber. Improvement over the conventional wrapped V-Belt is the so called raw edge V-Belt(Fig. 1(b)). In raw edge V-Belt, the body of belt is no longer wrapped with cotton and hence more tension members can be imbeded, and therefore carry more loads over the conventional velts. Instead the compression rubber is reinforced with short fibers. In addition, due to the difference in manufacturing processes between the two types of belt, the elongation at break is reduced in raw edge V-Belt.[7]

The prime purpose of short fiber reinforced rubber for V-Belt finds in the efficiency of power transmission, from driver to driven pulley. Power transmission occurs via friction between pulley and belt. Friction coefficient in cotton fabric-pulley combination is approximately 0.2~0.25, whereas that in short fiber reinforced rubber-pully is approximately 0.3~0.35. Therefore, the efficiency of power transmission is greatly improved in raw-edge V-Belt together with the abrasion resistance. However, the heat buildup is more in the raw edge type due to higher friction, and this actually imposes the limitation of short fiber reinforcement.

Typically, compression rubber in V-Belt has been prepared from chloroprene rubber(CR) due mainly to its high heat resistance. This paper considers the use of SBR composites, instead of CR, to reduce the production cost of V-Belt. At a specific fiber loading(16 wt%), effects of fiber surface treatment on physical properties of the composites were examined, and the use of short nylon fiber reinforced SBR for compression rubber was positively considered.

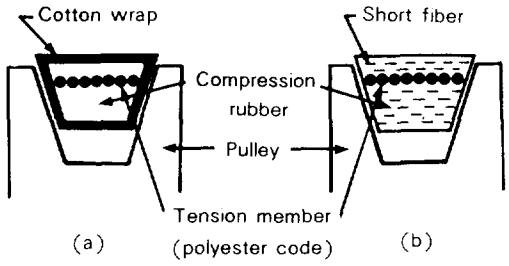

Fig. 1. Cross section of V-Belt ; (a) wrapped V-Belt, (b) raw edge V-Belt.

EXPERIMENTAL

Materials and Fiber Surface Treatment

Basic formulations of the rubber mix used in these experiments are given in Table 1. Commercial grade SBR(styrene content ; 23.5%, sp.gr. ; 0.93, Kumho SBR1502) and nylon fibers chopped to 4~6 mm (Tongyang Nylon, tire cord grade, dia= 1.2mm) as received were used for compounding. Technical grades of other ingredients, as footnoted in Table 1, were used without further treatment. In the table, mix A is unreinforced, mix B is reinforced by untreated nylon, and mix C is reinforced by surface treated nylon, respectively. For mix C, nylon was precipitated in resorcinol-formaldehyde-latex(RFL) solution. For the improvement of compatibility with SBR matrix, styrene-co-butadine

Table 1. Formulations of Rubber Mix

Sample Code	A	B	C
Coupling Agent[a]	–	–	RFL
SBR 1502[b]	100	100	100
Nylon[c]	–	16	16
Stearic Acid	2	2	2
ZnO	5	5	5
3C[d]	2	2	2
HAF[e]	50	50	50
DM[f]	1.5	1.5	1.5
Sulfur	2	2	2
Total PHR	162.5	178.5	178.5

A : unreinforced SBR
B : untreated short fiber-reinforced SBR
C : treated short fiber-reinforced SBR
[a] RFL(Resorcinol Formaldehyde SB-Latex)
[b] styrene content 23.5%, specific gravity 0.93, Kumho
[c] chopped fiber, tire cord grade, Tongyang Nylon
[d] N-isopropyl-N'-phenyl-P-phenylenediamine, antioxidant, Sumitomo
[e] High Abrasion Furnace Carbon
[f] Dibenzothiazyl Disulfide Accelerator

(SB) latex was used in the preparation of RFL.

Mixing

Mixing operation was carried out on a laboratory open mill(150×330mm) at 100±5℃. To achieve better wetting of the ingredients with rubber, we lowered the plasticity of rubber by means of mastication of SBR for 25min on a tight mill prior to the addition of other ingredients.[8] At this stage the nip gap was 1.5mm, and the ratio of roll speed was 1 : 1.20.

For mix B and C, nylon fibers were subsequently fed, evenly spreaded on the rubber sheet for better dispersion. The orientation of fibers during mixing is obtained by shearing action.[9~11] On the other hand, the shearing is controlled by the ratio of roll speed and nip gap.[12~14] Higher speed ratio and close nip gap should give more orientation but undoubtedly subject to more breakage of the fibers.[10~12] In this experiment, the ratio of roll speed and nip gap were respectively kept at 1 : 1.25 and 3mm.

After the fiber orientation is accomplished, other ingredients were added. Also, sulfur and DM(Dibenzothiazyl Disulfide), to avoid scorching, were added at the last stage of mixing. It should be mentioned that homogeneous mixing was not successfully done for mix B(untreated fiber reinforced SBR) with basic formulations, and hence a small amount of lubricant(naphthalic oil) and tackifier(petro resin) was additionally added. Surfaces of the sheets were still seriously distored. Therefore, samples for mix B were also prepared by using a Banbury for curing.

Curing

The rubber mix was vulcanized at 155℃. Optimum cure time at 155℃ was determined by using a Rheometer(Monsanto R-100). Cure Characteristics including Mooney viscosities, ML_{1+4}(100℃), are summarized in Table 2.

Morphology

Fiber orientation, dispersion and adhesion to the rubber matrix were observed from scanning electron microscopy(SEM). Fracture surfaces were prepared in liquid nitrogen, and sputtered with gold before viewing.

Table 2. Cure Characteristics of the Rubber Mix

	ML_{1-4}(100℃)[a] (dN·m)	ML[b] (dN·m)	Ts1[c] (min)	Tc(90)[d] (min)	MH[e] (dN·m)
A	62	12	3 : 00	12 : 15	50
B	138	21	1 : 00	11 : 15	48
C	112	14	1 : 15	9 : 15	51

[a] : Mooney viscosity
[b] : Mooney viscosity low
[c] : time for torque=0.1×Maximum torque
[d] : time for torque=0.9×Maximum torque
[e] : Mooney viscosity high

Mechanical Properties

Tensile and tear strength of the vulcanizates was measured by using a Instron tensile tester, following the standard procedures described in ASTM(D 412-51T, and D624-54, respectively). The crosshead speed was 500± 25 and 50mm/min respectively. Abrasion and Shore A hardness were obtained following the NBS(KSM 6518) and ASTM D676-52T procedures, respectively. All of the above tests were done at room temperature. Heat buildup was determined from a rubber cylinder(12.7mm(dia)×25.4mm(height)) at 100℃, 1800rpm, 8.75% stroke for 25min. The compression set(KSM 6581) was determined on a disk sample (12.7mm(thickness)×28.7mm(dia)). Sample was inserted between two parallel plates, and compressed to the spacer thickness at 70℃ for 22 hrs. Sample was released and then thickness(t_1) retained in 30min at room temperature was measured, and the compression set(C_s) was calculated from

$$C_s = \frac{t_0 - t_1}{t_0 - t_2} \times 100$$

where t_0 is the original thickness of the sample and t_2 is the spacer thickness.

To determine the retention of mechanical properties after ageing, tensile, tear and hardness specimens were aged for 96 hrs at 70℃ in a Blue MFG 712 air oven, and the properties were mea-

sured following the respective procedures described earlier. When it was possible, the mechanical properties were measured both in longitudinal(L) and transverse(T) directions. Other cases assumed the fiber orientation random.

RESULTS AND DISCUSSION

Fig. 2 shows the cure curves of mix prepared on a open mill. Maximum torque value of mix C, surface treated nylon reinforced, is higher than that of mix A(unreinforced), as expected. However, the maximum torque of mix B, where bonding agents are absent and prepared in the open mill, is lower than that of mix A. This, in part, is due to the addition of lubricant to mix B in mill operation but mostly caused by the poor adhesion between fiber and matrix leading to interfacial slip.[15~18] For more information concerning the cure characteristics, the readers are referred to Table 2.

Fig. 3 and 4 show the Mooney viscosity and rheographs of the mix, where mix B was prepared in a Banbury and no lubricant was added. Reduction of scorch time is obtained with fiber reinforcement. Like in Fig. 2, the maximun torque is in the order of mix B < mix A < mix C implying that the viscosity of composite would be greater or smaller than that of matrix depending on the interfacial adhesion, like in inorganic filler reinforced plastics.

SEM micrographs of the composites are shown in Fig. 5. Spatial distributions as well as the orientation of the fiber are seen in Fig. 5(b) to 5(d). In L direction, fibers are imbedded perpendicular to the plane(Fig. 5(b) and (d)), whereas in T direction long cylindrical imprints, left upon fiber pullout, are clearly seen(Fig. 5(c)).

The effectiveness of fiber surface treatment is seen in Fig. 5(b) to 5(d). The fracture surface of mix B(untreated) show long strands of fiber pulled out(Fig. 5(b) and(c)). On the contrary, such pull out of fiber is much less, instead most fibers break at the fracture surface in mix C, RFL treated sample. Debonding in mix B is clearly seen in Fig. 5(e), and this phenomenon in not prominent in mix C(Fig. 5(f)).

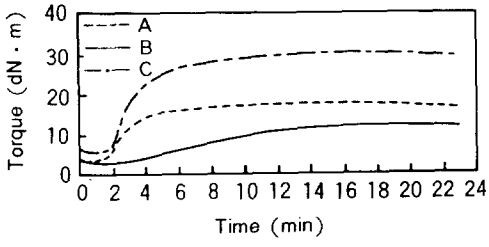

Fig. 2. Cure curves for the rubber mix.

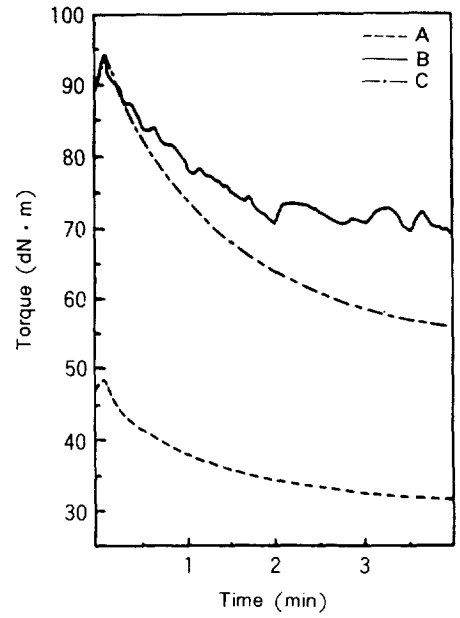

Fig. 3. Mooney viscosities for the rubber mix.

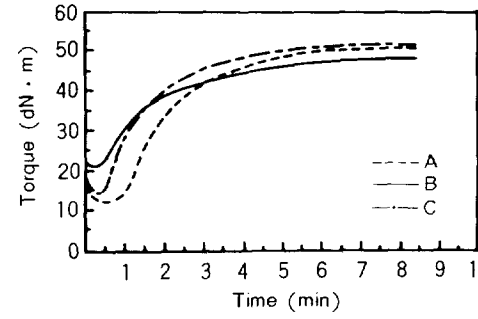

Fig. 4. Rheographs for the rubber mix.

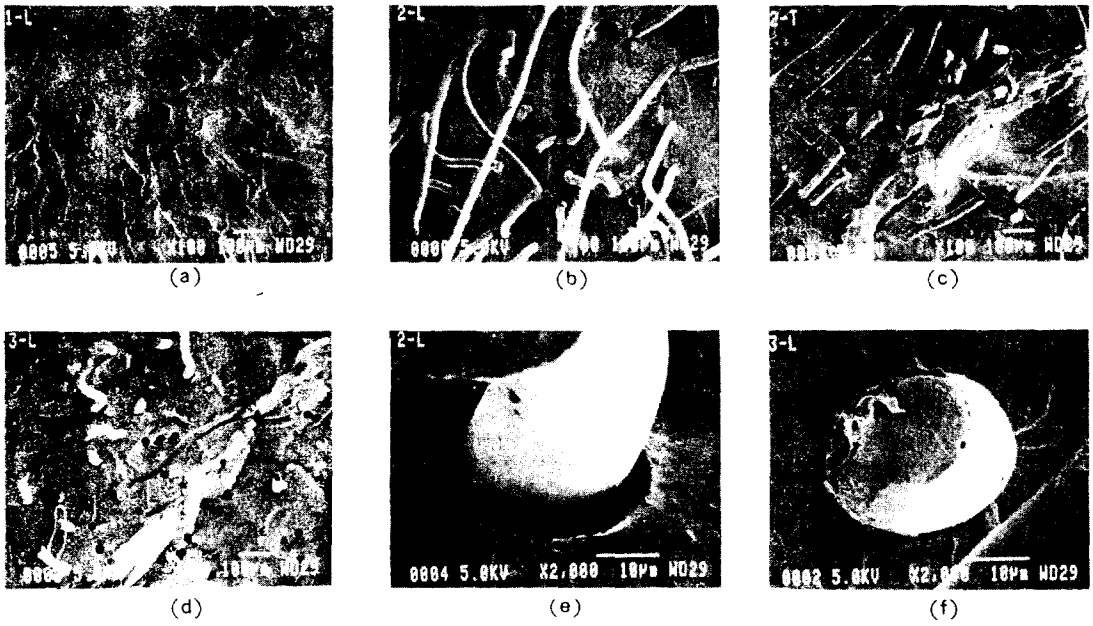

Fig. 5. SEM micrographs for the fracture surfaces : (a) SBR matrix, (b) B in L direction, (c) B in T direction, (d) C in L direction, (e) B in L direction, (f) C in L direction.

Table 3. Mechanical Properties of the Vulcanizates

		A	B		C	
			L	T	L	T
Tensile Strength (kg/cm²)		247.7	67.5	66.4	178.8	120.7
100% Modulus (kg/cm²)		31.7	43.5	23.8	–	83.65
Elongation (%)		415	590	817.5	32.5	200
Tear (kg/cm)		74.1	59.6	56.4	80.8	79.2
Hardness (Hs)*		68	65			80
Specific Gravity		1.16	1.05			1.15
DIN Abrasion		96	182	230	52	61
Compression Set(70℃, 96hr)		18.8	30.5	67.7	28	37.1
Heat Build-up (90℃×25min)	⊿T(℃)	19.1	32.5	31.1	27.5	25.9
	⊿Hd(Hs)	(−2)	(−4)	0	(−4)	(−3)
	⊿Comp. Set (70℃, 22hr)	0.94	12.01	11.36	4.23	1.60
After Ageing (70℃×96hr)	Tensile strength (kg/cm²)	225	80	–	180	123
	Elongation (%)	320	530	690	20	150
	Hardness (Hs)	70	66		86	

L : longitudinal, T : transversal, * : assumes random orientation

The mechanical properties of the vulcanizates, are tabulated in Table 3, and the stress-strain behavior is shown in Fig. 6. As expected, the initial modulus of the composite, regardless of surface

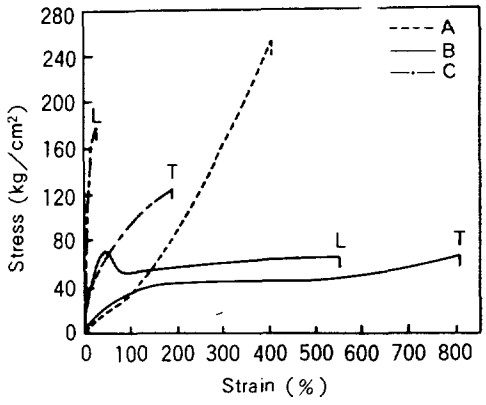

Fig. 6. Stress vs. strain curves for the vulcanizates.

treatment, is improved significantly with fiber addition(see the initial slope of stress vs. strain curves in Fig. 6).

Tensile strength of the composites, both for mixes B and C, is lower than that of matrix. This simply indicates that the fiber loading, 16 wt% in this experiment, is lower than the critical concentration. The critical concentration of fiber reinforced rubber in most cases fall in 15~20 vol%.[2] Below the critical loading, fibers do not control the matrix elongation and break with small load. This is known as the dilution effect, which often is observed in hybrid composites.[19,20]

It is obvious from the table that the tensile strength of mix C is much higher than that of mix B in both directions, indicative of improved interfacial adhesion due to the surface treatment, as was seen from the SEM micrographs. It is worth to note that the anisotropy is more pronounced with mix C(178.8/120.7) than with mix B (67.5/66.4).

Elongation at break is increased in mix B, due probably to the slippage of the fiber, and decreased in mix C, especially in L direction viz. from 415 to 32.5%. This implies that the concentration of 16 wt% should be very close to the critical concentration. It is indicated that the critical concentration is a function of bonding level, also.

Tear strength of the composite is a function of fiber loading, alignment, bonding level, and elastomeric nature of the matrix. At low fiber loading, the tear strength of composite is generally elevated.[1,2] However, at high loading of fiber, tear strength of composite is decreased below the matrix value due probably to the strain amplification of the matrix between closely packed fibers. In our experiment, the tear strength is increased in mix C, and decreased in mix B. This is again due to the improved adhesion between fiber and matrix in mix C[15], and partial slip of the fibers in mix B. In both of the composites, tear strength in L direction is higher than that of T direction. In L direction, tear propagates across the fiber, and is hindered by the fibers bridging. On the contrary, tear propagates along the fiber direction in transversely oriented sample, and fibers do not significantly disturb the tear growth.

Hardness and abrasion resistance in addition to the transverse stiffening are of most important properties in V-belt production.[7] Hardness is significantly improved in mix C, and the abrasion resistance in mix B compared to the unreinforced matrix. Notably, the abrasion resistance in T direction is higher than in L direction in both of the composites. In transversely oriented sample, more fiber surfaces are exposed to the abrader, and give more resistance to abrasion compared to the longitudinally oriented sample.

Compression set and heat buildup are inevitably increased with fiber addition to rubbery matrix, and these actually impose a limitation to apply the fiber reinforced rubber for V-belt application.[7] In both of the composites, compression set and heat buildup are increased, more in mix B and less in mix C. With more heat buildup than the unreinforced rubber, the composites lose hardness more than the unreinforced rubber through the test. The same is true for resilience.

Upon ageing the samples for 96 hrs at 70℃, tensile strength as well as the elongation at break was decreased significantly for the unreinforced rubber. However, tensile strength is slightly increased, and elongation at break is decreased in composites. Hardness is slightly increased in all of the mixes upon ageing.

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