Durability of Radiation-Sterilized Polymers, XI. The Effect of Irradiation on Rubber Gloves

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Synopsis

The effect of both gamma ray and electron beam irradiations on three rubber gloves are compared in relation to sterilization. Two of these gloves are sulfur vulcanized and the other is radiation vulcanized. It was found that the radiation-vulcanized rubber gloves could be used, even at 25 kGy, the sterilization dose used. For all three gloves, it was found that the tensile strength and elongation at break are not significantly affected after irradiation in either gamma rays or electron beam or during storage. The tear strengths, however, decrease with increasing dose and storage, and it was found that degradation was higher in gamma rays than electron beam. The chemiluminescence data show that the rate of degradation is the highest in latex film followed by radiation-vulcanized and sulfur-vulcanized gloves.

INTRODUCTION

Medical products sterilization using radiation has increased rapidly since its introduction in about 1960. The medical products that have been sterilized include syringes, catheters, sutures, and rubber gloves. The success of radiation sterilization is due to its outstanding reliability, inherent simplicity, continuous sterilization process, applicability to the sterilization of single-use medical products, freedom in selection of product and packaging materials, and high degree of sterility assurance.[1]

In view of these advantages, there has been a further marked swing toward radiation for the sterilization of medical devices encouraged by the problems that have arisen from ethylene oxide residuals. The kinds of articles that can be sterilized by radiation also increase by the year. Polymers that are accepted for use in medical applications include fluorocarbons, polycarbonates, polyethylene, polypropylene, and natural rubber.[2] Many of these polymers used in the medical field show various degrees of degradation after radiation exposure. The sterilizing radiation effect on selected polymers is described in detail by Skiens.[3] From our previous work,[4,5] we have also shown that polypropylene and copolypropylene degrade to a certain extent during irradiation. However, no work has been carried out so far to study the effect of irradiation on rubber gloves.

In our present work, we report on the effects of gamma-ray and electron beam radiation on rubber gloves. These gloves are made from natural rubber latex. They are, however, vulcanized differently. Two of these gloves are vul-

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canized conventionally, that is, by using sulfur as the curing agent, while the other is vulcanized by using radiation.

Extensive work has been carried out to study the mechanism of sulfur-vulcanized natural rubber latex.[6-9] The mechanism of sulfur-vulcanized natural rubber latex has been a subject of some controversy. A summary of the overall mechanism of accelerated sulfur vulcanization has been published in a review by Porter.[10] It is now generally accepted that the precursor to the formation of crosslinks in accelerated sulfur vulcanization is the rubber-bound intermediate and the crosslinks occur via the sulfur bond (—C—S—C—). In contrast, the study on radiation vulcanization of natural rubber latex with the addition of a sensitizer has received little attention. However, our laboratory has done substantial work in this area to render the radiation vulcanization of natural rubber latex a potential process for producing good-quality products. Earlier work has been dedicated to finding the best sensitizer,[11-14] and we found that 2-ethylhexyl acrylate has many advantages over other sensitizers. Rubber products from this process have low toxicity due to the absence of carbon tetrachloride, high heat resistance and no SO gas, and ashes are formed from burning these products. A mechanism for radiation vulcanization of natural rubber latex using 2-ethylhexyl acrylate monomer has been proposed by Makuuchi et al.[14] Based on their gel permeation chromatograph study, they suggested that the main part of the vulcanization is attributed to the entanglement of natural rubber molecules and poly-2-ethylhexyl acrylate molecules. Crosslinks of the —C—C— bond type were also found to occur in the latex particles.[15] Rubber gloves have been treated by radiation vulcanization of natural rubber latex with the addition of 2-ethylhexyl acrylate monomer sensitizer. In order to evaluate the physical properties of these rubber gloves made from radiation vulcanization of natural rubber latex, we compare their performance with commercially produced rubber gloves made by using sulfur vulcanization. In this article, we also report on the effects of radiation on rubber gloves vulcanized by both sulfur and radiation. Their stability in radiation will be compared from their tensile test and chemiluminescence measurement.

EXPERIMENTAL

Materials

Summary of sample used is shown in Table I. The two commercially produced gloves (called S1 and S2) were made from sulfur vulcanization while the third (called R) was made from radiation vulcanization natural rubber latex with the addition of 2-ethylhexyl acrylate (2EHA) monomer and carbon tetrachloride (5 : 1 phr) as sensitizer. Since R gloves are prepared by radiation vulcanization with the monomer, vulcanization accelerators and zinc oxide that are used in sulfur vulcanization are not contained. On the contrary, S1 and S2 gloves contain some additive such as vulcanization accelerators and zinc oxide. However, the rubber formulation is not clear for commercial rubber gloves. Radiation-vulcanized films were also prepared in order to compare their radiation stability with R gloves. For the preparation of these films, the NR latex used was a commercially available centrifuged latex (FELDA HA) from Malaysia. The

TABLE I
Summary of Samples

	Preparation of samples		Physical properties			
Samples	Vulcanization method	Additive	Tb (MPa)	M_{100} (MPa)	Eb (%)	Tr (Nmm^{-1})
R gloves	Radiation vulcanization	Antioxidant[a]	36.9	0.68	906	70.9
Latex film	Radiation vulcanization	None	30.4	0.70	898	40.5
S1 gloves[b]	Sulfur vulcanization	Some additives	48.7	1.34	788	79.0
S2 gloves[b]	Sulfur vulcanization	Some additives	51.9	1.01	894	76.7

[a] 2,2-Methylene bis(4-ethyl-6-butylphenol), 0.5 phr.
[b] Commercial rubber gloves.

latex was diluted with 1% aqueous ammonia solution to a rubber content of 53%. Chemically pure 2-ethylhexyl acrylate was used without further purification. Reagent grade toluene was used for estimation of swelling ratio and gel fraction in vulcanized rubber.

Preparation of Latex Films

The radiation-vulcanized latex were cast onto glass plates at room temperature and dried at this temperature for 4 days. The films were then washed in 1% aqueous ammonia solution for one night before drying for another night at room temperature (RT) and a further drying for 1 h at 80°C.

Irradiation

All three types of rubber gloves were irradiated in both gamma-ray and electron beam radiation. In the case of latex, only gamma-ray irradiation was used. The doses used were 10, 25, 50, and 100 kGy. For the gamma-ray irradiation, the dose rate used was 10 kGy/h except for the 25-kGy dose, whereby the samples were irradiated for 2 h at 10 kGy/h and for 1 h at 5 kGy/h. For the electron beam irradiation, the beam current used was 2 mA, and the acceleration energy was 2 MeV. The rate of irradiation was 5 kGy per pass.

Measurements after Irradiation

The tensile properties such as tensile strength (Tb), elongation at break (Eb), modulus (M_{100}), and tear resistance (Tr) of the rubber gloves and latex film were determined in accordance with the ASTM standard D3577. For all of these test, the Toyoseiki Strograph-R1 tensometer was used. Extraction was carried out to measure the gel fraction by immersing the sample in boiling toluene for 24 h. For the latex film, however, the samples were immersed in boiling toluene for 48 h. The swelling ratio of both the rubber gloves and latex film were measured after the samples were immersed in toluene at room temperature for one day. The three gloves and the latex film were cut into 4-cm diameter disks for chemiluminescence (CL) measurements. These samples were irradiated in gamma rays at 50 kGy dose and stored at −78°C before CL measurements were carried out by using the CL Analyzer OX-7 made by Tohoku Electronic Industrial Co. The gate time used for these measurements was 1 s.

RESULTS AND DISCUSSION

Physical Properties of the Rubber Gloves and Latex Film

The absolute values of Tb, M_{100}, Eb, and Tr of the rubber gloves and latex film before irradiation are given in Table I. It can be seen that the Tb value of the latex film (ca. 30.4 MPa) is the lowest compared to the three rubber gloves. R rubber gloves vulcanized by radiation has Tb value (ca. 36.9) higher than the latex film. The difference between R gloves and latex film is in their preparation conditions. For the latex film, raw vulcanized latex was cast onto glass plates without any other additive. For the R glove, vulcanized latex used to make gloves include the addition of antioxidant and coagulant. Apart from this, the thickness of the latex film and R glove for tensile test were different for both samples (0.15 mm for R glove and 1.35 mm for latex film). It has been shown previously[16] that in latex film, thickness and moisture content affect the tensile strength. With increase in thickness and moisture content, the Tb decrease. This is due to lower cohesion between the latex particles. These two factors, difference in preparation conditions and thickness, are the reasons why the Tb of R gloves is higher than that for latex film, even though both latexes were radiation vulcanized. The Tb of R gloves shows that radiation-vulcanized gloves are also acceptable as rubber gloves since according to ASTM standard D3577, the minimum value acceptable is 24 MPa.

Comparing the Tb of sulfur-vulcanized gloves and radiation-vulcanized samples (Table I), it was found that the sulfur-vulcanized gloves give higher Tb. This is due to the difference in crosslinking bonds. For sulfur-vulcanized gloves crosslinking occurs via —C—S—C— bonds, while for radiation-vulcanized gloves crosslinking occurs via the —C—C— bonds. The covalent bond energies[17] of —C—S—C— and —C—C— are 285 and 351 kJ/mol, respectively. Since the covalent bond energy of the —C—S—C— bond is lower than the —C—C— bond, the mobility of the —C—S—C— bond is higher than the —C—C— bond. It has been shown previously[17] that the higher the mobility of the crosslinking bond, the higher will be the tensile strength. Hence, there is a higher Tb in the S1 and S2 gloves compared to R gloves. For the values of Eb, all the rubber gloves meet the requirement of the ASTM standard D3577, which is 750% minimum. The M_{100} of latex film is similar to R gloves and lower than S1 and S2 gloves. This difference is due to the different vulcanization methods employed in these samples, and it can be concluded that radiation vulcanization of natural rubber latex gives lower value compared to sulfur vulcanization. This data shows that R gloves are superior to S1 and S2 gloves since they are more sensitive and cause less fatigue on the fingers, and these qualities are required especially if the gloves are used for a long time. From

Table I, it can also be seen that the Tr of R gloves is higher than the latex film. The difference between these two samples lies in their preparation conditions. The presence of antioxidant and the preparation conditions in producing rubber gloves causes the Tr value of R gloves to increase dramatically compared to the cast-vulcanized latex film. The Tr value of R gloves, on the other hand, is lower than the Tr value of S1 and S2 gloves. Here, it can be deduced that the sulfur-vulcanized gloves give higher Tr compared to the radiation-vulcanized gloves due to the difference in the mechanism in sulfur vulcanization.

Effect of Gamma-Ray Irradiation on the Rubber Gloves and Latex Film

Figure 1 shows the relative changes of Tb, M_{100}, Eb, and Tr with dose after irradiation in gamma rays for rubber gloves and latex film. From Figure 1a, the slope of the graph for latex film is very small while the slope of the graph for R groves is the largest. Comparing R and S1 and S2 gloves, it can be seen that degradation occurs more in R gloves than S1 and S2 gloves. Even though degradation that has occurred in R gloves is the highest, at 50 kGy Tb is only reduced to 10% (ca. 33.1 MPa). This indicates that at 25 kGy, the sterilization dose used, R gloves can still be accepted as rubber gloves. From Figure 1b, 1c, and 1d, it can be seen that Eb is not affected with increasing dose, but M_{100} and Tr decrease markedly at low dose especially in R gloves. This shows that degradation occurs most with the R gloves, followed by latex film, and S1 and S2 gloves. The Tr data also indicates that in the sulfur vulcanization method, the bonding between latex particles is stronger since the values of Tr are higher in S1 and S2 gloves compared to R gloves and latex film. Our data, however, is not in agreement with Kohjiya et al.[18] In their study, natural rubber was cured by sulfur and accelerator to give rubber vulcanizates. The Tb and Eb of this rubber vulcanizate decreased with 10 kGy irradiation in gamma rays. M_{100}, on the other hand, did not change with increasing dose. The discrepancy between our results and Kohjiya et al.[18] could be due to different compounding recipes and curing conditions. This shows that the effects of irradiation on natural rubber latex is very sensitive to the preparation conditions on the latex. The swelling ratio and gel fraction results are shown in Figures 2a and 2b, respectively. From the swelling ratio results (Fig. 2a), the crosslinking density of radiation-vulcanized samples before irradiation is lower than that of sulfur-vulcanized ones. In sulfur-vulcanized samples, higher crosslinking density reflects in higher physical properties compared with that of radiation-vulcanized samples. This data further suggest that the bonding between latex particles in sulfur-vulcanized gloves are stronger than R gloves. For the latex film, degradation occurs at a lower dose and crosslinking occurs after 100 kGy irradiation. From the swelling ratio graphs for the three rubber gloves, it can be observed that the swelling ratio increases with increasing dose. This finding indicates that degradation increases with dose. Further, crosslinking did not occur in the rubber gloves. The gel fraction results (Fig. 2b) confirm this. It should be noted that degradation that has occurred was minimal. Our result is in agreement with Kohjiya et al.[18] who also found that degradation has occurred in their sulfur-vulcanized samples irradiated up to 100 kGy. The different behavior

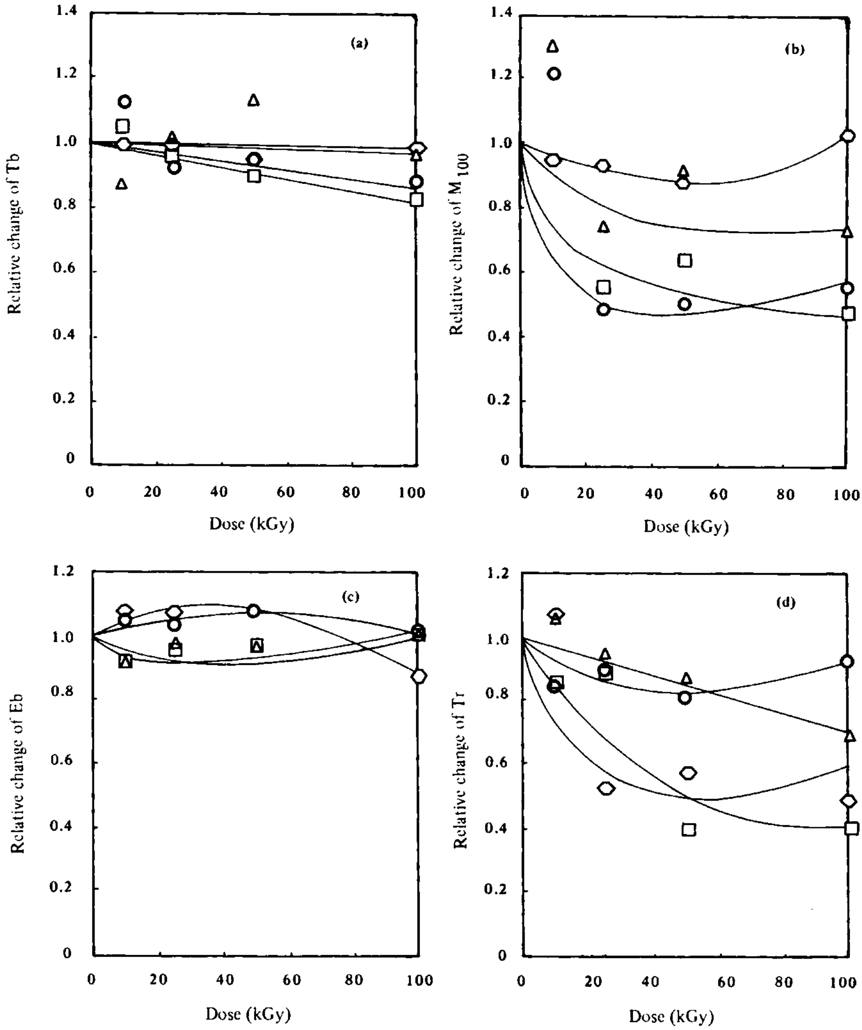

Fig. 1. Relative change of (a) tensile strength, Tb; (b) modulus at 100% elongation, M_{100}; (c) elongation at break, Eb; and (d) tear strength, Tr; with dose after irradiation in gamma rays for rubber gloves and latex film: (○) S1 gloves; (△) S2 gloves; (□) R gloves; (o) latex film.

between the three rubber gloves and the latex film could be due to the presence of antioxidant in the gloves, suggesting that the antioxidant inhibits both degradation and crosslinking.

Effect of Electron Beam Irradiation on the Rubber Gloves and Latex Film

The effect of electron beam on the degradation of the three rubber gloves has also been studied. Figure 3b shows typical effects of electron beam radiation on the Tb, M_{100}, Eb, and Tr of R rubber gloves at different doses. From Figure 3b, it can be observed that Tb and Eb are hardly affected with increasing dose. A similar tendency has been observed in gamma rays (Fig. 3a). M_{100} and Tr,

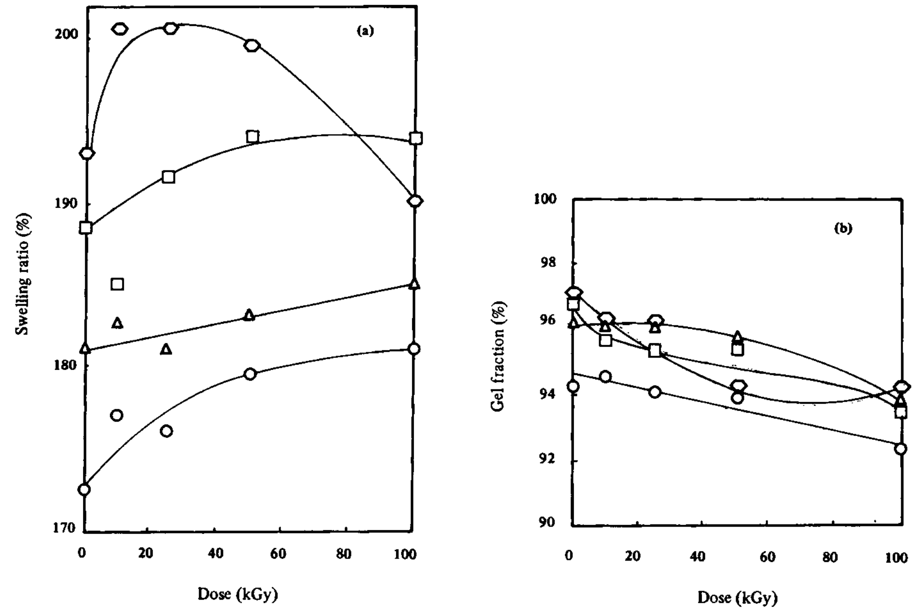

Fig. 2. The (a) swelling ratio, Sw; and (b) gel fraction, Gr; of rubber gloves and latex film at different doses after irradiation in gamma rays: (○) S1 gloves; (△) S2 gloves; (□) R gloves; (o) latex film.

however, decrease slightly with increasing dose after irradiation in electron beam. Comparing Figures 3a and 3b, it can be seen that M_{100} and Tr decreased more in gamma rays than in electron beam, indicating that degradation is higher in gamma-ray than electron beam radiation. This is expected since in gamma rays, the penetration is deeper and, hence, oxygen can diffuse into the

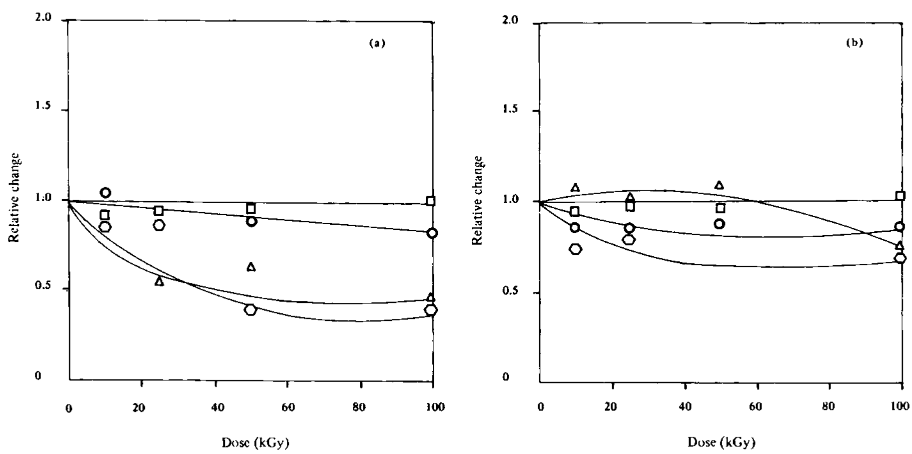

Fig. 3. Relative changes of (○) Tb, (△) M_{100}, (□) Eb, and (o) Tr with dose after irradiation in (a) gamma rays and (b) electron beam.

sample. It can be concluded that electron beam would be a better choice for the sterilization of rubber gloves.

Effect of Storage on the Rubber Gloves

It is well known that some polymer such as polyethylene and polypropylene degrade by residual peroxy radical during storage after irradiation. In order to confirm degradation during storage, physical properties on irradiated rubber gloves were measured. Figure 4 shows the Tb of the three rubber gloves during storage after 25 and 50 kGy irradiation in gamma rays and electron beam. There is no significant change in the Tb of the three rubber gloves during storage. Similar tendency was observed for the Eb of the rubber gloves during storage. However, Tr decrease with storage (Fig. 5). For the R gloves, since after 50 kGy irradiation in gamma rays Tr value is low before storage, there is practically no change in Tr during storage (Fig. 5). Comparing the effects of gamma-ray and electron beam radiation on the storage of rubber gloves, only

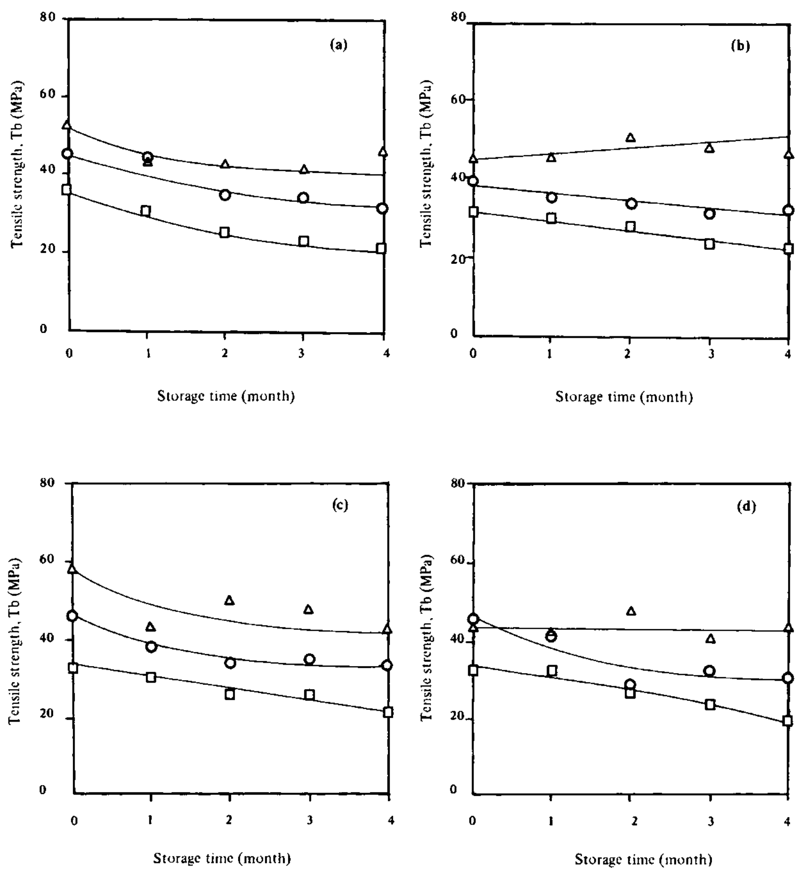

Fig. 4. The change in Tb of the three rubber gloves during storage: (○) S1 gloves; (△) S2 gloves; (□) R gloves. (a) 25 kGy in gamma rays; (b) 25 kGy in electron beam; (c) 50 kGy in gamma ray; (d) 50 kGy in electron beam.

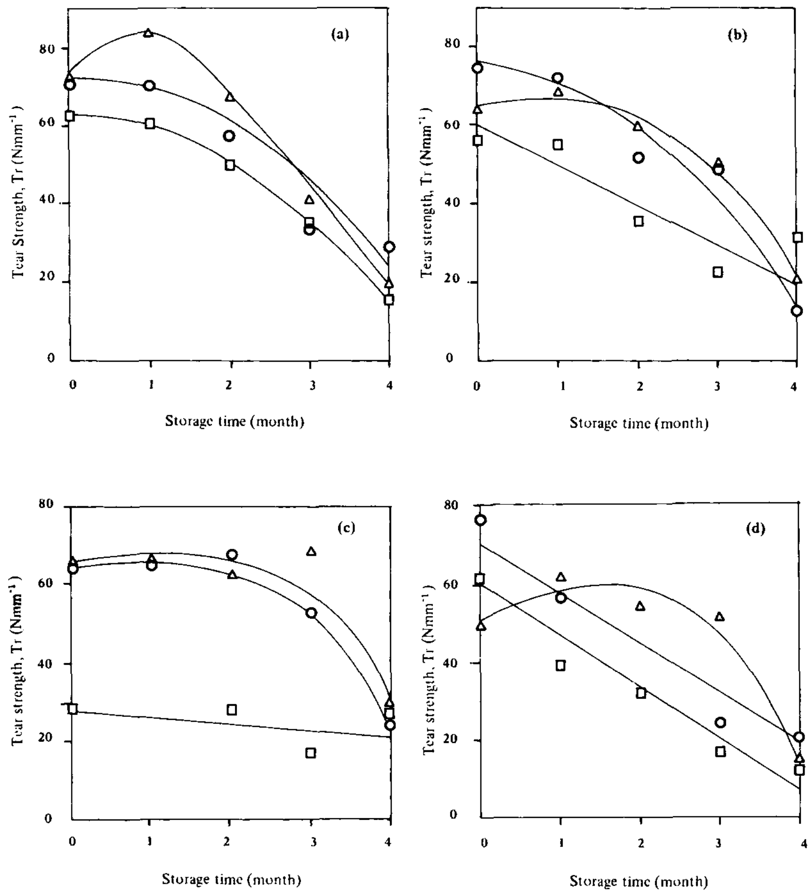

Fig. 5. The change in Tr of the three gloves during storage: (○) S1 gloves; (△) S2 gloves; (□) R gloves. (a) 25 kGy in gamma rays; (b) 25 kGy in electron beam; (c) 50 kGy in gamma rays; (d) 50 kGy in electron beam.

the Tr after 50 kGy irradiation is different. In gamma rays the Tr decrease slightly with storage (Fig. 5), but in electron beam the Tr decrease significantly with storage (Fig. 5). Degradation has occurred in the rubber gloves after 50 kGy irradiation in gamma rays before storage, and hence the decrease of Tr is very low with storage. On the other hand, after 50 kGy irradiation in electron beam, the degradation that has occurred was not complete. Thus, storage causes the Tr to decrease further. This data clearly shows that degradation occurs easier in gamma rays than electron beam irradiation.

Chemiluminescence (CL) Measurement of Rubber Gloves and Latex Film

CL measurement was useful for analysis of oxidative degradation of polypropylene.[19,20] A review article on the applications of CL by Mendenhall[21] explains the correlation of CL measurements in polymeric samples and the formation of peroxy radicals. The CL is emitted from an excited ketone formed by recombination of the peroxy radical in the termination step and the following reaction schemes are presented:

$$RH \xrightarrow{\text{Irradiation}} R\cdot$$

$$R\cdot + O_2 \rightarrow RO_2\cdot$$

$$2\,RO_2\cdot \rightarrow \begin{array}{c} R''-\overset{\overset{\large O^*}{\|}}{C}-R' + ROH + O_2 \\ \downarrow \\ R''-\overset{\overset{\large O}{\|}}{C}-R' + h\nu \end{array}$$

where $RO_2\cdot$ is the peroxy radical and $R''-CO^*-R'$ indicates an excited ketone. The intensity of the CL would be proportional to the concentration of peroxy radicals. Degradation of polymeric materials during storage after irradiation is caused by residual peroxy radical. Thus, correlation of CL intensity and degradation of rubber gloves during storage was confirmed. Figure 6 shows the CL decay curves of the R gloves and the latex film at 40°C after 50 kGy irradiation in gamma rays. The CL intensity is found to be higher in the latex film than the R gloves. Latex film without the presence of antioxidant degrades the most. This is in accordance with our earlier data (swelling ratio and gel fraction). The concentration of peroxy radicals found in the latex film is higher compared to R gloves, and because of this, it is expected that the latex film will degrade further and faster on storage than the rubber gloves. Comparing S1, S2, and R gloves, it is found that S1 gloves degrade the most while S2 the least. The concentration of peroxy radicals that remain in S1 glove is more than either S1 or R gloves. It is expected that S1 glove will degrade further on storage. S2 gloves, on the other hand, have low concentration of peroxy radicals indicating that they will not degrade much on storage. The rate of degradation of R gloves falls in between S1 and S2 gloves. The CL data is not in agreement with the tear strength data. According to the tear strength data, the order of degradation after 50 kGy irradiation in gamma rays is highest in the R glove, followed by latex film, S1, and S2 gloves. Mendenhall[21] found that the presence and amount of antioxidant affect the CL intensity. This discrepancy could be due to the different antioxidant and amount of antioxidant used in the rubber gloves.

CONCLUSION

From the data obtained, it can be concluded that R gloves made by radiation vulcanization of natural rubber latex with the addition of 2-ethylhexyl acrylate sensitizer can be used as rubber gloves. At 25 kGy, the sterilization dose used, R rubber gloves are still acceptable for use as surgical rubber gloves. For sensitivity and long duration of use, R gloves are superior to the sulfur-vulcanized gloves. It was also found that for the three rubber gloves, the tensile strength and elongation at break were not significantly affected after irradiation either

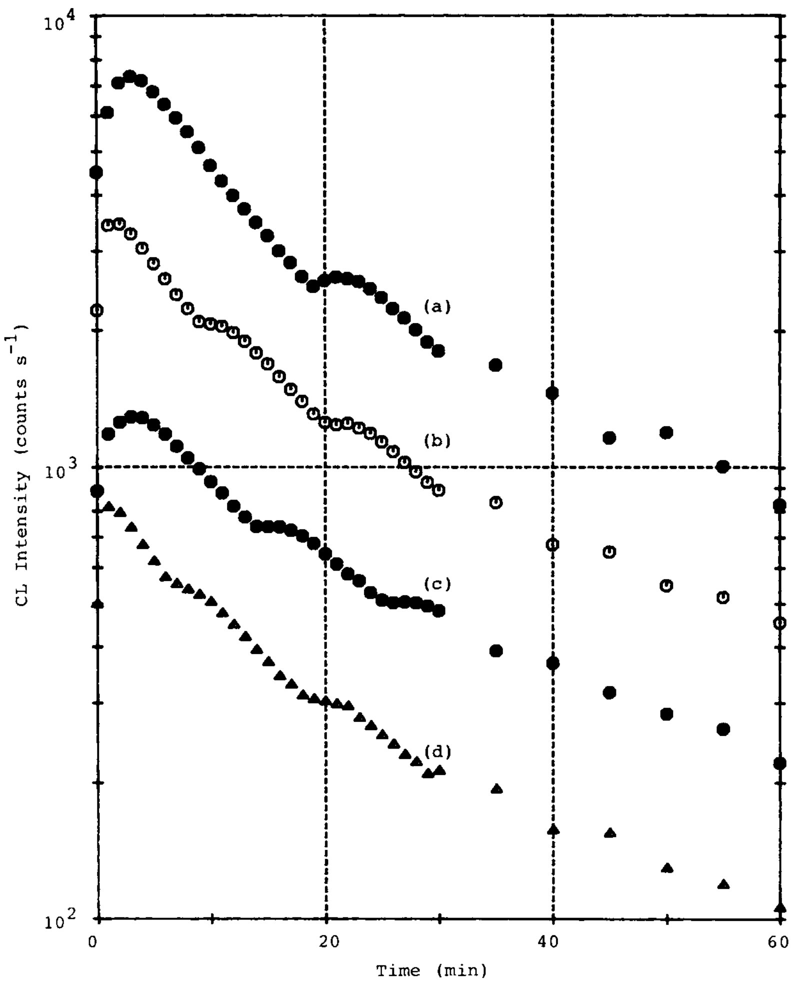

Fig. 6. Chemiluminescence decay curves of the rubber gloves and latex film after 50 kGy irradiation in gamma rays. The measurement temperature was 40°C: (a) latex film; (b) S1 gloves; (c) R gloves; (d) S2 gloves.

in gamma rays or electron beam and also during storage. Tear strength, on the other hand, decreases with increasing dose and storage for all of the rubber gloves. From this data, it was found that degradation is higher in gamma rays than electron beam. From swelling ratio and gel fraction results, it was found that minimal degradation occurs in all the rubber gloves. For the cast latex film, however, degradation occurs at low dose, but crosslinking occurs after 100 kGy irradiation. The CL data shows that the rate of degradation is highest in latex film followed by S1, R, and S2 rubber gloves.

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