

Radiation Vulcanization of Natural Rubber Latex with Polyfunctional Monomers

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Synopsis

Natural rubber latex was irradiated with γ -rays from Co-60 in the presence of polyfunctional monomers to accelerate crosslinking of rubber molecules. Hydrophobic monomers were more effective in accelerating the vulcanization than were hydrophilic monomers. This was ascribed to high solubility of hydrophobic monomers in rubber particles. Among the hydrophobic monomers, neopentylglycol dimethacrylate (NPG) exhibited the highest efficiency in accelerating the vulcanization. Advantages of using NPG are (1) high colloidal stability of the irradiated latex and (2) high thermal stability of dried rubber film.

INTRODUCTION

Vulcanization of natural rubber latex (NR Ltx) can be performed by the irradiation with ionizing radiation, but it requires more than 30 Mrad,¹ which is too high to be used for industrial application. Halogenated hydrocarbons such as carbon tetrachloride (CCl₄) and chloroform have been used as sensitizers to reduce the required dose.²⁻⁶ The best vulcanized NR Ltx can be produced below 3 Mrad with 5 phr of CCl₄. Halogenated hydrocarbons, however, are often toxic. The toxicity of chemicals is generally evaluated by the threshold limit value (TLV), which is a tolerable concentration for an 8-h workday. The TLV of CCl₄, for instance, is 10 ppm.⁷ Few other sensitizers have been investigated. Divinylbenzene (DV) reported by Tatrov⁸ and Laizier et al.⁹ is the only polyfunctional monomer (monomer containing more than two polymerizable C=C double bonds in a molecule, PFM) that has been investigated as a sensitizer for this purpose. It was found that DV had a lower accelerating efficiency than CCl₄. But certain PFMs have been reported to act as excellent sensitizers for the radiation-induced crosslinking of polyethylene¹⁰⁻¹² and poly(vinyl chloride).^{13,14}

The accelerating efficiency of PFM depends not only on its reactivity with a polymer to be crosslinked but also on its solubility in the polymer.¹⁵ For instance, when sufficient amount of PFM cannot enter the inside of rubber particles, crosslinking of rubber molecules cannot be accelerated, even though the reactivity of PFM is high. On the contrary, when the reactivity of PFM is low, it is also difficult to accelerated the crosslinking even though the solubility of the PFM in NR is high.

In the present paper, the efficiencies of various PFMs were investigated as a sensitizer for radiation vulcanization of NR Ltx from the viewpoints of their solubility in NR and reactivity with NR molecules.

TABLE I
 Polyfunctional Monomers Used in This Work

Trade name	Chemical type	f^a	Supplier
1G	Ethyleneglycol dimethacrylate	2	Shin-Nakamura Chemical Co., Ltd.
2G	Diethyleneglycol dimethacrylate	2	
3G	Triethyleneglycol dimethacrylate	2	
4G	Polyethyleneglycol (# 200) dimethacrylate	2	
9G	Polyethyleneglycol (# 400) dimethacrylate	2	
14G	Polyethyleneglycol (# 600) dimethacrylate	2	
A-4G	Polyethyleneglycol (# 200) diacrylate	2	
P-9G	Polypropyleneglycol (# 400) dimethacrylate	2	
BG	1,3-Butyleneglycol dimethacrylate	2	
NPG	Neopentylglycol dimethacrylate	2	
HD	1,6-Hexanediol dimethacrylate	2	
A-BG	1,3-Butyleneglycol diacrylate	2	
A-NPG	Neopentylglycol diacrylate	2	
TMET	Trimethylolethane trimethacrylate	3	
TMPT	Trimethylolpropane trimethacrylate	3	
A-TMPT	Trimethylolpropane triacrylate	3	Nippon Kayaku Co., Ltd.
D-330	Dipentaerythritol triacrylate	3	
D-320	Dipentaerythritol tetraacrylate	4	
D-310	Dipentaerythritol pentaacrylate	5	
DPHA	Dipentaerythritol hexaacrylate ^b	5.5	
T-603	Dimethylolchloroendate	2	Wako Pure Chemical Industries, Ltd.
T-605	Diallylchloroendate	2	
DAF	Diallylfumarate	2	Kurogane Chemical Co., Ltd.
DAI	Diallyitaconate	2	
DAP	Diallylphthalate	2	Wako Pure Chemical Industries, Ltd.
DAIP	Diallysophthalate	2	
TAIC	Triallylisocyanurate	3	Musashino Chemical Research Institute
T-705	Triallytrimellitate	3	
			Wako Pure Chemical Industries, Ltd.

^a Functionality (numbers of unsaturated C=C bond).

^b Containing 50% of D-310.

EXPERIMENTAL

Materials. The NR Ltx used was a commercially available double centrifuged high-ammonia latex (H & C) imported from Malaysia. The PFMs used are listed in Table I with their trade name and number of polymerizable C=C bond in a molecule, f . They were all chemically pure (except for an inhibitor present in 50–100 ppm) and used without further purification. Reagent grade benzene, toluene, xylene, other organic solvents, and *n*-octyl mercaptan (*n*-OMP) were used as obtained.

Solubility of PFM in NR. The solubility of PFMs in the natural rubber was estimated by measuring the weight increase in an air-dry NR Ltx film after immersion in PFMs for a certain period at 30°C.

Irradiation. Measured volume of PFM was added to measured weight of

TABLE II
Absorption of PFM by NR sheet

PFM	Absorption (%)		HLB ^a	Viscosity (cP)	Molecular weight
	4.5 h	120 h			
2G	10.5	12.7	8.35	5	242
3G	5.6	7.8	8.70	9	286
4G	2.5	4.7	9.05	14	336
9G	0.3	—	10.80	35	536
14G	0.0	—	12.55	64	736
A-4G	0.8	—	10.0	24	308
P-9G	6.0	—	7.95	25	536
BG	45.3	68.5	7.05	4	226
NPG	46.2	87.6	6.575	6	240
HD	70.1	165.2	6.1	4	254
A-BG	13.2	17.3	8.0	4	198
A-NPG	15.2	23.8	7.525	4	212
T-603	25.8	—	—	1100	499
T-605	24.3	—	—	410	469
DAF	21.9	23.9	—	2	196
DAI	8.6	—	—	3	210
TMPT	5.8	11.0	7.075	42	338
TMET	4.7	8.6	7.55	35	324
A-TMPT	1.6	—	8.5	95	296
T-705	3.4	—	—	28	330
D-330	0.0	—	13.6	954	416
D-320	0.6	—	13.15	1167	470
D-310	0.3	—	12.7	2743	524
DPHA	0.0	—	12.25	5320	551

^a Calculated by Davies equation.¹⁶

NR Ltx and mixed with a magnetic stirrer for one hour. The mixture was then kept standing for 16 h at room temperature (25°C). About 80 mL of the mixture was irradiated in a 100-mL glass bottle with a plastic screw cap in an environment of air (about 20 mL of air above the surface of the mixture). Irradiation was carried out with 10 kCi of Co-60 at room temperature. The dose rate measured with cobalt glass dosimeter was 1 Mrad/h.

Measurements after Irradiation. Conductivity and pH of the irradiated latex were measured at room temperature. The viscosity was measured at 30°C with a cone and plate type viscometer, Model EMD, of Tokyo Keiki Co., Ltd. Dried films were prepared from the irradiated latex by casting it onto a glass plate and drying the same at room temperature. Some of the films were further treated in a forced convection oven.

The tensile properties such as tensile strength, elongation at break, and tear resistance of the films were determined in accordance with Japanese Industrial Standard JIS K 6301, which is similar to ASTM D 412 and D 624. Aging test was performed through air heating at 100°C for 48 h.

Disc specimens having a diameter of 15 mm were cut from the films and the gel fraction was determined. Unless otherwise noted, the gel fraction measurement was carried out by immersing the specimens in a boiling toluene for 20 h.

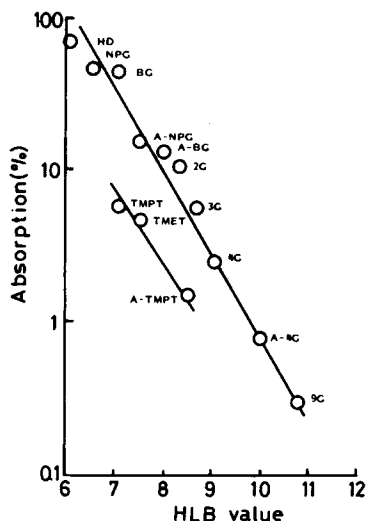


Fig. 1. Relationship between HLB value and absorption (%) of PFM in NR: absorption (%), measured at 30°C for 4.5 h.

RESULTS AND DISCUSSION

Solubility of PFM in NR. Table II shows the percent absorption of PFM in NR sheet after immersion for 4.5 hours and 120 h. As the data for poly(ethylene glycol dimethacrylate) with varying the number of oxyethylene groups (from 2G to 14G) indicates, the percent absorption decreased with increasing number of oxyethylene groups. Since the oxyethylene group is hydrophilic, the richer the oxyethylene groups in the PFM is, the more hydrophilic PFM is. The data of Table II show that, with decreasing the hydrophilicity of PFM, its solubility in NR increases.

Poly(ethylene glycol diacrylate) (A-4G) has many oxyethylene groups as poly(ethylene glycol dimethacrylate) (4G), but its percent absorption is lower than 4G. The absence of two methyl groups seems to increase the hydrophilicity of the PFM. The same tendency is observed by comparing between BG and A-BG and between NPG and A-NPG.

The hydrophilicity or hydrophobicity of PFM can be expressed by its hydrophilic-lipophilic balance (HLB) value. Low HLB value indicates strong lipophilic tendency. Davies has suggested that it is possible to allocate HLB numbers to component groups of a molecule.¹⁶ According to Davies, the HLB value of a molecule can be calculated by using the following equation,

$$\text{HLB value} = 7 + \Sigma H + \Sigma L$$

where ΣH and ΣL are the sums of hydrophilic group numbers and lipophilic group numbers, respectively. The hydrophilic groups in acrylates and methacrylate used in this work are ester and ether, and their hydrophilic group numbers are 2.4 and 1.3, respectively. Carbon atoms at the end and the center of the chain are calculated to be lipophilic, the lipophilic group numbers being -0.475 in either case. The HLB values thus calculated are listed in Table II.

Figure 1 shows the relationship between HLB values of acrylates and

methacrylates and the percent absorption by NR after 4.5 h. It is clear that the percent absorption increases with decreasing HLB value. Percent absorption of trifunctional monomers such as TMPT, TMET, and A-TMPT are extremely low for their HLB values. This seems to be due to steric and viscosity effects of these high molecular weight monomers. The low percent absorption of tetra-, penta-, and hexafunctional monomers could be explained by their high HLB values.

From the above results, it is reasonable to conclude that the PFMs which can be absorbed easily by NR particles in latex are dimethacrylates having HLB values lower than 7.05. The typical examples of these dimethacrylates are HD, BG, and NPG.

Effect of PFM on Vulcanization of NR Ltx. A series of polyethylene glycol dimethacrylate was investigated to study the effect of the solubility on the radiation vulcanization and also to compare those with the effect of CCl_4 . All HLB values of these dimethacrylates fall in a range from 8.35 to 12.55, indicating that they belong to the hydrophilic monomers. The results are shown in Table III.

The viscosity of the latex in the presence of 4G increased gradually, and it totally coagulated after standing for one night. The increase in viscosity was also observed with 2G, 3G, and 9G after irradiation. In the case of 3G, total coagulation occurred after the irradiation. Probably, a certain amount of these PFMs remained in aqueous phase and at the interface between NR particle and surrounding aqueous phase because of their high hydrophilicity. The amount of PFMs is considered to decrease at the interface and increase in aqueous phase with increasing hydrophilicity. The reason for the coagulation of NR Ltx with 4G is not clear, but it may be due to the changes in the structure of hydrated layer on the surface of NR particles. The coagulation after the irradiation in the presence of 3G seems due to the property change in hydrated layer by the formation of polymers of 3G at the interface. On the other hand, water-soluble 14G, which is expected to polymerize in aqueous phase, gave a stable latex even after irradiation.

The tensile strength of the films prepared from the latex irradiated in the presence of these PFMs are inferior to those of the films from the latex irradiated in the presence of CCl_4 .

The appearance of the film from the latex irradiated with hydrophilic PFM is opaque (less transparent), suggesting that the polymerization occurred mainly in aqueous phase to form homopolymers of the PFM.

The effect of HD having the lowest HLB value on the radiation vulcanization was compared with that of CCl_4 . The standing stability of the latex after mixing

TABLE III
Properties of NR Ltx Mixed with 5 phr of Poly(ethylene Glycol Dimethacrylate)^a

Properties	2G	3G	4G	9G	14G	CCl_4
Standing stability	A	A	C	A	A	A
Radiation stability	B	C	—	B	A	A
Film appearance	B	—	—	B	B	A
Tensile strength (MPa)	13.6	—	—	10.6	10.2	25.3

^a A: excellent; B: good; C: bad; —: not measurable because of coagulation of latex.

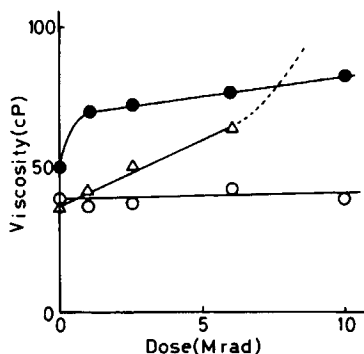


Fig. 2. Changes in viscosity of NR Ltx with dose in the presence of sensitizers: (O) control; (●) 10 phr of NPG; (Δ) 5 phr of CCl_4 .

with 10 phr of HD was excellent. Figure 2 shows the change in viscosity of the latex containing 10 phr of HD, 5 phr of CCl_4 , and the control latex as a function of dose. The viscosity of the latex containing CCl_4 increased with increasing dose. At 10 Mrad the latex coagulated during the measurement of viscosity with a rotational viscometer. This is probably due to enhancement of radiation damage of protective colloids (adsorbed protein) on the surface of the particles by the presence of CCl_4 . Large number of radicals from CCl_4 may attack the proteins as well as rubber molecules, and the proteins may preferentially enter into decomposition.

The viscosity of the latex containing 10 phr of HD gradually increased with dose, but the latex was stable even after irradiation up to 10 Mrad. However, the tensile strength of the film prepared from the irradiated latex is not high compared with that of the film from the latex irradiated in the presence of CCl_4 as shown in Figure 3. When CCl_4 was used, the tensile strength of dried latex film becomes 23.5 MPa at a maximum point at 6 Mrad. While, in the case of HD, the tensile strength increased gradually with dose and was still lower than

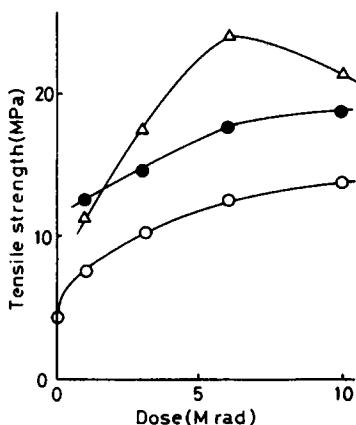


Fig. 3. Changes in tensile strength of NR film prepared from the latex irradiated in the presence of sensitizers: see the caption for Figure 2 as to symbols.

TABLE IV
Effect of Extracting Solvent on Gel Fraction of NR Film from Radiation Vulcanized Latex

Sensitizer		Dose (Mrad)	Gel (%) ^a			Δ gel ^b (%)
Name	phr		Benzene	Toluene	Xylene	
None		1	87.3	74.0	0.0	87.3
		3	88.9	79.9	35.1	53.8
		6	93.5	88.9	60.6	32.9
		10	93.9	91.4	71.7	22.2
CCl ₄	5	1	89.6	75.8	9.3	80.3
		3	95.0	90.9	51.0	44.0
		6	96.0	94.8	74.7	21.3
		10	97.2	95.5	76.8	20.4
HD	5	1	88.9	81.6	49.9	39.0
		3	91.9	90.8	71.8	20.1
		6	95.5	93.4	81.6	13.9
		10	95.6	94.5	84.1	11.5

^a Extracted for 20 h in boiling solvent.

^b Difference in gel fraction between benzene and xylene.

20 MPa even at 10 Mrad. The acceleration by HD is clear from comparison with the case for control latex, but the efficiency is not high.

Table IV shows the relation between dose and gel fraction. The gel fraction depends on extracting solvent. It was high when boiling benzene (80°C) was used, but low when boiling toluene (110°C) or xylene (140°C) was used. This means that the gel fraction decreased as extracting temperature increased. It seems due to the thermal decomposition of NR during the extraction at high temperature for a relatively long period (20 h). The difference in the apparent gel fractions between benzene and xylene as extracting solvents, Δ gel, as shown in Table IV, decreased with increasing dose. This is reasonable because it is generally accepted that the degradation of polymers depends on molecular weight, i.e., the apparent rate of degradation decreases with increasing degree of crosslinking when the degradation is evaluated with the decrease in gel fraction. It is interesting to note that the Δ gel obtained for CCl₄ is higher than that for HD at every dose, even though the gel fraction is higher in the case of CCl₄ than HD. This may be caused by the difference in thermal stability of cross-linked rubber, and it may be said from the above results that HD provides

TABLE V
Accelerating Effect of HD, BG, and NPG^a

Sensitizer	Dose (Mrad)	gel (%)	Tensile Strength (MPa)
HD	1.5	83.0	—
	3.0	89.4	12.3
BG	1.5	87.6	—
	3.0	88.4	12.3
NPG	1.5	84.4	—
	3.0	90.5	13.7

^a 5 phr of PFM was added to latex.

TABLE VI
Colloidal and Film Properties of Radiation Vulcanized Latex in the Presence of CCl_4 and NPG

Sensitizer	Dose (Mrad)	Viscosity (cP)	Film treatment conditions ^a								
			Air-dried			100°C for 30 min			100°C for 48 hr		
			T_b	E_b	Tr	T_b	E_b	Tr	T_b	E_b	Tr
CCl_4 5 phr	1	44	9.6	1200	15	7.8	1100	6	0.3	230	1
	3	65	16.7	1150	29	11.6	1150	12	2.6	950	9
	6	154	15.8	980	22	24.1	1090	20	12.6	950	9
	9	—	—	—	—	—	—	—	—	—	—
NPG 10 phr	1	62	9.8	1000	8	8.7	990	9	1.6	390	4
	3	64	16.0	950	12	14.3	980	14	4.5	500	7
	6	64	14.4	850	13	15.9	950	16	7.6	530	12
	9	64	16.3	840	21	19.5	830	21	14.0	670	16
	12	65	16.1	790	21	22.7	800	23	20.5	690	18
	16	79	16.6	730	26	22.9	750	24	21.7	680	23

^a T_b = tensile strength (MPa); E_b = elongation at break (%); Tr = tear resistance (kg/cm); —: not measured due to coagulation of latex

thermally more stable crosslinking than CCl_4 . This will be discussed later in connection with the aging properties of the film.

Table IV also shows that a degree of crosslinking as high as 87% is obtained at 1 Mrad without any sensitizing agent. It is likely that such a high efficiency of crosslinking can be achieved because the molecular weight of NR is very high, suggesting the existence of gel.¹⁷

Effect of NPG. Although HD has high solubility in NR, it is less effective than CCl_4 for the radiation vulcanization of NR Ltx. It may be due to its low reactivity with NR molecules. In this section, the effectiveness of two other PFMs, BG and NPG, having high solubility in NR, was investigated. Table V shows the accelerating effects of BG and NPG in comparing with HD. It is clear that BG and NPG are almost equal to HD in the crosslinking efficiency in term of the gel fraction while NPG gave the highest tensile strength. This results suggests that the solubility of NPG is enough to accelerate crosslinking and that its reactivity with NR is higher than that of HD.

Table VI compares the effectiveness of NPG and CCl_4 . The viscosity of the latex irradiated in the presence of NPG did not increase remarkably with dose and the latex keeps lower viscosity at a dose of 16 Mrad than the value obtained at a dose of 6 Mrad in the presence of CCl_4 .

Table VI also shows the tensile strength (T_b), elongation at break (E_b), and tear resistance (Tr) of the films treated at three different temperatures. No significant difference in T_b was observed between the two sensitizers when the films were dried at room temperature. However, T_b increased remarkably by heating the films at 100°C for 30 min. This is probably because the mobility of molecular chain of rubber increased at high temperature to enhance the entanglement of the molecular chains between rubber particles, i.e., coalescence of rubber particles becomes complete.^{18,19} By the heat treatment a film having a T_b of 24.1 MPa was obtained by the irradiation up to 6 Mrad in the presence of CCl_4 while 10 Mrad or more dose was necessary for obtaining a T_b above 20 MPa by using NPG.

Table VI also shows the aging properties of the films. When the films from the latex irradiated with CCl_4 was aged at 100°C for 48 h, they were colored, and

TABLE VII
Effect of Post-Addition of Solvent on Tensile Strength of Latex Film^a

Solvent	TLV (ppm) ⁷	bp (°C)	T_b (MPa)
None	—	—	13.3
CCl ₄	10	77	21.9
CH ₃ CCl ₃	350	74	21.3
<i>n</i> -Pentane	500	36	24.6 ^b
<i>n</i> -Hexane	500	69	21.4
<i>n</i> -Heptane	500	98	21.1
Cyclohexane	300	84	21.6
Ligroin	500	80–110	23.7
Petroleum ether	500	30–80	23.6 ^b
Petroleum benzene	500	50–90	23.0

^a Solvent, 10 phr; irradiation, 6 Mrad in the presence of 10 phr of NPG; film treatment, dried at room temperature.

^b Bad appearance with pinholes.

their surface became sticky, indicating noticeable degradation; but the films from the latex irradiated with NPG showed no coloration and surface degradation.

The superior aging property of NPG was also clear from the data of T_b and Tr after aging treatment. Their residual rates were about 50% at 6 Mrad in the case of CCl₄. On the contrary, in the case of NPG they were nearly 100% at 16 Mrad, which gave the highest gel fraction.

The inferior aging properties of CCl₄ may be due to the formation of thermally unstable bonds such as allyl-type chlorine and tertiary chlorine of a branched structure. These are considered as weak points to initiate the thermal decomposition of poly(vinyl chloride).^{20,21} These structures were not detected by infrared spectroscopy because of low concentration. By an elemental analysis of a film of the latex irradiated with 5 phr of CCl₄ up to 6 Mrad, 0.55 wt % of chlorine was detected.²²

Addition of Solvent for Film Formation. As can be seen from the above discussion, T_b of vulcanized film depends on the mobility of rubber molecules during film formation, and it is necessary to increase the coalescence of rubber particles to enhance the T_b . One such possibility is to add a good solvent for NR to the irradiated NR Ltx. This is a popular process in the organic coatings industry to add a solvent to latex to enhance the coalescence of latex particles.²³ Also in radiation-induced crosslinking of poly(vinyl chloride), it is well known that the crosslinking efficiency is increased by addition of solvent after irradiation²⁴ because of the enhancement of chain mobility. In this section, the effect of post-addition of solvent to the vulcanized NR Ltx on T_b was investigated.

Table VII shows the effect of the addition of various solvent to the latex vulcanized with 10 phr of NPG at 6 Mrad. The T_b increased from 13.3 MPa to above 21 MPa by the addition of solvent. However, when *n*-pentane and petroleum ether having low boiling points were used, small craters or pinholes were formed in the surface of dried film to impair their appearance. Table VII also shows TLV values of the solvent.⁷ It is preferable to use a solvent having a TLV value more than 300 ppm. Thus, ligroin was selected as an optimum solvent, and, in the subsequent experiments, 10 phr of ligroin was added to the irradiated NR Ltx before film formation.

TABLE VIII
Effect of *n*-Octyl Mercaptan on Radiation Vulcanization of NR Ltx with 10 phr of NPG^a

<i>n</i> -OMP (phr)	T_b (MPa)	E_b (%)
0.0	21.0	950
0.1	15.9	750
0.5	16.1	930
1.0	10.3	1300

^a Irradiation dose, 6 Mrad; heat treatment of film, 30 min at 100°C.

Effect of Chain Transfer Agent. Radiation-induced crosslinking of polymers with PFMs has been established by Salmon and Loan.²⁵ The rapid polymerization of the PFMs takes place in a matrix of the original polymers with forming a 3-dimensional network, by which the original polymers can be bridged. The mechanical properties such as T_b and E_b probably depend on the molecular structure or chain length of the bridge. To study the relationship between the chain length of NPG polymers in the bridge and the mechanical properties, a typical chain transfer agent, *n*-OMP was added to reduce the chain length.

The tensile strength was found to decrease with increasing concentration of *n*-OMP as shown in Table VIII. This suggests that T_b decreases with decreasing chain length of NPG polymers, or stated conversely, long NPG polymer chain is advantageous for achieving higher T_b .

From the results described above the conditions for preparing vulcanized latex film of high T_b with using PFMs could be summarized as follows:

- (1) Irradiation in the presence of 10 phr of NPG.
- (2) Addition of 10 phr of ligroin before film formation.
- (3) Treatment of film at 100°C for 30 min.

In Figure 4, T_b and E_b of the films thus prepared were plotted against irradiation dose. E_b decreased with increasing dose while T_b increased with increasing dose up to 26 MPa at 10 Mrad and decreased with further increase in dose. The decrease in T_b in the higher dose range is due to overcuring. Ex-

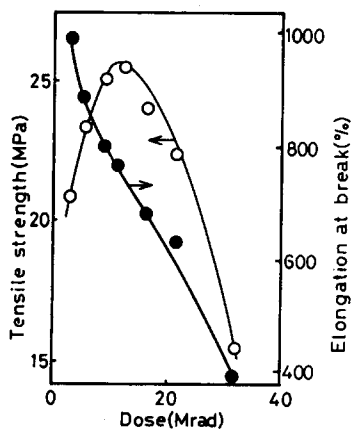


Fig. 4. Changes in tensile strength and elongation at break of the film prepared from the latex irradiated in the presence of 10 phr of NPG and mixed with 10 phr of ligroin after irradiation: heat treatment of film, 30 min at 100°C.

cessive crosslinking suppresses the mobility of rubber molecules so that the interparticle chains are not adequately entangled.

The maximum T_b was obtained at 10 Mrad. This dose is still high for industrial application. Further investigation to reduce the required dose by using PFM will be reported at a later date.

CONCLUSION

Various kinds of PFMs were investigated to accelerate the radiation vulcanization of NR Ltx. The relationship between the solubility of PFM in NR and the effectiveness of vulcanization was studied because PFM must be located in the NR particles to accelerate the vulcanization. Hydrophilic PFMs having low solubility in NR reduced the colloidal stability of the latex and did not show any significant acceleration for the vulcanization. On the other hand, hydrophobic PFMs accelerate the vulcanization. Among the hydrophobic PFMs, NPG exhibited the most effective acceleration. The advantages of NPG as an accelerating agent for the vulcanization of NR Ltx compared with CCl_4 were as follows:

- (1) High colloidal stability of the irradiated latex.
- (2) High thermal stability of the dried NR film.

Addition of solvent to the irradiated latex before film formation and heat treatment of film were effective to enhance tensile properties of the film.

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