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Studies on the γ-Irradiation of Natural Rubber Latex

YUJI MINOURA
Department of Chemistry, Research Institute for Atomic Energy, Osaka City University, Osaka, Japan
MAMORU ASAO
Foundation for Natural Rubber Research and Development, Tokyo, Japan

INTRODUCTION

Since 1943, when Burr and Garrison[1] carried out an experiment on the irradiation of rubber, it has been known that high-energy radiation crosslinks rubber molecules and thus vulcanizes rubber, and many theoretical and technological studies have been made in this field.

When rubber is irradiated by high-energy radiation, hydrogen atoms of the trunk chain, mainly of methylene groups α to double bonds, are ejected and radical sites are formed, and these radical sites are combined into C—C crosslinks.[2-5]

Heat-vulcanizing ingredients such as sulfur, accelerators, benzoyl peroxide, and other peroxides are known to have little effect on this reaction,[6-7] but it is possible that these ingredients, acting as radical acceptors,[8] hinder the radicals from combining with each other and thus retard irradiation vulcanization. In some cases, however, these ingredients are mixed into the compounds to be irradiated in order to induce vulcanization of the compounds partly by heat, because the temperature of any material irradiated adiabatically rises, sometimes even to 140°C., which is a standard vulcanization temperature.[7,9]

Irradiation curing of high polymers has not yet been widely adopted on an industrial scale, mainly for economic reasons; however, certain companies[9-12] are now vulcanizing tires and cables by high-energy radiation. Because these vulcanizates have superior aging properties[11] and because the product can be obtained uncontaminated by poisonous ingredients, the future of radiation curing looks bright.

High-energy radiation is used in various other fields of high polymer chemistry, such as irradiation polymerization and degradation. The graft copolymerization of methyl methacrylate and styrene onto natural rubber both in the solid state[13,14] and as latex[15,16] has been studied, and it is reported that the graft copolymerization of natural rubber and methyl methacrylate takes place with a very high yield of grafting.[16]

In recent years, vulcanized latex has been playing a more and more important role in rubber industry, as the demand for foam rubber and various dipped goods has increased. However, in spite of the earnest investigations into the radiation curing of solid rubber mentioned above, no reports have been published on the radiation curing of latex.[17]

It is known that when there is water in the system, the irradiation decomposes the water into radicals, which influence the reaction.[18-20] We have studied the irradiation curing of natural latex, considering the influence of water on the crosslinking reaction.

EXPERIMENTAL

Materials

The properties of the latex used (R.C.M.A. concentrated latex) were as follows: viscosity of 60% latex, 52.8 cpoise; mechanical stability (51.5% latex), 550 sec.; pH, 10.65; KOH number, 0.853.

Centrifuged latex (R.C.M.A.) was diluted with distilled water, if necessary, and then irradiated.

Methods

Radiation. One kilocurie of Co^{60} in the form of wire 15 cm. long was used as the radiation source. About 15 ml. of latex sample in a corked, hard-glass test tube (diameter 1.2 cm., length 15 cm.) was irradiated at room temperature. The dose rate was 1–2.5 × 10^5 r/hr.

In order to measure properties of latex such as mechanical stability, viscosity, etc., another sample was irradiated in a 500-ml. bottle.

The properties of the irradiated latex were measured as follows:

Viscosity. Viscosity was measured with an Ostwald viscometer at 20 ± 0.2°C.

pH. A calomel electrode pH meter (ASTM D 1076-54T) was used to measure pH.

pH at Gel Point. In order to find out whether the protein in latex is deteriorated by γ-irradiation, the pH at the gel point, which corresponds to the isoelectric point of protein, was measured.

Latex containing 3 g. of total solids was diluted to 300 ml. with distilled water, and titrated with 0.1*N* HCl under constant stirring. The pH value at the point where rubber coagulates and separates from the serum was read with a calomel-electrode pH meter.

KOH Number. Fatty acids in the latex were determined in accordance with the KOH number determination described in ASTM D 1076-54 T.

Mechanical Stability. The time required for the flocculation of latex stirred at high speed was measured in seconds, in accordance with ASTM D 1076–54 T. For this measurement the concentration of latex was 51.5%.

The irradiated latex was dried on a glass plate 7 cm. × 12 cm., first at room temperature for 48 hr. and then at 50 ± 2°C. to constant weight. The time required for the latter stage of drying was about 10 hrs. The thickness of the latex film was adjusted to 1 ± 0.2 mm. with the amount of the latex, and the properties of the film were measured as follows.

Tensile Test. A dumbbell-shaped specimen, 5 mm. × 20 mm. × ca. 1 mm., was stretched at 20°C. on a Schopper testing machine at the rate of 20 cm./min. Moduli at 300 and 500% elongation, elongation at break, and tensile strength were measured.

Equilibrium Swelling Ratio. The film was immersed in benzene at 25°C. for 40 hr. and the volumetric swelling ratio was calculated from

$$Q = V_2/V_1 = 1 + (\rho_R/\rho_B)(W_2/W_1) - (\rho_R/\rho_B)$$

where Q is the equilibrium swelling ratio, V_1 and V_2 are the volumes of the film before and after immersion, respectively, W_1 and W_2 the weights of the film before and after immersion, respectively, and ρ_R and ρ_B the density of rubber and benzene, respectively. ρ_R and ρ_B had been measured previously and the following values were used: ρ_R = 0.93, ρ_B = 0.87.

Hardness. The hardness of the film was measured with the rubber hardness tester in accordance with JIS-K-6351.

RESULTS AND DISCUSSION

Crosslinking of Rubber in Latex

Forty per cent latex was irradiated with various dosages, and the properties of the film were measured. The results obtained are given in Table I and Figures 1–4. The modulus (Fig. 1) increased with the dose, and it was found that rubber in natural latex is crosslinked by γ-irradiation. The tensile strength (Fig. 2) first increased with the dose and then decreased after a maximum of ca. 180 kg./cm.^{2} This maximum tensile strength was higher than the 130–140 kg./cm.^{2} obtained for solid rubber radiation-cured in air.[5,7,21]

It was found that the equilibrium swelling ratio of γ-irradiated latex films decreased with the dose, as shown in Table I, and that the rubber crosslinking increased with the dose.

Flory and Rehner[22] have shown that for highly swollen gels, for which terms of higher order than $(1/Q)^2$ can be neglected, the volume swelling ratio Q in a pure solvent is given by

$$Q^{5/3} = (0.5 - \mu)M_c/\rho v \qquad (1)$$

TABLE I
Properties of the Film from γ-Irradiated Natural Latex

Radiation dose,[a] r	300% Modulus, kg./cm.^{2}	500% Modulus, kg./cm.^{2}	Tensile strength, kg./cm.^{2}	Elongation break, %	Hardness (JIS)	Swelling ratio Q	$\nu_0 \times 10^{-18}$[b]	Viscosity of 40% latex, cpoise
0	3.7	5.3	18.9	770	27	56.6	—	5.9
5×10^6	6.4	10.5	77.3	880	32	—	—	5.1
1×10^7	7.9	11.9	—	930	35	—	—	4.3
1.2×10^7	—	—	146	1000	—	11.5	8.1	—
5×10^7	8.5	13.7	115	850	37	6.7	19.8	4.5
7.5×10^7	15.6	27.1	60.9	670	47	5.5	27.6	5.0
1×10^8	15.6	—	16.9	330	—	4.8	34.6	5.3

[a] Dose rate ≒ 10^5 r/hr.

[b] ν_0 = Number of crosslinked units per cc. of rubber.

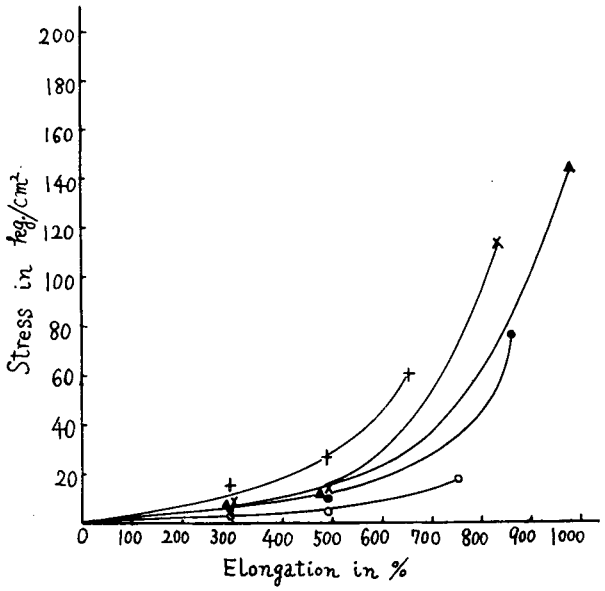

Fig. 1. Stress–strain curves of the film made from γ-irradiated natural rubber latex at irradiation. Cases of (○) 0, (●) 5×10^6, (▲) 1×10^7, (×) 5×10^7, and (+) 7.5×10^4 r/hr.

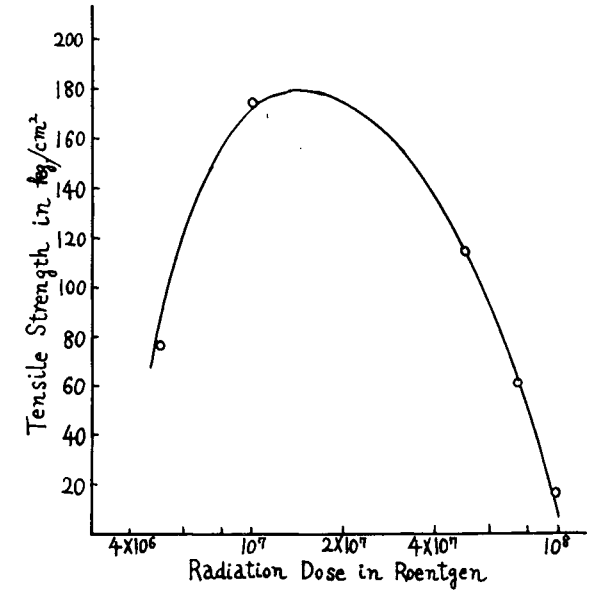

Fig. 2. Tensile strength vs. radiation dose (40% latex).

where μ is the parameter of the solvent–polymer interaction, M_c is the average molecular weight of chain between two crosslinks, ρ is the density of the polymer, and v is the molar volume of the solvent. For natural rubber and benzene, the following values were used:

$$\mu = 0.43$$
$$\rho = 0.93$$
$$v = 89.6$$

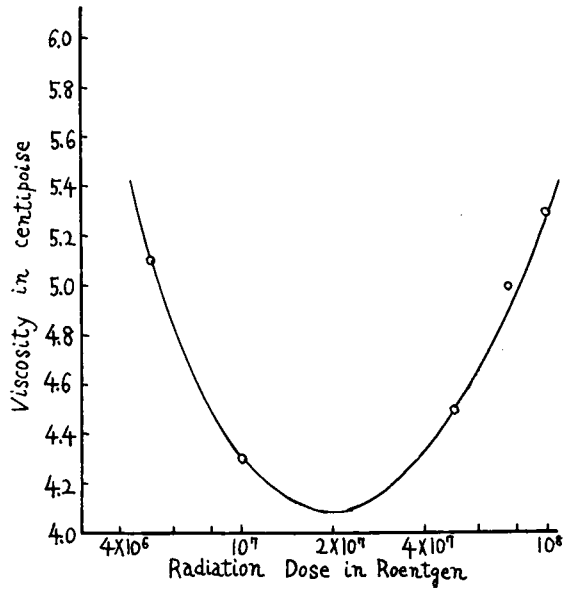

Fig. 3. Viscosity of γ-irradiated latex (40%).

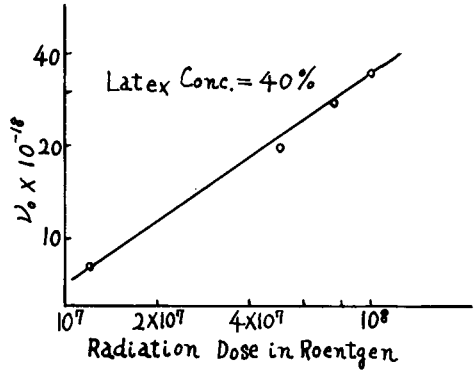

Fig. 4. Density of crosslinking vs. radiation dose.

On the other hand, the number of crosslinked units ν is given by

$$\nu = N_0 M_0 / M_c \tag{2}$$

where M_0 is the molecular weight of an isoprene unit, and N_0 is the total number of isoprene units concerned. Therefore, the number of crosslinked units per unit volume (1 cm.^{3}) of the polymer, ν_0 is

$$\nu_0 = N_A \rho / M_c \tag{3}$$

where N_A is Avogadro's number. Equation (1) then becomes

$$\nu_0 = [(0.5 - \mu) N_A / v] Q^{-5/3} = K Q^{-5/3} \tag{4}$$

where $K = 4.71 \times 10^{20}$.

From the results, it was found that for 40% latex the relationship between the crosslinking density and the dose is expressed by

$$\nu_0 = 1.15 \times 10^{14} (\text{dose}, \gamma)^{0.685} \doteqdot k(\text{dose}, \gamma)^{2/3} \tag{5}$$

The viscosity of the latex (Fig. 4) first decreased with the dose and then, after a minimum, increased. The decrease in the first stage may have been due to the reduction in particle size caused by the crosslinking. The time required for drying was shortened slightly when the latex was irradiated with more than 5×10^7 r, and latex irradiated to this extent had a putrid smell. These phenomena might be due to γ-deterioration of the protein in the latex and the deterioration might possibly correspond to the increase in viscosity in the later stage.

Brown but transparent film was obtained from γ-irradiated natural latex.

Effect of Latex Concentration on Crosslinking

Latex (60%) was diluted with distilled water to various concentration and γ-irradiated with a dose of 1.2×10^7 r. The equilibrium swelling ratio of the film and the calculated ν_0 are shown in Figure 5.

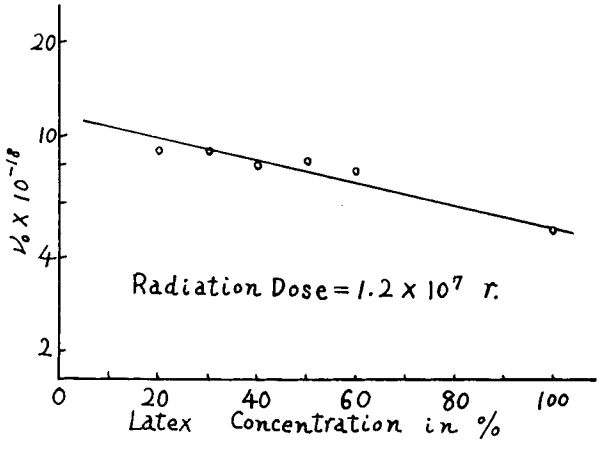

Fig. 5. Density of crosslinking vs. latex concentration.

The value at 100% latex was obtained on film that was irradiated after drying to constant weight.

It was found that water accelerated the crosslinking reaction, that the diluted latices had higher values of ν_0, and that it was more advantageous to irradiate latex than dried film. Moreover, it was shown that the curve, Figure 5, is expressed by

$$\nu_0 = 4.94 \times 10^{18} \exp \{[H_2O]/1.20\}$$

where $[H_2O]$ is the concentration of water in latex in g./cm.[3]

TABLE II
Relation of Latex Concentration to Density of Crosslinking[a]

Concentration, %	Swelling ratio, Q	$M_c \times 10^{-4}$[b]	$\nu_0 \times 10^{-18}$
20	11.0	6.4	8.88
30	11.0	6.4	8.88
40	11.5	7.1	8.03
50	11.3	6.8	8.28
60	11.9	7.6	7.61
100	15.4	11.5	4.95

[a] Dose rate = 5.3×10^4 r/hr.; total dose = 1.2×10^7 r.
[b] M_c = Average molecular weight of chain between two crosslinks.

Properties of Latex

Since a large amount of latex was needed for testing the properties, 60% latex was irradiated in a 500-ml. bottle, the diameter of which was about 8 cm. The latex sample in the bottle was irradiated with a wide range of intensities; the doses shown in Table III were measured at the center of the bottle. As in the case of 40% latex, the viscosity of 60% latex (Fig. 6) passed through a minimum

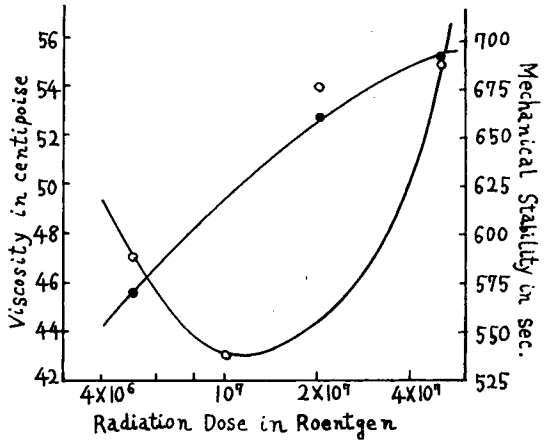

Fig. 6. Viscosity (O) and mechanical stability (●) of γ-irradiated latex.

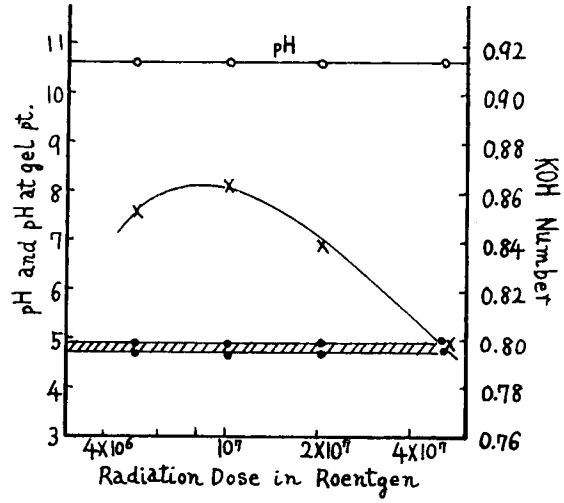

Fig. 7. pH (O), pH at gel point (●) and KOH number (×) of γ-irradiated latex.

TABLE III
Properties of γ-Irradiated Latex

Radiation dose,[a] r	Viscosity of 60% latex, cpoise	Mechanical stability,[b] sec.	pH	pH at gel point	KOH number	Swelling ratio Q
0	52.8	550	10.65	4.9–4.7	0.853	57
5×10^6	47.2	570	10.65	4.9–4.7	0.852	31
1×10^7	43.4	660	10.65	4.9–4.7	0.863	23
2×10^7	54.4	660	10.65	4.9–4.7	0.839	24
5×10^7	55.3	690	10.70	5.0–4.8	0.779	16

[a] The radiation dose shown is the value at the center of the bottle. The dose rate is 4.3×10^4 r/hr.
[b] The mechanical stability was measured at 51.5% of total solids.

in the course of irradiation, whereas the mechanical stability continuously increased. With a larger dose (ca. 10^8 r) the latter property decreased to 240 sec. without coagulation.

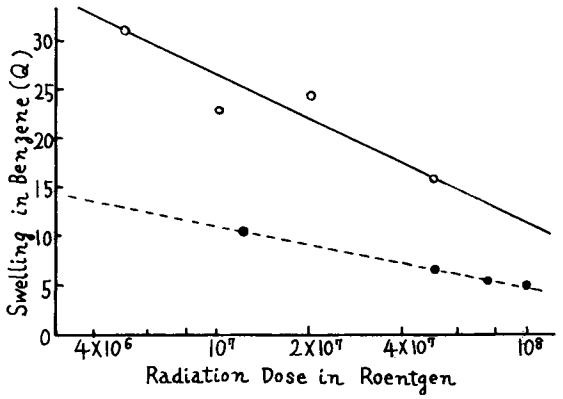

Fig. 8. Swelling of films that were γ-irradiated (O) in a 500-ml. bottle and (●) in a test tube (for comparison).

The pH and the pH at the gel point of the irradiated latex (Fig. 7) were scarcely affected by irradiation.

The KOH number (Fig. 7) increased slightly at first, and with further irradiation decreased slightly. It is thought that the fatty acids in the latex may have been decomposed.

The above results do not show quantitative relationships, however, because the mean dose throughout the bottle was far less than the dose at the center, as is shown by the results of swelling test (Fig. 8).

Infrared Spectra Analysis

Thin films (ca. 0.01 mm. thick) were prepared from nonirradiated latex and irradiated latex (5×10^7 r) in a vacuum desiccator, and an infrared spectra analysis was made. The spectra were obtained with a Baird Type D double-beam spectrophotometer equipped with a sodium chloride prism. No difference was found between the spectra of the two samples. The absorption chart and the analysis of the irradiated sample are shown in Figure 9 and Table IV, respectively. From the above results, it was concluded that no change in the spectrum due to irradiation had occurred,

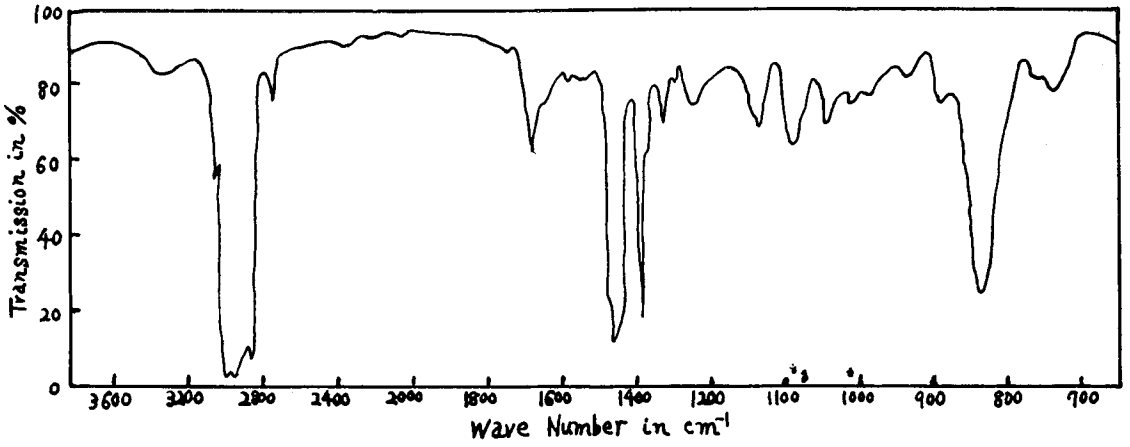

Fig. 9. Infrared spectrum of the γ-irradiated latex film.

and hence no oxidation or other side reactions had taken place during the γ-irradiation of rubber in latex.

TABLE IV
Infrared Spectra Analysis

Wave number, cm.$^{-1}$	Intensity[a]		Assignment[b]
837	s	r	(CH_2), *cis*-1,4-addition
888	vw	r	(CH_2), *cis*-3,4-addition
927	vw		?
1009	w		?
1038	w		?
1088	m		?
1127	m	δ	(CH_3) or w_a (CH_2), *cis*-1,4-addition
1245	w	w_a	(CH_2)
1308	w	w_a	(CH_2)
1377	s	δ_s	(CH_3)
1449	s	δ	(CH_2) or δ_a (CH_3)
1535	vw		COO^-, protein and amino acids
1636	m(sh)	ν	(C=C)
1661	m	ν	(C=C)
1730	vw	ν	(C=C)
2030	vw		?
2315	vw		?
2680	vw		?
2720	w		
2850	vs	ν_s	(CH_2)
2920	vs	ν_a	(CH_2)
2960	vs	ν_a	(CH_3)
3030	w(sh)	ν_a	(CH_3)
3310	vw	ν	(OH) or CH stretching of "lone" hydrogen on the double bond

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder.

[b] ν = stretching vibration, ν_s = symmetric stretching vibration, ν_a = antisymmetric stretching vibration, δ = bending or deformation, δ_s = symmetric deformation, δ_a = antisymmetric deformation, r = rocking, w_a = wagging.

The infrared spectra of irradiated rubber have already been investigated by many authors; it has been reported that when solid rubber is irradiated in air, side reactions, namely, disappearance of double bonds,[23] appearance of carbonyl and hydroxyl groups, etc.,[5] and cyclization[24] as with the sulfuric acid treatment, occur, and that the maximum tensile strength of this irradiated rubber is ca. 130–140 kg./cm.,[2,5,7,21] i.e., much lower than that of the usual vulcanizate. This lower tensile strength may be due to scissions of rubber molecules occurring simultaneously with the above-mentioned side reactions.

The present results show that in our experiments, the irradiation of latex, even in air, did not produce these changes in rubber, and gave the film higher tensile strength (i.e., ca. 180 kg./cm.^{2}).

Aging

The 60% latex sample, which was irradiated with 5×10^7 r at the dose rate of 5.3×10^4 r/hr. (at the center of the 500-ml. bottle) and which gave a film with tensile strength of 180 kg./cm.^{2}, was regarded as the optimum vulcanizate.

Dumbbell-shaped specimens of this film were kept at 100 ± 1°C. for 24 hr. in an air oven equipped with a temperature regulator and a fan for circulation of air. The tensile strength before and after aging was measured; the results are given in the last column of Table V. For comparison, the results of the same aging tests for ordinary sulfur-vulcanized latex films[25] are also given.

TABLE V
Results of Aging Tests[a]

	Samples				
	A	B	C	D	E
Recipe, parts by wt.					
Rubber (in latex)	100	100	100	100	100
KOH	—	0.5	0.5	0.5	—
Ammonium caseinate	—	0.5	0.5	0.5	—
Zinc oxide	—	2	2	2	—
Sulfur	—	1	1	1	—
Setsit-5	—	—	1.5	1.5	—
Age-Rite White	—	—	—	1	—
Total	100	104	105.5	106.5	100
Tensile strength, kg./cm.^{2}					
Before aging	113	148	387	368	180
After aging	42	68	141	219	235
Swelling ratio Q					
Before aging	—	—	—	—	6.17
After aging	—	—	—	—	6.10

[a] Samples A, B, C, and D were cured in hot air (90°C.) for 30 min.; sample E was γ-irradiated to 5×10^7 r.

The tensile strength of the γ-irradiated latex film before aging, 180 kg./cm.^{2}, was the lowest in the groups of films tested, whereas its tensile strength after aging, 235 kg./cm.^{2}, was the largest, which indicates superior aging of γ-irradiated latex film.

The increase in tensile strength during aging might perhaps be a result of new crosslinks arising from some functional group such as hydroperoxide which is produced in rubber molecules by γ-irradiation; actually, however, the density of crosslinking did not alter, as was shown by the swelling

ratios of the film before and after aging (Fig. 8). The inadequacy of the above hypothesis was shown also by the analysis of infrared spectra, in which no absorption, either of hydroperoxides or of other products appeared.

Therefore, the larger tensile strength may be due to more complete fusion of the rubber molecules with the latex particles, which could, perhaps, have occurred during the heating in this test, making the film stronger.

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Synopsis

Vulcanized latex was obtained by the γ-irradiation of natural rubber latex. The optimum cure was attained with ca. 2×10^7 r, in the case of 40% latex. Owing to the acceleration action of the water present, rubber in latex crosslinked more easily than it did in previously dried latex film, but no appreciable difference was found between the crosslinking in latices of various water contents. The protein in the latex deteriorated under γ-irradiation, but the properties of the latex were not damaged. The maximum tensile strength of the film obtained by drying this irradiated latex was larger than that of solid rubber irradiated in air; this may correspond to the fact that the irradiation, even when carried out in air, brought about no side reactions such as oxidation, etc., of rubber in latex. The aging behavior of the irradiated film was quite superior, the tensile strength being greater after aging than before.

Résumé

On obtient du latex vulcanisé par irradiation γ de latex de caoutchouc naturel. On obtient le meilleur résultat avec environ 2×10^7 roentgens dans le cas du latex 40%. L'eau accélérant la réaction, le caoutchouc dans le latex ponte plus facilement que dans un film de latex sèché au préalable; toutefois, on ne trouve pas de différence notable entre les réseaux des différentes concentrations. Les protéines présentes dans le latex sont détériorées par irradiation γ, mais les propriétés du latex ne sont pas modifiées. La force de tension maximum du film obtenu par sèchage du latex irradié est plus grande que celle du caoutchouc solide irradié à l'air et ceci correspond au fait que l'irradiation n'entraine pas de réactions secondaires comme l'oxydation etc. du caoutchouc dans le latex, même à l'air. Les propriétés au vieillissement du film sont nettement supérieures et même meilleures après vieillissement qu'auparavant.

Zusammenfassung

Vulkanisierter Latex wurde durch γ-Bestrahlung von Naturkautschuk-Latex erhalten. Das beste Ergebnis wurde bei ca. 2×10^7 Röntgen im Falle eines 40% igen Latex erreicht. Wasser beschleunigt die Reaktion und daher vernetzte sich Kautschuk im Latex leichter als in einem vorgetrockneten Latexfilm; zwischen Latices mit verschiedener Konzentration wurde jedoch kein erheblicher Unterschied gefunden. Durch γ-Bestrahlung wurde das Protein im Latex angegriffen, die Eigenschaften des Latex aber nicht geschädigt. Die maximale Zugfestigkeit des durch Trocknung dieses bestrahlten Latex erhaltenen Films lag höher als diejenige von festem, unter Luft bestrahlten Kautschuks, was durch den Umstand bedingt sein kann, dass die Bestralung des Kautschuks im Latex auch unter Luft keine Nebenreaktionen, wie Oxydation u.s.w. hervorruft. Die Alterungsbeständigkeit des Films war ausgezeichnet und er war nach der Alterung sogar noch fester als vorher.

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