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Studies on the Preparation and Uses of Co-60 Gamma-Ray Irradiated Natural Latex

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Synopsis

The properties are described of low-ammonia latex concentrates produced by gamma-ray irradiation (0.5–2.0 Mrad dose) in the presence of carbon tetrachloride or chloroform as sensitizer. Dipping trials with irradiated concentrates and irradiated field latex, for the preparation of condoms and medical gloves, gave products with high ultimate elongation, low modulus, and high permanent set. A change from straight dipping to coagulant dipping and a heat treatment after drying resulted in improved physical properties. A notable feature of products prepared from these materials is their purity, i.e., low content of rubber chemicals. An economic disadvantage, at the present time, is the high initial cost of the irradiation equipment.

Introduction

Organic halogen compounds (carbon tetrachloride or chloroform) were successfully used as sensitizers for the crosslinking of rubber in natural latex concentrates. A dose of 1 Mrad appeared adequate for optimal crosslinking, in the presence of 5% w/w carbon tetrachloride in the latex, as compared with a dose of 10–15 Mrad normally needed in the absence of sensitizer.

Laizier et al.[2] found that the presence of sulfur or certain thio-organic compounds enabled films with low permanent set to be obtained from natural latex concentrates irradiated with doses no higher than 1 Mrad. Puig[3] reported that effective crosslinking of rubber in latex could be achieved with doses of 2.5 Mrad, in the presence of carbon tetrachloride. The physical properties of the films from such latex were considered to be as good as those from vulcanized latex, while the aging properties were better.

Morganstern[4] has also claimed that radiation vulcanization of rubber in latex concentrates can be achieved with a dose of 1 Mrad in the presence of a suitable sensitizer.

Sumarno and Sundardi[5] found that the rate of crosslinking in natural latex concentrates was not significantly affected by the presence of sensitizer when the radiation dose exceeded 4 Mrad. They also showed that crosslinking efficiency (number of crosslinks per 100 eV absorbed) increased with sensitizer concentration until the efficiency reached a maximum value, which was about 10.7 using carbon tetrachloride and about 8.0 using chloroform as sensitizer.

The present paper describes irradiation on both natural latex concentrates

TABLE I

Properties of Natural latex (60% DRC, 0.3% w/w NH_3) After Irradiaton, with Chloroform and Carbon Tetrachloride as Sensitzers

Property	Age of Irradiated latex, weeks	0.5 Mrad[a]						1.0 Mrad						2.0 Mrad					
		3.0 phr[b]		7.5 phr		9.0 phr		3.0 phr		7.5 hr		9.0 phr		3.0 phr		7.5 phr		9.0 phr	
		$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4	$CHCl_3$	CCl_4·	$CHCl_3$	CCl_4
MST, min	1	520	1540	195	400	180	280	375	850	225	480	210	280	400	430	310	410	210	280
	12	739	993	353	843	180	660	1190	1030	250	825	285	560	783	997	366	506	314	393
Viscosity,	1	48.0	59.1	72.3	72.6	107.4	74.5	63.2	10.7	104.2	88.0	123.4	100.8	60.0	62.0	116.8	110.5	83.5	95.3
centipoises	12	54.6	54.7	74.1	76.5	104.8	75.2	58.9	66.2	110.4	99.9	141.7	118.1	56.4	66.0	122.9	290.9	89.9	118.9
KOH	1	0.60	0.98	0.62	0.62	0.85	0.82	0.35	—	0.43	—	0.53	—	0.68	0.68	0.61	0.66	0.75	0.85
Number	12	0.69	0.95	0.88	1.05	1.15	0.92	0.75	0.82	0.96	0.89	0.97	0.88	0.80	0.85	0.78	0.89	0.87	0.83
VFA	1	0.10	0.16	0.13	0.09	0.26	0.11	0.04	0.11	0.25	0.15	0.41	0.17	0.17	0.20	0.24	0.07	0.32	0.30
Number	12	0.07	0.25	0.26	0.17	0.59	0.16	0.19	0.22	0.55	0.30	0.43	0.38	0.18	0.16	0.30	0.16	0.35	0.34

[a] Radiation dose.
[b] Sensitizer content.

TABLE II
Properties of Dried Films from Irradiated Latex (60% DRC, 0.3% w/w NH_3, 0.1–0.3% w/w Sulfur) Using Carbon Tetrachloride (5 phr) as Sensitizer

	1.0 Mrad[a] 0.1%[b]	1.0 Mrad 0.3%	2.0 Mrad 0.1%	2.0 Mrad 0.3%	2.5 Mrad 0.1%	2.5 Mrad 0.3%
Modulus 300%, kg/cm^2	2.2	2.0	2.5	3.0	2.7	3.1
Modulus 500%, kg/cm^2	2.8	2.8	3.4	4.4	4.7	4.7
Tensile Strength, kg/cm^2	110	145	230	220	205	210
Elongation at break, %	1070	1140	1150	1060	1090	1100
Permanent set, %	30	25	12	10	9	9
		After Seven Days of Aging at 70°C in Geer Oven				
Modulus 300%, kg/cm^2	1.2	2.0	1.7	2.0	2.6	2.9
Modulus 500%, kg/cm^2	1.9	2.5	2.8	3.0	3.3	4.1
Tensile strength, kg/cm^2	72	90	160	205	200	250
Elongation at break, %	1100	1080	1110	1150	1150	1160
Permanent set, %	24	20	12	10	10	8

[a] Radiation dose.
[b] Sulfur content.

and field latex, and describes the properties of dried films and dipped goods (medical gloves and condoms) obtained from them.

Experimental

A Co-60 gamma-ray irradiator, "Gamma-Cell No. 220" (made in Canada), with a dose rate of ca. 4.2×10^5 rads/hr was employed. The latex used was from the experimental garden of the BPP Bogor at Ciomas (Bogor) and was preserved and concentrated as required. In these experiments, irradiation was conducted under air (the stoppered bottles were filled up to the neck with latex), and no antioxidant was employed.

The sensitizers carbon tetrachloride and chloroform were employed in the form of 40–50% w/w emulsions in water. Sulfur dispersions (50% w/w) were prepared by ball-milling for 48 hr with 4% w/w Dispersol LR (I.C.I. Ltd.) as dispersing agent.

The KOH number, VFA number, and MST of latex samples were determined in accordance with ASTM procedures,[6] and viscosities were measured with a capillary viscometer as described by Van Gils.[7]

Dried films of latex samples were prepared by spreading the latex on glass plates and drying at ca. 33°C to constant weight.

For the preparation of gloves, the straight dipping method was used with a porcelain former. After preliminary drying at 40°C, the glove was stripped, soaked in water for two to three days, and finally dried in a circulating air oven at 40°C for 2–3 hr unless stated otherwise.

Condoms were made on a glass former using either the straight dipping or coagulant dipping method. In the latter case, the formers were first coated with a coagulant solution consisting of calcium nitrate, ethyl alcohol, and water in the ratios of 1:1:3 by weight. After preliminary drying at 40°–45°C, the condoms were stripped, soaked in water for two to three days and dried in an air oven at 40°C. In some experiments, specified in the text, the condoms were given a final treatment in a steam autoclave at 100°C for 1–2 hr.

TABLE III
Properties of dipped Gloves from Irradiated Latex (Straight-dipping method)

	0.3% w/w[a]		0.7% w/w[a]		Commercial medical gloves[d] A	Commercial medical gloves[d] B
Radiation dose, Mrad	2.5	3.0	3.0	3.0	—	—
Sulfur content, % w/w of latex	0.25	0.25	—	—	—	—
Carbon tetrachloride, phr	5.0	5.0	4.0	5.0	—	—
Modulus 300%, g/cm^2	6.3[b]	6.6[c]	4.5[c]	5.6[c]	10.1	16.0
Modulus 500%, kg/cm^2	—	—	—	—	18.5	36.2
Modulus 600%, kg/cm^2	11.5	11.5	7.6	8.5	—	—
Tensile strength, kg/cm^2	135	147	194	176	195	225
Elongation at break, %	1010	930	1000	980	750	710
Permanent set, %	22	22	—	—	5	5

[a] Ammonia content of original latex.
[b] Final heat-treatment given (2–3 hours at 40°C in an air-circulated oven).
[c] No inal heat-teatment iven.
[d] Different commercial gloves purchased in Jakarta.

All measurements of modulus, ultimate elongation, tensile strength, and permanent set were made in accordance with ASTM procedures.[6] The bursting strength of condom samples and the testing for holes were determined by British Standard procedures.[8]

RESULTS

Properties of Irradiated Latices and Films

Table I shows the effect of radiation dose and sensitizer content on the physical properties of latex concentrate stabilized with 0.3% w/w ammonia, using chloroform or carbon tetrachloride as sensitizer.

A main feature of the table is the increase in viscosity and the large reduction in mechanical stability which occurs when the sensitizer content is raised from 3.0 to 9.0 phr. However, with a radiation dose of 2.0 Mrad and 3.0 phr of either chloroform or carbon tetrachloride as sensitizer, the mechanical stability, KOH number, and VFA number of the irradiated latices remain within British Standard specification limits[9] for a period of at least 12 weeks.

TABLE IV
Propertes of condoms Prepared from Irradiated Low-Ammonia (0.3% w/w) Latex Concentrate (60% DRC) Containing 0.25% W/w Sulfur and 5% w/w Carbon Tetrachloride as Sensitizer (Straight-Dipping Method)

Radiation dose, Mrad	Modulus 300%, kg/cm^2	Modulus 600%, kg/cm^2	Tensile strength, kg/cm^2	Ultimate elongation, %	Pemanent set, %	Bursting stength, liters of water
2.5	6.7	10.0	176	1000	20	3.95
3.0	7.3	11.1	136	920	19	2.40

If stability proves a problem, it could easily be overcome by the incorporation of stabilizers and/or secondary preservatives where appropriate. In this case, for appreciably longer periods of storage, a higher concentration of ammonia than 0.3% w/w would presumably be necessary to give satisfactory long-term stability.

Table II shows the effect of radiation dose on the properties of dried films of irradiated latices using carbon tetrachloride (5 phr) as sensitizer. In these experiments, small amounts of sulfur were added to the latex before irradiation to determine their effects, if any, on film properties. An increase in the sulfur content from 0.1 phr to 0.3 phr appeared to produce little change in the film properties.

The results of Table II demonstrate the increase in modulus and tensile strength and the decrease in permanent set caused by increasing the radiation dose. Elongation at break shows little change. A radiation dose of at least 2.0 Mrad appears necessary to obtain appreciable crosslinking of the rubber in these experiments. The best heat-aging resistance was obtained at the highest radiation dose employed (2.5 Mrad).

By comparison with conventional sulfur-cured latex films, the films from the irradiated latices are characterized by low modulus, fairly low tensile strength, high elongation at break, and high permanent set.

Dipped Medical Gloves

Table III typifies the properties of dipped medical gloves prepared from irradiated concentrates containing 0.3% or 0.7% w/w ammonia as preservative, and using radiation doses of 2.5–3.0 Mrad with 4.0–5.0 phr carbon tetrachloride as sensitizer. The permanent set figures were unexpectedly high for the radiation doses employed. In comparison with the commercial gloves A or B, gloves from the irradiated latices possessed lower modulus, somewhat lower tensile strength, and appreciably higher elongation at break.

Gloves prepared from the high-ammonia latex with 4.0 phr sensitizer were subjected to 20 sterilizations (½ hr each time) in a steam autoclave at 120°C; 85% of the samples so treated showed no signs of deterioration (a leakage test similar to that applied to condoms was employed).

Condoms from Irradiated Latex Concentrates

Typical properties of the condoms obtained from low-ammonia latex concentrates irradiated in the presence of sulfur, with carbon tetrachloride as sensitizer, are given in Table IV. The products (0.06–0.07 mm thick) were made by the straight-dipping method and were finally heated for 1–2 hr in a steam autoclave at 100°C.

Physical properties were again characterized by low modulus and tensile strength, high ultimate elongation, and high permanent set. The bursting strength of the products approximated the minimum requirement of British Standard 3704,[8] which specifies a figure of 3.0 liters water.

Condoms were also prepared by the same dipping technique from irradiated high-ammonia latex (0.7% NH_3, 60% DRC) concentrate, in the absence of sulfur, using a radiation dose of 3 Mrad and 4% w/w carbon tetrachloride as sensitizer.

TABLE V

Effect of Storage on he Viscosity and mst of irradiated Field latex at 30°C (4 phr CCl_4)

Radiation dose, Mrad	Total solids content, %	NH_3 Content, %	3 Weeks		5 Weeks		7 Weeks		9 Weeks		12 weeks		15 Weeks	
			Visc.[a]	M.S.T.[b]	Visc.	M.S.T.	Visc.	M.S.T.	Visc.	M.S.T.	Visc.	M.S.T.	Visc.	M.S.T.
1.0	41.8	0.42	5.2	810	5.3	1620	5.2	>1800	5.3	>1800	5.4	>1800	5.3	>1800
2.0	41.2	0.43	5.4	1350	5.2	>1800	5.3	>1800	5.3	>1800	5.4	>1800	5.5	>1800
3.0	41.3	0.40	5.4	>1800	5.4	>1800	5.2	>1800	5.3	>1800	5.5	>1800	5.4	>1800
4.0	41.6	0.42	5.3	>1800	5.2	>1800	5.4	>1800	5.4	>1800	5.5	>1800	5.4	>1800

[a] Viscosity, in centipoise.

[b] Modified ASTM D 1076 procedure (without dilution, 0 ± 1 g latex, 14000 ± 200 rpm).

TABLE VI
Properties of dipped Films Prepared from Irradiated Field Latex (ca. 30% DRC and 0.6% w/w Ammonia Content) with 5% w/w Carbon Tetrachloride as Sensitizer

Radiation dose, Mrad	Type of film[a]	Modulus 300%, kg/cm²	Tensile strength, kg/cm²	Ultimate elongation, %	permanent set, %
1.0	A	9.0	157	908	9.1
	B	3.8	83	1082	12.5
2.0	A	12.4	159	809	8.2
	B	4.5	122	1080	10.7
3.0	A	12.8	194	803	7.1
	B	5.5	112	973	8.7
3.0	A[b]	13.3	250	896	5.8
4.0	A	13.8	164	752	6.1
	B	5.7	98	925	7.5
6.0	A	14.9	147	730	5.2
	B	6.6	87	814	6.5

[a] A = coagulant-dipped film; B = straight-dipped film.
[b] Film finally heated at 100°C for 15 min.

The bursting strength of these products was 3.0–4.0 l. water, and could be further increased by a final heat treatment in a steam autoclave at 100°C for 15–60 min. Still higher bursting strengths (6.0–7.0 l. water) could be achieved by diluting the latex with 10% w/w water before irradiation and using two dips instead of a single dip to obtain the required thickness of product (0.06–0.07 mm). The bursting strengths, considering the smaller size (volume = 80 cm^3, diameter = 2.8 cm), compared well with commercial samples (volume = 150 cm^3, diameter = 3.3 cm, bursting strengths = 4.4–6.0 l. water). No holes were detected in any of the samples when tested in accordance with British Standard 3704.

Dipped Films and Condoms from Irradiated Field Latex

The latex used in this series of experiments was field latex of approximately 30% DRC stabilized with ca. 0.4% w/w ammonia, and irradiated in the presence of ca. 5% w/w carbon tetrachloride as sensitizer. No significant change in the viscosity of the irradiated latex could be detected after 15 weeks of storage, and a high mechanical stability could be maintained (Table V).

Dipped films were prepared with glass formers, using both straight dipping and coagulant dipping techniques. The films were soaked in water for ca. 48 hr and dried at 45°C; where specified, the films were finally heated at 100°C for 15 min. Results are given in Table VI.

The best balance of physical properties appears from Table VI to be achieved with a radiation dose of 3 Mrad. Coagulant-dipped films had considerably higher modulus and tensile strength than those prepared by straight dipping. The effect of a final heat treatment at 100°C on a coagulant-dipped film from latex irradiated with 3 Mrad was to increase tensile strength and ultimate elongation and to reduce the permanent set. Whether or not equally good physical properties could be obtained from irradiated latex concentrates diluted to ca. 30% DRC remains to be established.

TABLE VII
Properties of Condoms Prepared from Irradiated Field Latex (ca. 30% DRC and 0.6% w/w Ammonia Content) by Coagulant Dipping

Radiation dose, Mrad	Time of heating at 100°C, min	Modulus 300%, kg/cm²	Modulus 500%, kg/cm²	Tensile strength, kg/cm²	Ultimate elongation, %	Permanent set, %
1.0	0	9.9	17.6	156.9	904	9.0
	15	12.6	22.2	151.6	852	8.4
	30	11.6	19.5	123.3	838	7.2
2.0	0	12.4	22.2	158.4	810	8.0
	15	13.3	23.4	166.4	820	7.4
	30	13.7	23.6	142.3	852	5.4
3.0	0	13.0	27.5	193.7	802	7.2
	15	14.7	27.8	249.5	896	5.8
	30	13.6	24.9	192.2	860	4.2
4.0	0	15.0	38.6	147.2	730	6.3
	15	18.9	35.4	144.7	720	4.8
	30	18.5	33.5	135.5	666	3.8

With the same irradiated field latex, samples of condoms were prepared on glass formers using the coagulant dipping method. Results are shown in Table VII. In the table, the best balance of physical properties again appears to be obtained at a radiation dose of 3 Mrad. In this case, final heating of the products at 100°C for a period of 15 min increased tensile strength and ultimate elongation, in addition to reducing the permanent set. The bursting strength of these condom samples (thickness ca. 0.10 mm) averaged 7.4 l. water, i.e., considerably higher than the minimum of 3.0 l. required by British Standard 3704.[8]

CONCLUSIONS

1. Irradiated low-ammonia (0.3% w/w) latex concentrates can be prepared, using a radiation dose of 2.0 Mrad and 3.0 phr of either chloroform or carbon tetrachloride as sensitizer, such that the mechanical stability, KOH number, and VFA number remain within British Standard specification limits for a period of at least 12 weeks.

2. Dried films, dipped gloves, and condoms prepared from such irradiated latices are typically of low modulus, fairly low tensile strength, high ultimate elongation, and high permanent set. An increase in modulus and a reduction in permanent set could usually be achieved by increasing the radiation dose.

The bursting strength of condomspprepared from irradiated high-ammonia (0.7% w/w NH_3) latex concentrate could be substantially increased by heating the condoms at 100°C for 15–60 min. Still higher bursting strengths were obtained by diluting the latex with110 water before irradiation.

3. Irradiated field latex containing ca. 0.4% w/w ammonia could be stored for more than three months without significant increase in viscosity; a high mechanical stability could be maintained. The physical properties of condoms prepared from such latices by the coagulant dipping technique could again be improved by a heat treatment at 100°C for 15 min.

4. The absence of conventional rubber compounding ingredients in products prepared from irradiated latex should be advantageous for many medical ap-

plications. An economic disadvantage arises from the high initial cost of the irradiation equipment.

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