The Effect of Compounding Ingredients on Microbial Degradation of Vulcanized Natural Rubber

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Synopsis

A series of natural rubber vulcanizates containing varied amounts of sulfur and an accelerator (N-cyclohexyl-2-benzothiazyl sulfenamide, CBS) were prepared and their resistance to attack by a strain of *Nocardia,* capable of utilizing natural rubber as carbon substrate, was examined. The higher the content of sulfur or CBS, the less the weight loss of the vulcanizates after microbial attack. In this system of curing without a filler, the rate of microbial degradation was suggested to depend on the cross-link density estimated from the swelling. Addition of calcium carbonate as a filler did not affect the microbial degradation, and in some cases slightly enhanced it. Addition of carbon black, however, made the vulcanizate apparently more resistant to microbial attack. The specimens with HAF grade carbon black loading were more resistant than those with SRF grade.

INTRODUCTION

We have isolated a strain of *Nocardia,* which grows on natural rubber as a carbon substrate, and have reported the mechanism of rubber degradation by this organism.[1] Not only unvulcanized but also various kinds of vulcanized natural rubber products were utilized by the organism to some degree. It was important to know the potential for microbial degradation from both the view point of prolongation of usage and of waste disposal problems. However, explanation of degradation test results on commercially available rubber products was difficult because the manufacturer is reluctant to disclose the details of his recipes and curing processes.

We prepare then a series of specimens with definite formulations to examine the effect of each compound on microbial attack. There have been a number of reports on microbial deterioration of rubber products, and some of them have referred to the effect of curing agent and fillers.[2] The methods employed in these degradation tests, however, were usually time consuming and inadequate for an accurate estimation of the resistance of many samples.

In this communication, *Nocardia* sp. 835A was used to examine microbial degradation of the vulcanizates under a confirmed experimental condition which gives a result with sufficient reproductivity in a relatively short time period.

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There are various kinds of rubber-degrading microorganisms with different characteristics and the different results may be obtained from the degradation test with different organisms. As reported previously, however, *Nocardia* sp. 835A was a very strong decomposer of solid rubber and was able to cause scissions of polymeric chains in natural rubber vulcanizates.[1] Consequently, the method described below was considered suitable for the comparison of a series of the vulcanizates and for the estimation of relative susceptibility of polymeric chains in the network structures.

EXPERIMENTAL

Preparation of the Vulcanizates

The formulations, cure times, and other properties of the rubber samples are shown in Tables I and II. All the mixes contained 5 phr (parts per hundred of rubber) of zinc oxide and 0.5 phr of stearic acid, varying contents of sulfur, an accelerator, and fillers. As rubber, ribbed smoked sheet RSS no. 1 was used.

TABLE I
The Compositions and Some Properties of the Vulcanizates without Fillers[a]

CBS content (phr)	Sulfur content (phr)	T_{95} (min)	Torque[e] (kgf cm)	V_r
0.2	0	60[b]	ND[d]	—[c]
	0.5	25	6	0.09
	1	24.8	9	0.15
	2	29.4	14	0.18
	3	35.0	16	0.19
	5	44.0	18	0.19
	10	120[b]	20	0.24
0.5	0	60[b]	ND	—[c]
	0.5	18	9	0.14
	1	15.4	13	0.17
	2	16.7	17	0.20
	3	19.0	20	0.23
	5	19.5	22	0.24
	10	19.0	22	0.25
1	0	60[b]	2	0.01
	1	15.3	14	0.20
	2	12.8	18	0.23
	5	11.8	24	0.26
	10	11.3	26	0.28
3	0	60[b]	ND	0.02
	1	15.5	18	0.22
	2	9.0	22	0.26
	5	7.8	33	0.31

[a] All the vulcanizates contained NR100, ZnO 5, and Stearate 0.5 (phr).
[b] The curing curve was not saturated.
[c] Dissolved in benzene.
[d] Not determined.
[e] Curelastometer tests were carried out at a stroke of ± 3°.

TABLE II
The Compositions and Some Properties of the Vulcanizates with Fillers

CBS–sulfur content (phr)	Filler content (phr)		T_{95} (min)	Torque[a] (kgf cm)	V_r	Weight loss (%)
0.5–2	Heavy $CaCO_3$	50	17	22	0.23	73 ± 13
		100	17	24	0.25	78 ± 5
	Light $CaCO_3$	50	16	24	0.23	75 ± 10
		100	14	32	0.25	97 ± 1
	Ultra fine $CaCO_3$	50	14	24	0.20	81 ± 10
		100	14	14	0.17	88 ± 10
1–5	Ultra fine $CaCO_3$	50	10	18	0.25	32 ± 10
		100	6	18	0.24	31 ± 10
3–5	Ultra fine $CaCO_3$	50	10	27	0.30	6
		100	6	30	0.29	8 ± 2
0.5–2	SRF	20	17	21	0.22	57 ± 10
		50	18	21	0.24	60 ± 11
		100	18	41	0.27	36 ± 13
	HAF	20	14	3[b]	0.26	67 ± 5
		50	14	6[b]	0.30	35 ± 2
		100	13	8[b]	0.31	1 ± 1

[a] Curelastometer tests were carried out at a stroke of ± 3°.
[b] At a stroke of ± 1°.

Zinc oxide no. 1 was obtained from Sakai Chemical Industry Co. Ltd., stearate from Japan Oils and Fats Co. Ltd., sulfur from Hosoi Chemical Industry Co. Ltd., and *N*-cyclohexyl-2-benzothiazyl sulfenamide (CBS) from Ouuchi Shinkou Chemical Industry Co. Ltd. Heavy calcium carbonate (Whiton SB), light calcium carbonate (Silver W), and ultra fine calcium carbonate (Hakuenka cc) were from Shiraishi Industry Co. Ltd. Carbon black SRF (Asahi 50, ASTM no. N-770) and HAF (Asahi 70, ASTM no. N-330) were from Asahi Carbon Co. Ltd.

Mixing of compounding ingredients was carried out according to Japan Industrial Standards (JIS) K6300. Cure time at 140°C was selected for a 95% of maximum torque (T_{95}) determined by a Curelastometer type III (JSR).

Determination of Crosslink Density

The test specimens were preserved in benzene for 2 days at 30°C. The volume fraction of the rubber network (V_r) in the swollen gel was estimated, assuming that the change in thickness and width were proportional to the change in length. The crosslink density (ν_c) was calculated by the modified Flory–Rehner equation

$$[\ln(1 - V_r) + V_r + \mu V_r^2] = \nu_c V_s (V_r^{1/3} - \tfrac{1}{2} \cdot V_r)$$

where μ is the interaction parameter and V_s is the molar volume of the solvent.[3]

Methods of the Degradation Tests

The conditions of the degradation tests have been reported previously.[1] Each rubber specimen was cut into strips with a diameter of about 0.5 mm and a length of 120 mm, and each of the strips (80–90 mg) was added to 100 mL of mineral salt medium. After inoculation with the organism, the flasks were aerated using a magnetic stirrer at 600 rpm (30°C) for 8 weeks. After the incubation period, the culture medium was filtered through gauze and the strip was collected and weighed after being dried *in vacuo.*

RESULTS AND DISCUSSIONS

The Effect of Sulfur and an Accelerator (CBS)

The results of samples without filler are summarized in Figure 1. With a CBS content of 0.2 phr, the vulcanizates having sulfur content up to 3 phr were degraded rapidly by the organism. At 5 phr sulfur level, the degradation rate was slow and at sulfur level of 10 phr the sample was hardly degraded. With a CBS content of 0.5 or 1.0 phr, a considerable depression of microbial degradation was observed at a sulfur level of 2 or 3 phr. With a 3 phr CBS content, the vulcanizate having 1 phr sulfur was substantially resistant to microbial attack and there was little degradation observed at the 2 phr sulfur level. In any case, either an increase in sulfur content or that in CBS content of rubber formulations made the vulcanizate more resistant to microbial attack.

The depression of microbial activity by increasing sulfur content was also reported by Stanescu and Cirlan[4] and Cundell et al.[5] The curing agent concentration was reported, however, not to influence the rate of microbial deteriorations.[6]

The Effect of Crosslink Density

The data in Figure 1 was rearranged in Figure 2 according to the crosslink densities of the vulcanizates estimated from swelling. The weight losses of all

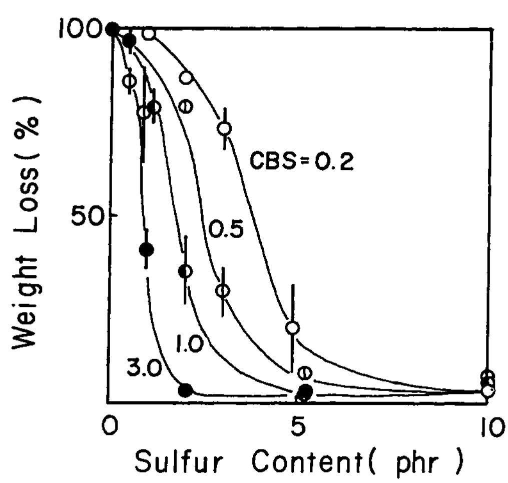

Fig. 1. The effect of sulfur and CBS content on the microbial degradation of the vulcanizates. CBS content (phr): (○) 0.2; (◐) 0.5; (◐) 1.0; (●) 3.0. Vertical lines in the figure indicate the deviation of values in duplicate experiments.

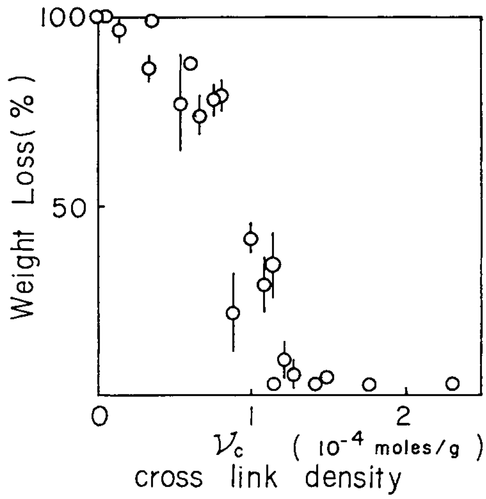

Fig. 2. The relationships between the crosslink density and microbial degradation.

the samples examined were in good correlation with the crosslink densities, regardless of the content of sulfur or CBS. In a curing system with sulfur and CBS, the crosslink density can be considered as a principal limiting factor of the resistance of vulcanizates to microbial attack.

It has been reported that various numbers and amounts of curatives influence the resistance of rubber rings[7] and that the different types of crosslinks were present in the case of accelerated sulfur vulcanization of natural rubber.[8] The relative proportion of mono-, di-, and polysulfidic crosslinks may effect the microbial activities. The effect of crosslink density in the different curing systems and the effect of the different types of cross links in the vulcanizates require further studies.

The Effect of Calcium Carbonate

Three kinds of calcium carbonate filler up to 100 phr in content have little or no effect on the microbial degradation of those vulcanizates with the formulation of CBS 0.5 and sulfur 2 phr (Table II). The weight losses of the samples with varying amounts of ultra fine calcium carbonate (Hakuenka cc) are shown in Figure 3. The effect of the filler was negligible in the samples with a formulation of CBS 0.5 and sulfur 2 phr, or CBS 3 and sulfur 5 phr. Only with the formulation of CBS 1 and sulfur 5 phr were the specimens with calcium carbonate loading more readily degraded than unfilled rubber.

The Effect of Carbon Black

The effect of two kinds of carbon black, SRF, and HAF can be seen in Figure 4. The depression of microbial activity by increasing filler content was observed with the addition of both the carbons. In both cases, the higher the content of carbon black in the rubber, the lower the weight loss of the vulcanizates. Although a specimen with SRF filler loading of 100 phr was degraded to some extent, the vulcanizate containing 100 phr of HAF hardly degraded.

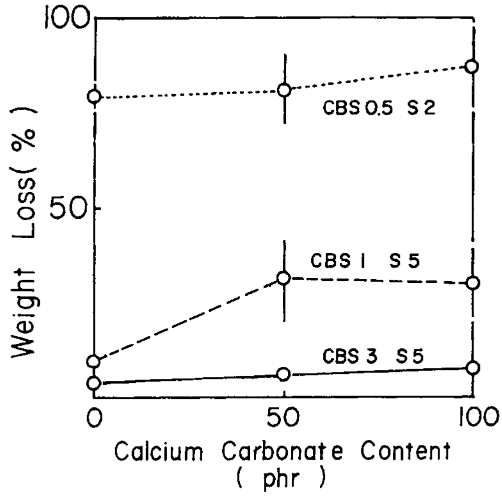

Fig. 3. The effect of calcium carbonate loadings. CBS, sulfur contents (phr): (· · ·O· · ·) 0.5, 2; (- -O- -) 1, 5; (— O —) 3, 5.

The vulcanizates with carbon black loading have already been reported to be more resistant to microbial attack than unfilled rubber,[9] and our results concur with that. It was interesting that the resistance of filled rubbers to microbial attack was closely related to the reinforcing property of the fillers, and that the specimens containing HAF, which has a strong reinforcing effect, were most resistant to microbial attack.

We have reported here the relationships between the fundamental components in formulations of vulcanized natural rubber and its resistance to attack by a sellected strain of rubber-degrading microorganism. In many commercial

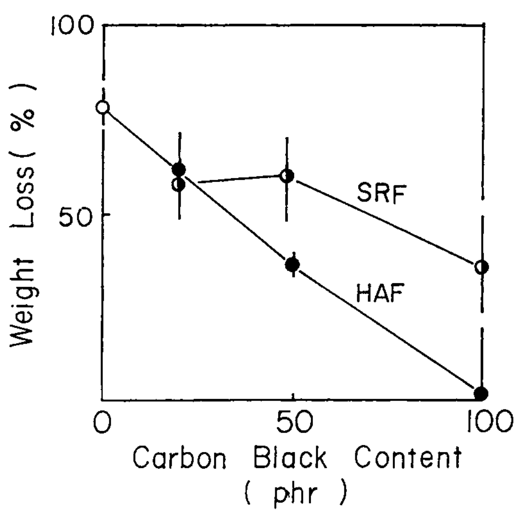

Fig. 4. The effect of carbon black loadings: (◑) specimens with SRF loadings; (●) specimens with HAF loadings.

products, synthetic rubbers are mixed with natural rubber and the compounding includes many kinds of additives such as oils and antioxidants. Microbial degradation of vulcanized rubber with formulations used practically will be a subject of further study.

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