Mechanical Properties of Styrene-Butadiene Rubber Cured by Ionizing Radiation in the Presence of Sulfur and Polyfunctional Agent

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ABSTRACT

The mechanical Properties of Styrene-Butadiene Rubber (SBR) samples cured by a combination of sulfur and ionizing radiation in the presence of polyfunctional crosslinking agent were studied. SBR formulations containing various concentrations of trimethyl propane triacrylate (TMPTA) were irradiated at absorbed doses in the range of 35-200 kGy. The influence of TMPTA on the mechanical properties, solubility % and swelling % were investigated. The various formulations were compared based on crosslink density expressed by 200% modulus (i.e. tensile stress at 200% elongation). The increase in TMPTA concentration has led to the decrease in the absorbed dose required to achieve full-cure conditions. Another set of SBR formulations containing partial levels of sulfur in the presence of the same TMPTA concentrations as the earlier formulations were irradiated at the same absorbed dose range. The presence of sulfur has further decreased the absorbed dose required to achieve full-cure conditions

INTRODUCTION

Vulcanized rubber, i.e. crosslinked rubber, can be prepared by different processes. Vulcanizing agents are necessary for the crosslink formation. These vulcanizing agents are mostly sulfur or peroxide or high energy radiation. In radiation vulcanization of rubber, a small concentrations of polyfunctional crosslinking agents are usually added to achieve reasonable crosslinking density at lower irradiation doses. Hence, to avoid damage of polymeric chains at high irradiation doses [1-3]. The resulting properties of the vulcanized rubber depend to some extent on the number and type of crosslinks.

SBR is the most widely produced elastomer. It has a vast range of applications and is relatively inexpensive compared to other elastomers. Sulfur curing of SBR has been the popular method by the industry. Vulcanization of SBR when cured with sulfur produces one crosslink per 200 structural units in most practical applications; the crosslink density (and thereby the modulus) can be changed by changing the sulfur content. Radiation dose can produce a crosslink density equivalent to the curing conditions obtained with sulfur. However, radiation has two potential advantages over sulfur; (1) the C-C crosslinks are expected to give radiation cured SBR better mechanical properties at higher temperature (e.g. high hot tear strength). (2) Radiation induced

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crosslinks can be produced in a truly random pattern with great uniformity in local concentration. In sulfur-cured systems, uniformity of crosslink density is more difficult to achieve due to heterogeneity in the mixing process. These advantages were demonstrated with the hot tear strength reported by Silverman and Lambert[4]. Moreover, work by Basfar and Silverman demonstrated that an absorbed dose of 150 to 200 kGy achieves full-cure conditions for sulfur-radiation cured SBR formulations containing a partial sulfur concentration of 0.5 phr [5-7].

This work explored the effect of γ-radiation on the physical and mechanical properties of SBR formulations containing different concentrations of TMPTA as polyfunctional crosslinking agent. Moreover, the influence of incorporating sulfur in the SBR compounds was also investigated.

EXPERIMENTAL:

Materials:

A commercial grade styrene-butadiene rubber (SBR-1502) with 23.5% styrene content was obtained from Copolymer Co.(COPO), USA. The polyfunctional crosslinking agent used is trimethylol propane triacrylate (TMPTA) from Cray Vally Co. in France.

Compounding and Vulcanization:

The various formulations utilized in this study are presented in Table 1. A Brabender Plasti-Corder Model PL-2000 and an internal mixer Model 3505 were used. The compounding was in accordance with ASTM D-3182. Vulcanization characteristics were measured using Monsanto-oscillating disk cure-meter Model ODR-2000E in accordance with ASTM D-2084. A hydraulic hot press by PHI Co. Model G236 H was used to press and vulcanize rubber sheets with an average thickness of about 2 mm in accordance with ASTM D-3191. The formulations containing sulfur were vulcanized at 150°C for 30 minutes whereas the formulations containing the polyfunctional crosslinking agent were sheeted at 100°C for 3 minutes, under 20 MPa pressure.

Irradiation

A Cobalt-60 gamma cell Model GC-220 manufactured by Nordion Int. Inc. in Canada was used for irradiation at a dose rate of 12.2 kGy/h, 40°C and in nitrogen atmosphere.

Physical Properties

The physical properties which were studied are as follows :

1. Solubility and swelling measurements were performed in toluene. The soluble fraction was calculated by extracting soluble part from each sample using soxhlet for 24 h, and drying the insoluble part completely in vacuum oven at 50 °C. The swelling measurements were performed in fresh toluene using the insoluble part after extraction for 24 h at 25 °C.

2. Mechanical properties measurements were carried out using an Instron Universal testing machine Model 4505 in accordance with ASTM D-412. Five samples from each batch were tested. Dumbbell shaped specimens were cut from sheets using a steel die with standard neck-width of 3mm and length of 20mm.

Results and Discussion

The mechanical properties of formulations containing the polyfunctional agent are shown in Figs. 1-3.

The modulus stress at 200% elongation (M200) of the samples S-1 to S-4 containing no sulfur and sensitized by different concentrations of TMPTA coagent are shown in Fig. 1 as a function of irradiation dose including the control sample (S-0). It can be seen from this figure that the values of M200 increased linearly with the increase of both the irradiation dose and the concentration of the coagent. The stress value at low elongation of a vulcanizate is proportional to its degree of crosslinking, i.e. crosslinking density. Hence, the incorporation of the crosslinking agent in the system leads to increase in the crosslinking density of the matrix and this increase depends upon the concentration of the added coagent.

The ultimate tensile strength (TS) of these samples are shown in Fig. 2. TS of the control sample increased linearly with increasing the irradiation dose. Moreover, addition of small concentrations of the coagent, i.e. up to 0.82 phr, leads to appreciable increase in TS at low irradiation doses, i.e. 50 kGy. The successive increase in the concentration of the coagent over 0.82 phr, resulted in a little increase followed by a decrease in TS. Moreover, the TS increased with increasing irradiation dose and the rate of increase declined above 100 kGy. In addition, this increase in TS diminishes as the concentration of the coagent is increased. At high irradiation doses, the values of TS are very close for the different sensitized samples. This may be explained as, when rubber is subjected to ionizing radiation, two processes simultaneously take place, i.e. crosslinking and scission, which affect its properties in opposite directions. These processes depend on the type of the sample, the incorporated additives and its susceptibility to radiation as well as the irradiation dose. The incorporation of the coagent has induced additional crosslinking in the rubber matrix, especially at lower irradiation doses. At higher irradiation doses and in presence of high concentration of the coagent, the probability of scission is predominant, hence, the tensile strength declined.

Elongation at break for the SBR samples containing different concentrations of TMPTA are shown in Fig. 3. The elongation at break decreased with increasing both the concentration of the coagent and the irradiation dose. The irradiated samples with no coagent have the highest ductility compared to those containing 6.67 phr of TMPTA. This can be also illustrated from the swelling and solubility measurements which are presented in Fig. 4 and Table 2, respectively.

The swelling measurements are shown in Fig. 4. It can be seen that a linear

relationship exists between the swelling % and the dose of irradiation for all samples. Moreover, the rate of decrease of the swelling depends on the concentration of the added coagent. Swelling is inversely proportional to the crosslink density. Hence, crosslink density increases with increasing both the irradiation dose and the content of the coagent. This is also concluded from the solubility measurements which is presented in Table 2 after applying Charlesby-Pinner Equation[8]:

$S+\sqrt{S} = p_o/q_o + 2/q_o\ U\ D.$

where S is the soluble fraction of the rubber sample in toluene, D is the dose of irradiation, p_o is the degradation density, average number of main chain scission per monomer unit and per unit dose; q_o is crosslinking density, proportion of monomer units crosslinked per unit dose; U is initial weight-average degree of polymerization (units per initial weight average molecule).

When polymers are subjected to ionizing radiation, crosslinking and main chain scission are among the chemical effects observed. The processes ultimately cause formation of insoluble gel if crosslinking predominates over scission [9]. These chemical effects are more pronounced in presence of the coagent, due to its susceptibility towards ionizing radiation. This could be explained from Table 2 as follows, when the content of the TMPTA coagent in the compounds is increased from 0.82 to 6.67 phr, the probability of scission increased about 3 times. In contrast, the probability of crosslinking increased about 2.6 times which affects negatively the mechanical properties at both high content of the coagent and high irradiation dose.

The mechanical properties as a function of irradiation dose for the formulations vulcanized by sulfur in absence and in presence of different concentrations of the polyfunctional agent TMPTA are shown in Figs. 5 - 7.

The M200 of samples containing sulfur and sensitized by different concentrations of TMPTA (S-6 to S-8) are shown in Fig. 5 as a function of irradiation dose including the control sample (S-0) and the sample S-5 without the coagent. It can be seen from the figure that the M200 increased linearly with the increase of irradiation dose, with the exception of S-7 which demonstrated polynomial relationship. Moreover, the vulcanization in presence of sulfur leads to increase in the M200 about 5 times compared with that in its absence at 40 kGy. Meanwhile, the combination of both sulfur and small concentration of TMPTA, namely 0.41 phr increased M200 about 5.7 times at the same irradiation dose, i.e. 40 kGy. However, the rate of increase in M200 with irradiation dose is 0.025 for both samples not containing TMPTA in absence or in presence of sulfur,i.e. S-0 and S-5 samples. Combining a small amount of 0.41 phr of the TMPTA with sulfur in the compound, i.e. S-6, improved the rate of increase of M200 with irradiation dose about 50%. This apparently means that the main effect of the radiation is on the rubber matrix and the polyfunctional coagent and not the sulfur, i.e. no synergistic effect on the stress property due to the combination of sulfur and irradiation dose was found in the range of irradiation dose studied. This can be seen also from the TS-irradiation dose relationship for the same samples shown in Fig. 6. The vulcanization of SBR by sulfur leads to increase in the value of TS about 14 times compared with that of the control

sample at 40 kGy. However, almost no change with the increase of irradiation dose was detected in those samples. Meanwhile, the combination of the coagent with sulfur in the SBR compounds resulted in a slight increase in the values of TS especially at lower irradiation doses, i.e. up to ~ 75 kGy. Increasing the irradiation dose higher than 75 kGy leads to decrease in the TS which is proportional to both the concentration of the coagent and the irradiation dose.

The elongation at break (E%) as a function of irradiation dose is shown in Fig. 7. In absence of the crosslinking agent, the values of E% steadily decreased with the increase of irradiation dose. The incorporation of sulfur leads to additional decrease in the values of E% and the rate of decrease with irradiation dose is almost similar to that in its absence. The incorporation of the coagent leads to a further decrease in the E%, which depends on the concentration of the added coagent as well as the irradiation dose.

The variation of swelling % with irradiation dose is shown in Fig. 8. It can be seen that that the swelling % for all the samples decreased linearly with different rates with the increase in irradiation dose. Moreover, the vulcanization by sulfur leads to appreciable decrease in the swelling %. At the same time, combination of sulfur and small concentration of the coagent, i.e. 0.41 phr, leads to a further decrease in the swelling %, ranging between about 39 % at 50 kGy and about 6 % at 200 kGy, compared with those of the corresponding samples not containing sulfur.

The soluble fraction (S_f)as a function of irradiation dose is shown in Fig. 9. It can be seen from the figure that the S_f of the SBR compound not containing vulcanizing agents decreased linearly with the increase of irradiation dose. However, when this SBR compound was vulcanized by sulfur and irradiated at 60 kGy, the value of S_f decreased about 72 %. Increasing the irradiation dose higher than 60 kGy, slightly affects the values of the vulcanized samples either in absence or in presence of the coagent.

Conclusions

The findings of this work can be summarized as follows:

1 The crosslink density (expressed by 200% modulus stress) of γ-irradiated SBR compounds containing TMPTA as crosslinking agent increased linearly with the increase of both the concentration of TMPTA and the irradiation dose in the range studied (35 -200 kGy).
2. Addition of small amount of TMPTA to the rubber compounds and irradiated at low irradiation dose, i.e. 50 kGy, leads to improving the TS while maintaining good elasticity, i.e. E% ~ 540.
3. The combination of both sulfur and a small concentration of TMPTA namely, 0.41 phr in the rubber compounds and irradiated at a low absorbed dose, i.e. 40 kGy, appreciably increased the M200 as well as the rate of increase of M200 with irradiation dose.
4. The vulcanization of SBR compounds by sulfur leads to an increase of TS about 14 times at 40 kGy compared with that in its absence. Moreover the combination of the coagent or increasing the irradiation dose resulted in no further improvement in TS.

On the other hand, scission predominates at both higher irradiation doses and higher TMPTA concentrations.

5. When the SBR compound is vulcanized by sulfur and irradiated at 60 kGy, the solubility in toluene decreased about 72%.

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Table 1: SBR formulations for radiation cured and sulfur-radiation cured systems.

Notation		Ingredients (phr)				
Code	**SBR-1502 (phr)**	**FEF-Carbon black**	**Additives**	**Polyfunctional X-linking agent (TMPTA)**	**Sulfur**	**CBS[b]**
S-0	100	50	6.0	--	--	--
S-1	100	50	6.0	0.41	--	--
S-2	100	50	6.0	0.82	--	--
S-3	100	50	6.0	1.64	--	--
S-4	100	50	6.0	6.67	--	--
S-5	100	50	6.0	--	0.5	2.0
S-6	100	50	6.0	0.41	0.5	2.0
S-7	100	50	6.0	0.82	0.5	2.0
S-8	100	50	6.0	1.64	0.5	2.0

a: The additives in phr, were ZnO 4.0, stearic acid 2.0, antioxidant (Winstay 100) 1.0.
b: CBS = N-c-Cyclohexyl-2-benzothiazole sulfenamide.

Table 2: Solubility parameters of irradiated SBR compounds containing different concentrations of TMPTA crosslinking agent.

Code	p_o/q_o	$*q_o$	$**p_o$
S-0	0.220	191	42
S-1	0.240	530	127.2
S-2	0.260	670	174.2
S-3	0.297	990	294
S-4	0.305	1740	530.7

$*q_o$ = Relative to crosslink density = q_o (UD)/2 x 10^{-4}
$**p_o$ = Relative to degradation density = p_o/q_o x $*q_o$

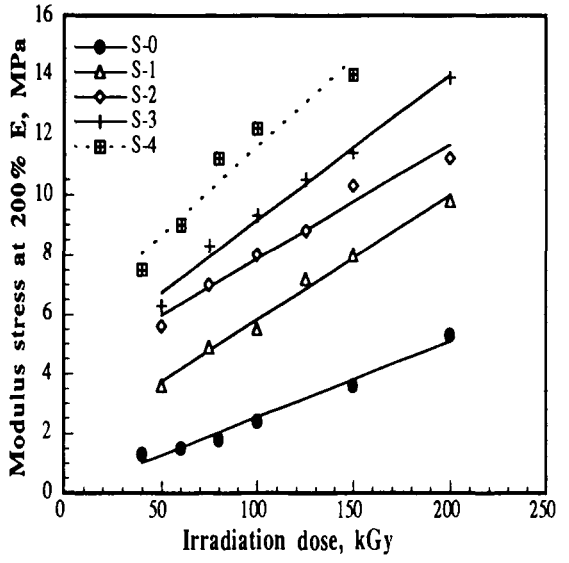

Fig. 1: The modulus stress at 200% elongation, as a function of irradiation dose for SBR compounds containing different concentrations of TMPTA coagent, including the control sample.

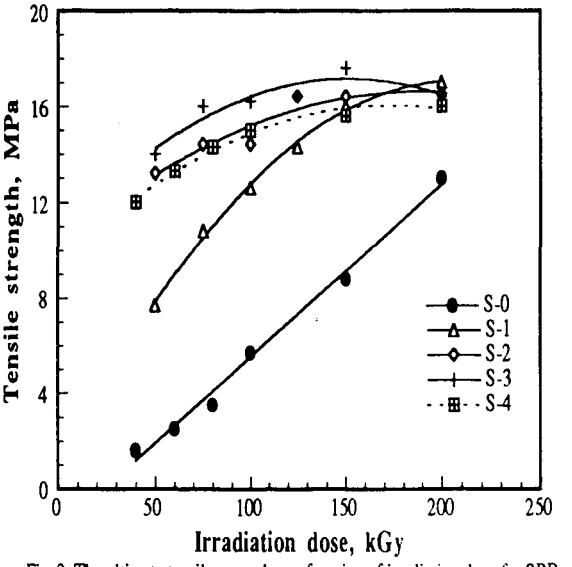

Fig. 2: The ultimate tensile strength as a function of irradiation dose for SBR compounds containing different concentrations of TMPTA coagent including the control sample.

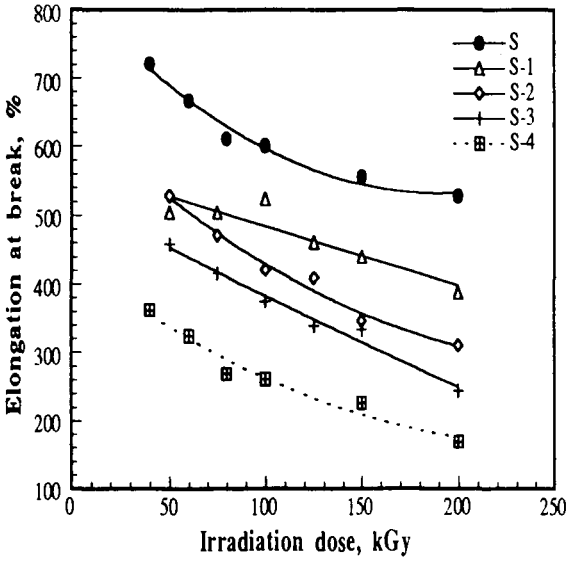

Fig. 3: The elongation at break as a function of irradiation dose for SBR compounds containing different concentrations of TMPTA coagent including the control sample.

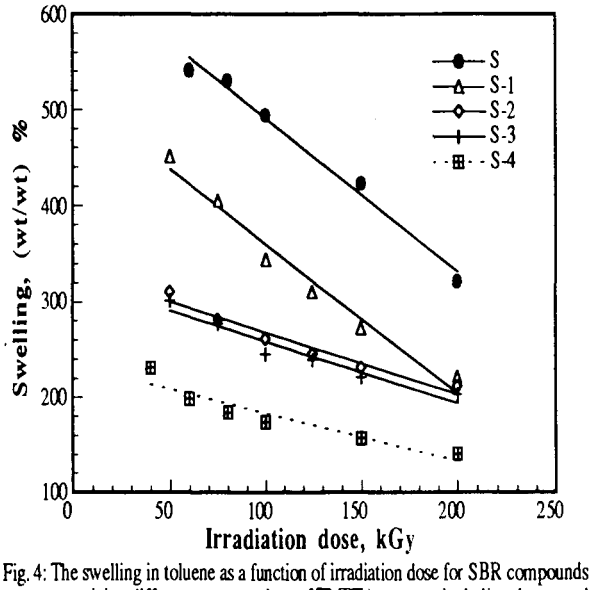

Fig. 4: The swelling in toluene as a function of irradiation dose for SBR compounds containing different concentrations of TMPTA coagent, including the control sample.

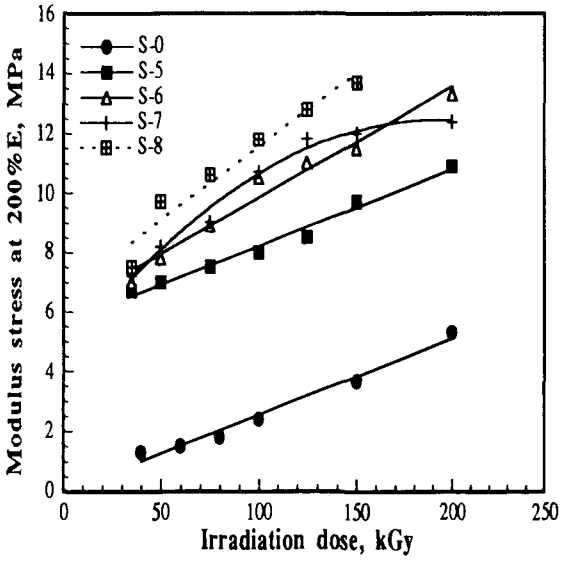

Fig. 5: The modulus stress at 200% elongation as a function of irradiation dose for SBR compounds vulcanized by sulfur and containing different concentrations of TMPTA coagent including the control samples.

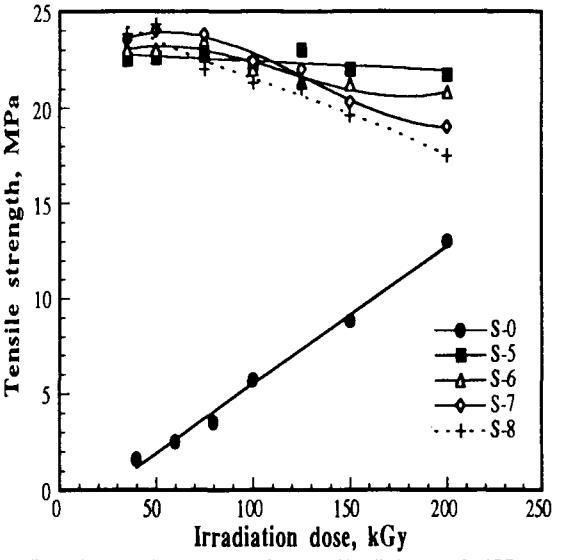

Fig. 6: The ultimate tensile strength as a function of irradiation dose for SBR compounds vulcanized by sulfur and containing different concentrations of TMPTA coagent including the control samples.

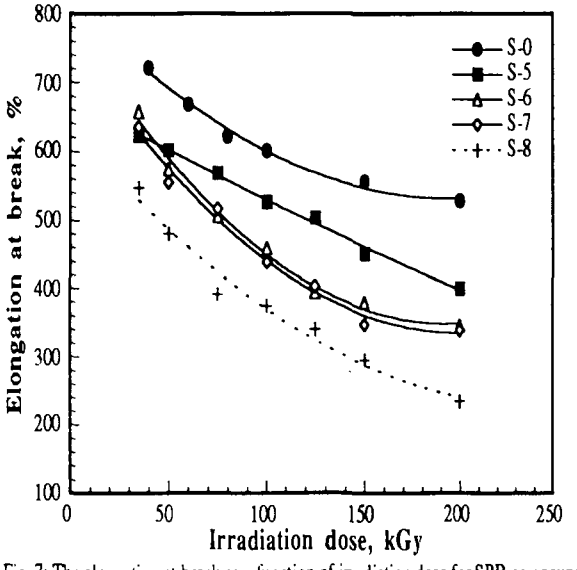

Fig. 7: The elongation at break as a function of irradiation dose for SBR compounds vulcanized by sulfur and containing different concentrations of TMPTA coagent including the control samples.

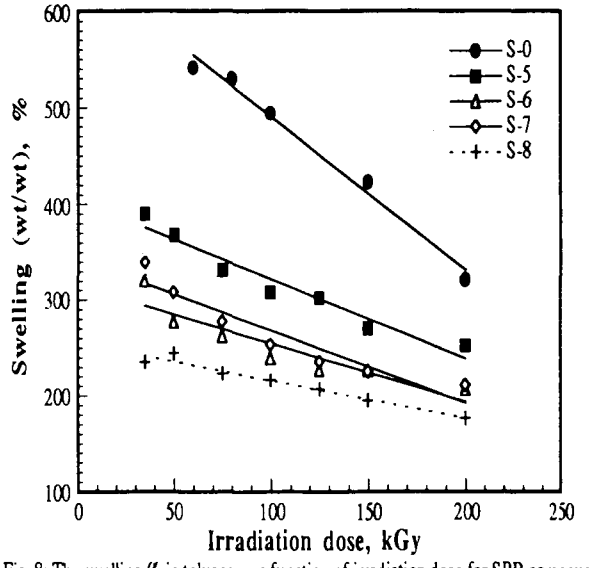

Fig. 8: The swelling % in toluene as a function of irradiation dose for SBR compounds vulcanized by sulfur and containing different concentrations of TMPTA coagent including the control samples.

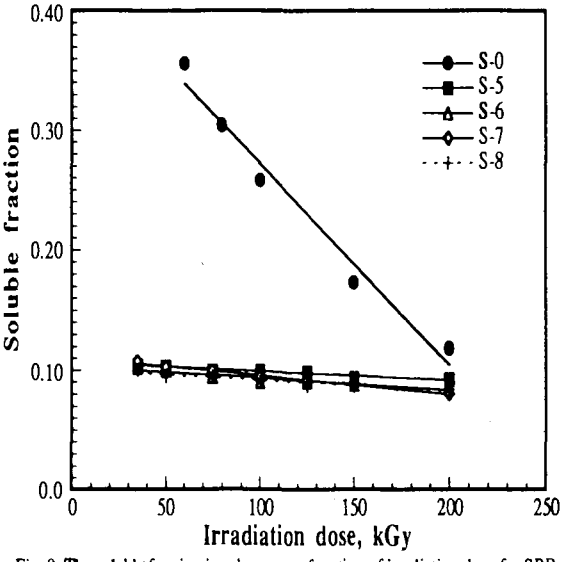

Fig. 9: The soluble fraction in toluene as a function of irradiation dose for SBR compounds vulcanized by sulfur and containing different concentrations of TMPTA coagent including the control samples.