

Studies on the Effects of Gamma Irradiation on Nontoxic PVC Formulations

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Synopsis

Thirty-five PVC formulations were compounded initially from which selected nontoxic formulations were subjected to studies in changes of mechanical, optical, migratory, viscosity, and toxicity properties due to gamma irradiation to 2.5 M rads. Degree of discoloration was found to vary from negligible to intense discoloration after irradiation on the selected samples. The nontoxic character of all samples was retained after irradiation. One formulation (R₂) showed excellent radiation resistance and minimum discoloration. Effects of various additives on PVC radiation stability is also discussed.

INTRODUCTION

Gamma irradiation for sterilization of polymeric medical devices has been established as a convenient and safe technique and is finding increasingly widespread use worldwide. An important feature of irradiation by gamma rays is that it generates no radioactivity in materials exposed to it. Irradiated polymers are reported to undergo¹ two basic structural changes (i) a chain scission mechanism occurring as a result of random rupturing of bonds resulting in a loss of molecular weight and (ii) a simultaneous cross-linking phenomenon resulting in formation of three-dimensional networks. Both these processes occur simultaneously during irradiation but one process frequently predominates over the other depending on the nature of the polymer.

Plasticized poly(vinyl chloride), (PVC) has been popularly used in a number of medical applications. As a low cost polymer amenable to widespread property modifications, it is highly popular as evidenced from tonnage and diversity of applications. It has been found that gamma irradiation affects the structural morphology of PVC to a great extent. It undergoes simultaneous degradation and crosslinking due to irradiation. Though virgin PVC resin does show moderate resistance² withstanding 1.9×10^9 ergs/g, plasticized polymer turns yellowish or brownish after exposure to a dose of 2.5 M rads (accepted dose for sterilization). The formation of gaseous hydrogen chloride due to dehydrohalogenation results in a conjugated polyene system³ which is readily attacked by atmospheric oxygen producing carboxyl groups and free radicals. Chain scission and cross linking also results in chromophoric color producing groups resulting in intense color formation. The final properties of the product

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TABLE I
Formulation of Compounding Samples R₁ to R₁₈

Composition	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	R ₈	R ₉	R ₁₀	R ₁₁	R ₁₂	R ₁₃	R ₁₄	R ₁₅	R ₁₆	R ₁₇	R ₁₈
PVC resin ¹	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Di octyl phthalate ²	25	50	25	25	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Secondary plasticizer ³	20	20	20	20	20	20	—	20	20	20	20	20	20	5	5	5	5	5
Ca/Zn stabilizer ⁴	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
Organic phosphite chelator ⁴	—	—	—	—	—	—	—	—	—	—	—	—	1	1	1	1	—	—
Polyethylene glycol-400 ⁵	—	—	—	1	—	10	10	5	—	—	—	—	—	—	—	—	—	—
Glycerol ⁶	—	—	1	—	0.4	—	—	—	—	—	—	—	—	—	—	—	—	—
Styrene ⁷	—	—	—	—	—	—	—	—	0.6	1.2	1.7	2.3	—	—	—	—	—	—
Lubricant ⁸	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.15	0.15	0.15	0.15

* All weights in grams taken in parts per hundred of PVC resin.

1. NOCIL Bombay
2. Indonippon Co., Bombay
3. Indofil Chemicals Ltd., Bombay
4. ALA Chemicals Ltd., Bombay
5. SD's Chemical Ltd., Bombay
6. Glaxo (BDH) Laboratories, Bombay
7. Amrut Industrial Products, Thane, Bombay
8. Local sources

TABLE I. (Continued from the previous page.)

Formulation	R ₁₉	R ₂₀	R ₂₁	R ₂₂	R ₂₃	R ₂₄	R ₂₅	R ₂₆	R ₂₇	R ₂₈	R ₂₉	R ₃₀	R ₃₁	R ₃₂	R ₃₃	R ₃₄	R ₃₅
PVC resin	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Plasticizer DOP	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50	50
Secondary plasticizer	10	15	20	20	20	15	5	5	5	5	5	—	20	20	15	20	20
Ca/Zn stabilizer	2	2	2	2	2	—	—	2	—	—	—	2	2	2	—	2	2
Glycine ⁹	—	—	0.4	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Pentaerythritol ¹⁰	—	—	—	0.4	1.0	—	—	—	—	—	—	—	—	—	—	—	—
Zinc octanoate ¹¹	—	—	—	—	—	2.5	2.5	0.5	0.5	1.5	1.5	—	—	—	—	1.5	—
N-N'Distearyl ¹²	—	—	—	—	—	—	—	0.5	0.5	0.25	0.25	—	—	—	—	1.2	—
ethylene diamine	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Calcium stearate	—	—	—	—	—	—	—	0.2	0.2	1.0	0.5	—	—	—	0.75	—	—
Styrenated phenol ¹³	—	—	—	—	—	—	—	—	—	—	—	—	0.25	0.5	—	—	—
Zinc stearate ¹⁴	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.75	—	—
Trinitrofluorenone ¹⁵	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.2	0.05

^aAll weights in grams taken in parts per hundred of PVC resin.

9. Wilson Laboratories, Bombay
 11. Research Org./Inor. Chemical Corpn., Calif., USA
 12. National Chemical Laboratory,
 Pune, India
 13. Fluka, A. G., Switzerland
 14. Kempasol, Bombay
 15. Fluka, A. G., Switzerland
 10. Wilson Laboratories, Bombay

are therefore considerably affected adversely as a result of these structural changes.

In this work, we are reporting the results of various studies conducted in our laboratory to develop certain radiation-resistant PVC formulations. The effect of gamma radiation on mechanical, optical, migratory, toxicological and viscosity properties of selected formulations is discussed.

EXPERIMENTAL

Dry blending of 35 different formulations of plasticized PVC was carried out in a high-speed mixer (Gunther Papepmier, TGEHK 20). Different re-

TABLE II
Visual Observations of Pre- and Postirradiated Samples

Batch	Preirradiated sample	Postirradiated sample
R ₁	Clear and transparent	Pale reddish yellow discoloration developed
R ₂	Clear and transparent	Clear and transparent
R ₃	Fogginess present	Pale yellow discoloration observed; fogginess present
R ₄	Mild foggy appearance; translucent	Mild foggy appearance and discoloration developed
R ₅	Completely foggy, oily appearance	Completely foggy; oily appearance
R ₆	Mildly foggy, translucent	Discoloration present; fogginess persists
R ₇	Completely foggy; Surface oily	Completely foggy; Surface oily
R ₈	Mild fogginess, translucent	Pale yellow discoloration present; mild fogginess
R ₉ , R ₁₀ , R ₁₁ & R ₁₂	Clear and transparent	Pale yellow discoloration present.
R ₁₃ , R ₁₄ & R ₁₅	Clear and transparent	Intense deep yellow discoloration observed
R ₁₆	Clear and transparent	More intense discoloration than batches R ₉ to R ₁₂
R ₁₇ , R ₁₈	Clear and transparent	Very pale yellow discoloration
R ₁₉	Clear and transparent	Highly yellowish discoloration observed
R ₂₀	Clear and transparent	Marginal discoloration observed compared to R ₂
R ₂₁	Yellowish tinge developed; translucent	Yellow color intensifies
R ₂₂ , R ₂₃	Clear and transparent; white embedded particles present	White particles persist; slight yellowish discoloration observed
R ₂₄ , R ₂₅	Clear and transparent	Marginal discoloration
R ₂₆ , R ₂₇	Yellowish color present	Yellowish color intensifies
R ₂₈	Foggy and yellowish appearance	Discoloration deepens, fogginess persists
R ₂₉	Yellowish appearance	Discoloration intensifies
R ₃₀	Clear and transparent	Marginal discoloration present
R ₃₁ , R ₃₂	Clear and transparent	Yellowish discoloration
R ₃₃	Yellowish discoloration	Yellowish color intensified
R ₃₄ , R ₃₅	Yellowish color	Develops orangish discoloration

ported⁴⁻¹¹ radiation stabilizers like Zinc Octanoate (ROC CO, California, U.S.A.), *N-N'*distearyl ethylene diamine (free sample from National Chemical Laboratory, Poona, India), Pentaerythritol and Glycine (LR grades, Wilson Labs, Bombay, India), Styrenated phenol and 2-4-7, Trinitro 9-fluorenone (Fluka AG, Buchs), Glycerol and Polyethylene glycol-400 (LR Grades, Glaxo Labs, Bombay, India) were tried independently in PVC resin along with other additives in differing compositions (Table I).

Small batches of 200 g were prepared for initial studies. PVC resin (M/s. NOCIL, Bombay) was heated initially to about 45–50°C in the blender and additives were added in order of decreasing viscosity while mixing was carried out at about 1500–1600 rpm. A maximum mix temperature of 125–130°C was achieved for each blending operation. The mixing process was conducted in a dust-free clean area and the whole operation lasted nearly 18 ± 2 minutes. Mix was cooled to room temperature and stored in airtight containers.

All samples for irradiation study were compression molded into disc forms of 5 cm diameter \times 0.2 cm thickness in a compression-molding machine (S.D. Dey & Co., Calcutta) at $175 \pm 3^\circ\text{C}$ at a pressure of nearly 2000 kg/cm². All irradiation work was carried out in a Co⁶⁰ Panoramic Batch Irradiator (Supplied by BARC, Trombay, India). Samples were exposed to a dose of 2.5 M rads at a constant dose rate of 0.47 M rads/h.

Samples R₂, R₁₅, R₁₇, and R₁₈ were selected for further studies out of the 35 irradiated samples. The selection was carried out on the basis of visual observations made on these samples (Table II). Rejected samples exhibited fogginess or developed intense discoloration. Incompatibility of additives with resin, oily and translucent appearance, or development of dark orange colors in certain batches also led to their rejection.

Tensile strength and elongation of pre- and postirradiated R₂, R₁₅, R₁₇, and R₁₈ samples were measured using a Universal tensile testing machine (INSTRON, Model 1193) as per ASTM procedure D 638-80 (Table III). A shore A hardness tester (Blue Steel Engineers, Model 734) was used to measure the hardness values as per ASTM D 676-69T procedure. At least six measurements were taken on each sample and the mean and standard deviation values calculated (Table IV).

Percentage transmission of visible light was measured (Table V) on cast films of pre- and postirradiated samples using a UV-VIS spectrophotometer (Shimadzu Model No. 240). Dimethyl formamide (Analar grade, Glaxo Labs, Bombay) was used as solvent for casting films. The solvent was completely removed by heating the cast films in a vacuum oven for 2–3 h. Similarly,

TABLE III
Stress-Strain Values for Pre- and Postirradiated Samples

Sample	Tensile strength (kg/cm ²)		Elongation (%)	
	Preirradiated	Postirradiated	Preirradiated	Postirradiated
R ₂	95.75	89.2	233.54	214.45
R ₁₇	101	98.6	164.47	115.54
R ₁₈	97.91	100	142.59	158.13
R ₁₅	75.53	74.49	194.47	150.98

TABLE IV
Hardness (Shore A°) Values for Pre- and Postirradiated Samples

Sample	Before irradiation		After irradiation	
	Mean	SD	Mean	SD
R ₂	76.43	± 0.98	76.39	± 0.6
R ₁₇	81.56	± 0.53	82.86	± 0.38
R ₁₈	76.17	± 0.98	76.16	± 0.41
R ₁₅	82.83	± 0.41	82.33	± 0.52

TABLE V
Percentage Transmission Values for Pre- and Postirradiated Samples

Sample	% Transmission	
	Preirradiated	Postirradiated
R ₂	84.5	84.5
R ₁₇	88.0	88.0
R ₁₈	90.0	90.0
R ₁₅	92.5	93.8

TABLE VI
Surface Gloss Values for Pre- and Postirradiated Samples

Sample	Preirradiated		Postirradiated	
	Mean	SD	Mean	SD
R ₂	63.2	± 1.28	59.4	± 0.91
R ₁₇	64.9	± 1.46	59.8	± 0.88
R ₁₈	64.3	± 1.25	60.4	± 3.00
R ₁₅	55.55	± 2.97	54.43	± 1.8

surface gloss of these films were measured using a gloss meter at 45°C (Pacific Scientific Co., U.S.A.). A minimum of six measurements were taken for each sample and mean and standard deviation calculated (Table VI).

Leaching of additives into simulated physiological media such as cotton seed oil and polyethylene glycol-400 were carried out in our laboratory for all pre- and postirradiated samples (refined cotton seed oil was procured locally and PEG-400 used was of laboratory reagent grade from M/s. SD. Labs Bombay).

Samples for leaching studies were prepared by injection-molding PVC compounds in disc form of 50 mm diameter and 2 mm thickness. Each disc was cut diametrically into four equal parts before use. All samples were cleaned thoroughly using soap and water, distilled water, and triple distilled water before use and dried. Nearly 5 g of each sample was weighed accurately and kept in a beaker containing 100 g of cotton seed oil or PGE-400 at 70 ± 1°C in an incubator. The samples were taken out at regular intervals, washed thoroughly again with soap and water, distilled water, and triple distilled water and dried in an oven before weighing. Measurements were made at intervals of 24 h, 48 h, and 72 h for both pre- and postirradiated samples. The difference in weight was calculated and percentage of loss of

TABLE VII
Leaching Values of Plasticizer from Pre- and Postirradiated Samples
Medium: Cotton Seed Oil, Temp: $70^{\circ} \pm 1^{\circ}\text{C}$

Sample	Preirradiated			Postirradiated		
	24 h %	48 h %	72 h %	24 h %	48 h %	72 h %
R ₂	7.049	9.519	9.791	6.927	10.233	11.369
R ₁₇	4.985	7.25	8.843	4.941	6.778	8.331
R ₁₈	4.832	6.88	8.075	4.957	6.754	8.125
R ₁₅	5.345	7.597	9.392	5.826	7.717	9.628

TABLE VIII
Leaching Values of Plasticizer from Pre- and Postirradiated Samples
Medium: Polyethylene Glycol 400, Temp. $70^{\circ} \pm 1^{\circ}\text{C}$

Sample	Preirradiated			Postirradiated		
	24 h %	48 h %	72 h %	24 h %	48 h %	72 h %
R ₂	4.643	7.336	9.318	4.876	7.521	9.533
R ₁₇	2.764	4.63	5.896	2.843	4.681	6.433
R ₁₈	2.826	4.529	5.882	2.899	4.708	6.284
R ₁₅	3.21	5.212	7.129	3.645	5.888	7.655

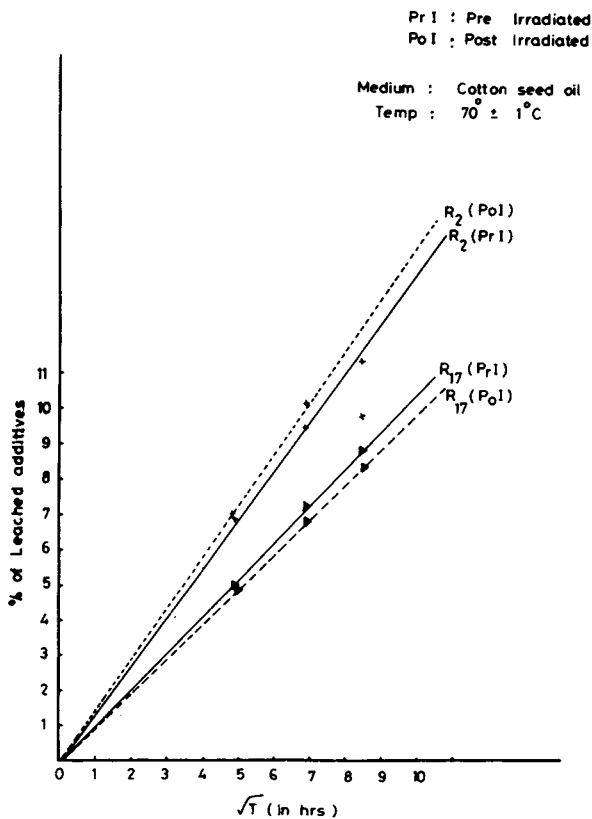


Fig. 1. Leaching curves for R₂ and R₁₇ in cotton seed oil.

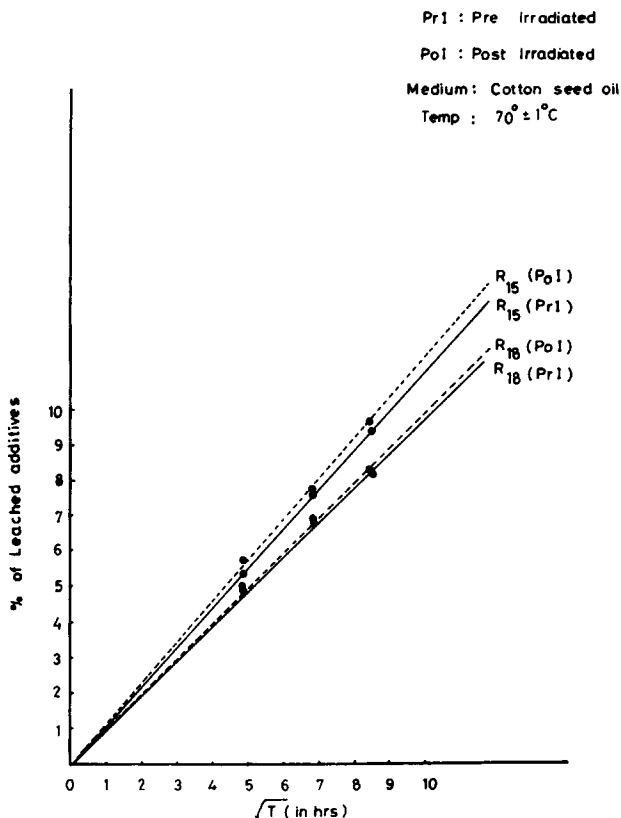


Fig. 2. Leaching curves for R_{15} and R_{18} in cotton seed oil.

additives was determined in each case. The values are given in Table VII and VIII. Figures 1 to 4 represent the leaching behavior exhibited by the samples before and after irradiation.

Viscosity measurements of all samples were carried out using an Ubbelohde viscometer at 25°C in a constant temperature water bath. Solutions of 0.5% PVC were prepared using DMF (analar grade) as solvent. Measurements of time were made for both pre- and postirradiated samples. Specific viscosity was calculated (Table IX) and compared.

Toxic responses of the samples R_2 , R_{17} , R_{18} , R_{15} , R_{20} , and R_{33} were carried out before and after irradiation. R_{33} was selected for toxicity studies additionally since a stabilizer recommended by European Pharmacopoeia was incorporated in this formulation. R_{20} was also tested since it had the same formulation as R_2 but with lower secondary plasticizer concentration. All samples were subjected to acute systemic toxicity test in mice, intracutaneous irritation test in rabbits, and in vitro hemolysis tests and these procedures have been described elsewhere.¹² Results are given in Table X.

RESULTS AND DISCUSSION

Irradiation of limited PVC formulations using various radiation stabilizers showed variations from reported observations. Our studies revealed that

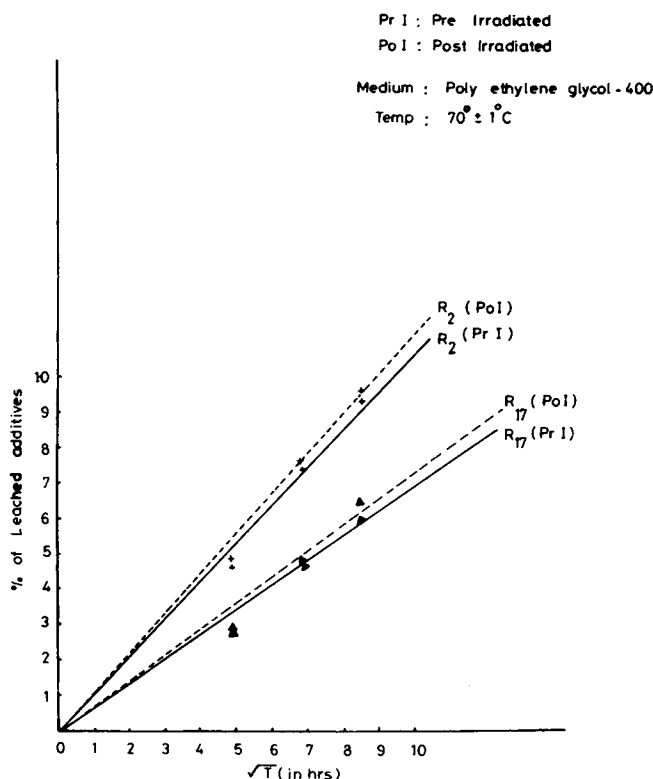


Fig. 3. Leaching curves for R_2 and R_{17} in polyethylene glycol-400.

PEG-400 and glycerol-incorporated PVC tend to produce oily appearance, fogginess, and translucency after molding these compounds, which increased in intensity after irradiation. Intense discoloration was observed after irradiation of compounds containing styrene, styrenated phenols, and 2-4-7, trinitro 9-fluorenone. Incompatibility with PVC resin resulted in elimination of samples containing glycine and pentaerythritol. Another surprising finding was the development of color formation after irradiation in samples incorporated with organic phosphite reported to be a good thermal stabilizer.

Intensity of discoloration varied in the order $R_2 < R_{15} < R_{17} < R_{18}$ among samples selected for further studies. In fact, R_2 practically showed no color difference before and after irradiation exhibiting excellent radiation resistance. Presence of 20 phr of epoxidized soyabean oil plasticizer seems to induce good radiation resistance to PVC. This also confirms the observations made by Lerke and Szymanski¹³ on their studies of effect of epoxy compounds on gamma-irradiated-processed PVC products.

R_{17} showed better radiation resistance than R_{18} and R_{15} . The lubricant stearates present in addition, acting as stabilizers may account for this as is deduced by a comparison of the formulations of R_{17} and R_{18} . The organic phosphite present in R_{15} tends to produce discoloration in the sample.

The tensile strength, and hardness values after irradiation do not show any appreciable change. Minor downward trend in values observed, however,

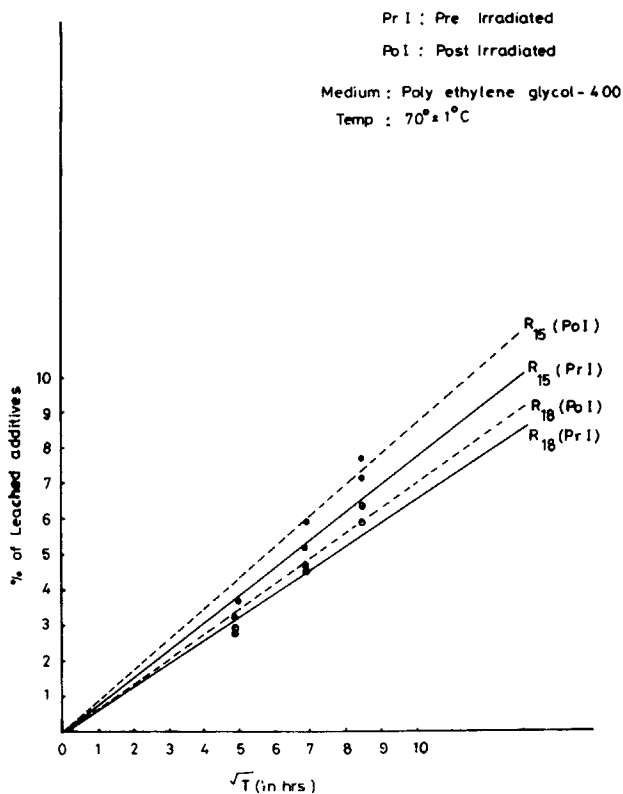


Fig. 4. Leaching curves for R_{15} and R_{18} in polyethylene glycol-400.

TABLE IX
 Specific Viscosity Values for Pre- and Postirradiated Samples

Sample	Before Irradiation		After Irradiation	
	Time in sec.	Spec. viscosity	Time in sec.	Spec. viscosity
R_2	302.22	24.62×10^{-2}	325.79	34.34×10^{-2}
R_{17}	314.97	29.876×10^{-2}	321.38	32.52×10^{-2}
R_{18}	312.17	28.723×10^{-2}	316.69	30.58×10^{-2}
R_{15}	305.91	26.14×10^{-2}	307.77	26.91×10^{-2}

indicates degradation in PVC after exposure to 2.5 M rads. The general trend toward a lower value is nullified by the extent of standard deviation and drawing any worthwhile conclusion is made more difficult. However, elongation values show a considerable decrease. Degradation crosslinking may account for this decrease. The negligible change in hardness values indicates that chemical changes induced by irradiation upon the thick samples used for hardness measurements are not significant enough to exhibit any appreciable change in indentation characteristics or behavior.

Comparison of the percentage transmission values show no appreciable change after irradiation. However gloss values show a uniform decrease after

TABLE X
Toxicity Studies conducted for Pre- and Postirradiated Samples

Sample nos.	Acute systemic toxicity test		Intracutaneous irritation test		Hemolysis test
	Cotton seed oil extract	Saline extract	Cotton seed oil extract	Saline extract	
R ₂	NT	NT	NI	NI	NH
R ₁₇	NT	NT	NI	NI	NH
R ₁₈	NT	NT	NI	NI	NH
R ₁₅	NT	NT	NI	NI	NH
R ₂	NT	NT	NI	NI	NH
R ₁₇	NT	NT	NI	NI	NH
R ₁₈	NT	NT	NI	NI	NH
R ₁₅	NT	NT	NI	NI	NH

Abbreviations: *Nontoxic-NT; Nonhemolytic-NH; Nonirritating-NI.

irradiation which may be attributed to the surface-induced chemical changes which do not considerably affect the bulk properties.

Viscosity values exhibit a uniform increase after irradiation. Predominance of crosslinking over degradation resulting in increase of molecular weight of the fractions may account for this observation. Leaching values for both pre- and postirradiated samples show a relative rate of leaching as $R_2 > R_{15} > R_{17} > R_{18}$. High leaching rate of R_2 may be explained due to the presence of 20 phr secondary plasticizer in addition to 50 phr of DOP. R_{15} , R_{17} , and R_{18} however contain only 5 phr of epoxidized oil while concentration of DOP remains the same as in R_2 . Postirradiated samples exhibited marginally higher leaching characteristics compared to preirradiated samples. The leaching behavior shown in both PEG-400 and cotton seed oil were found to be similar. The relative rate of leaching seems to be maximum during the initial 24 h for all tested samples before and after irradiation. Plot of percentage of leaching against square root of time as in Figures 1 to 4 indicated the process to be diffusion controlled¹⁴ though this fact is immaterial for the choice of optimal PVC composition.

Toxicity studies reveal the nontoxic, nonirritating, and nonhemolytic character of R_2 , R_{15} , R_{17} , and R_{18} and, in addition, both R_{20} and R_{33} are retained after irradiation. However, R_{33} being used as a radiation-stable formulation is highly doubtful as it tends to develop intense discoloration after irradiation.

CONCLUSION

Incorporation of additives such as styrene, polyethylene glycol-400, glycerol, glycine, penta erythritol, *N-N'* distearyl ethylene diamine, styrenated phenols, or trinitrofluorenone in limited formulations did not seem to improve radiation stability considerably. However, presence of 20 phr epoxidized oil in formulation R_2 seems to render excellent radiation resistance to PVC. Presence of marginal discoloration after irradiation in formulation R_{20} containing 15 phr epoxidized oil suggests an optimum concentration of 15–20 phr of oil for PVC radiation-stable compounds. Contrary to expectations, the commercial nontoxic organic phosphite stabilizer did not show good stabiliz-

ing action. However, the radiation stability seems to improve marginally in presence of lubricant. The effect of gamma radiation (2.5 M rad) on the mechanical, optical, and leaching characteristics of selected formulations seems to be marginal. The nontoxicity of the formulations studied is also not affected by gamma irradiation to 2.5 M rads.

The authors wish to thank the Board of Research in Nuclear Sciences, DAE, Govt. of India for funding this project. We wish to express our deep gratitude to Dr. N. G. S. Gopal, Head, ISOMED Division, BARC, Bombay for his valuable suggestions during the course of this work. We are grateful to Dr. M. S. Valiathan, Director, SCTIMST and Mr. A. V. Ramani, Head BMT Wing for providing us the facilities for doing this work. We are very much indebted to the valuable contributions made by Miss. Sarala Kumari and Miss. Mythili and our colleagues of Division of Polymer Technology towards the successful culmination of this work. Thanks are also due to the Laboratory for Technical Evaluation of Biomaterials for doing the tensile tests, the Division of Materials Toxicology for conducting the toxicity tests and Mr. K. P. R. Bhas for arranging the irradiation work.

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Received October 2, 1986

Accepted March 4, 1987