

High-Energy Radiation-Resistant Elastomeric Vulcanizates. I. Chlorosulfonated Polyethylene

CHAITANYA S. SHAH,¹ MAHENDRA J. PATNI,¹ MANISH R. DESAI,² and MADHAV V. PANDYA^{2,*}

¹Materials Science Centre and ²Chemistry Department, Indian Institute of Technology, Powai, Bombay 400 076, India

SYNOPSIS

In this article, a detailed study on the stabilization of chlorosulfonated polyethylene (CSP) vulcanizates in γ radiation is reported. The special additives (antirads) for the stabilization are synthesized from polynuclear aromatics and formulated in the laboratory. The effect of these antirad formulations on the physicochemical structure and performance properties of these materials is studied by monitoring the degradation in γ radiation using resistivity, wide-angle X-ray diffraction, and mechanical properties. Antirad formulations to stabilize CSP against a total dosage of 200 Mrads of γ radiation have been achieved. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Over the past decade, an increasing use of polymeric materials in nuclear installations has boosted the development of radiation-resistant materials. These efforts are directed to developing a special class of polymeric materials with inherent radiation resistance as well as for modification of the existing formulations of polymers. The interaction of nuclear radiation with polymeric materials is documented in detail mainly for space research.¹ These investigations are primarily for an inert environment, resulting in the paucity of data in the literature for the more important oxidative environment studies. The oxidation effects that are induced under these conditions dominate the degradation chemistry, resulting in very high radiation damage.¹⁻³ The current trends in the development of materials with enhanced resistance to degradation in environments of high-energy radiations have been critically reviewed by Clough and Gillen.^{4,5}

The interaction of polymer with high-energy radiation results in the formation of highly excited electronic states within the material, subsequently leading to bond scission to form free radicals. These are primary reactive species responsible for the ra-

diation-induced chemistry. The schematic presentation of the reaction mechanism for the polymer-radiation interactions is given in Figure 1. Keeping these reactions in view, mainly three types of stabilizers (termed as antirads) are used, namely, (a) energy scavengers, (b) radical scavengers, and (c) oxygen scavengers, for retarding the deterioration effects of γ radiation.

Energy scavengers are primarily aromatic molecules that can act as traps for the excited electronic states generated in the polymer. These energy scavengers, after absorbing energy, relax back to their ground state with a very high efficiency. The efficiency of absorbing radiant energy by such aromatic compounds is generally related to their size. Thorough care is required in selecting compounds used as energy scavengers. If the relaxation of the excited energy scavenger occurs as fluorescence or phosphorescence, it would be absorbed by the polymer molecule. This would lead to physicochemical changes and, hence, degradation would occur at the faster rate.

Radical scavengers reduce the radiation damage by trapping free radicals that are formed in the elastomer matrix. These types of stabilizers either continuously diminish or they may regenerate by redox coupling with the polymer. Many commercially available antioxidants have shown the radical and oxygen scavenging actions.^{6,7}

In our earlier work, we showed the importance of

* To whom correspondence should be addressed.

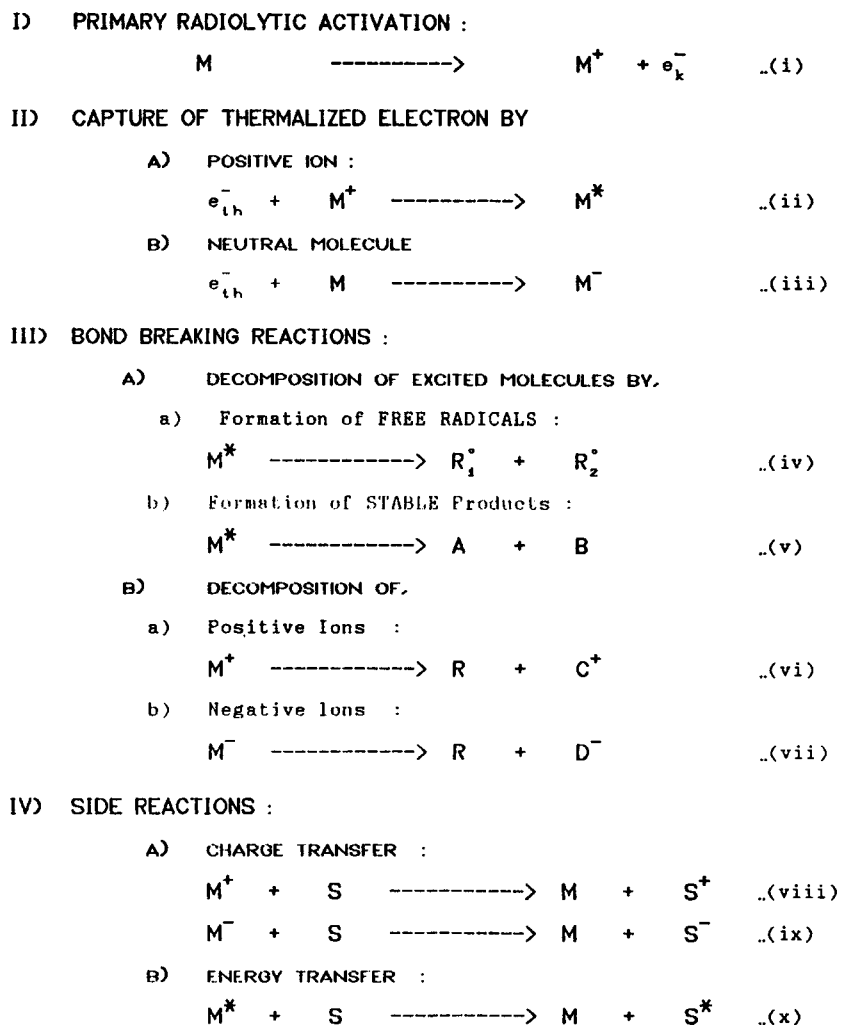


Figure 1 High-energy degradation mechanism—a schematic representation.

the antirad formulation consisting of energy scavenger, free radical scavenger, and oxygen scavenger molecules to achieve the stability of 100 Mrads in chlorosulfonated polyethylene (CSP) and EPDM vulcanizates.⁸ In this article, we present a study of variation in antirad formulations for CSP to achieve the stability to withstand 200 Mrads of γ radiation.

EXPERIMENTAL

Materials

Acenaphthene and pyrene (Py) were obtained from Aldrich and Fluka, respectively. Solvents were obtained locally and were used after fractional distillation. All other materials were obtained from the local chemical market and were used as received.

Synthesis of Antirads

Brominated acenaphthene (BrAc) was synthesized by reacting, in the dark, acenaphthene and excess bromine (1 : 6 mol) in carbon tetrachloride with anhydrous $FeCl_3$ as the catalyst for 4 h. The pentabromoacenaphthene product was washed with water to remove the $FeCl_3$ and recrystallized from benzene.⁹

Poly(acenaphthene sulfide) (PACSu) and poly(pyrene sulfide) (PPySu), adducts of acenaphthene and pyrene with sulfur, respectively, were synthesized by the following steps in an inert environment: (a) dry mixing of aromatics with sulfur in a 1 : 8 mol ratio, (b) slow heating to 120°C in 1 h followed by (c) slow heating up to 250°C in 3 hours, and further (d) heating at 350°C until evolution of hydrogen sulfide ceased, which is for 2–3 h. The prod-

Table I Recipe of CSP Vulcanizates

Material	Quantity (g)
Chlorosulfonated polyethylene ^a	100.0
Paraffin wax	4.0
China clay	20.0
Dibutyl lead phthalate	20.0
Aluminum silicate	30.0
Carbon black SRF	5.0
ARD resin	4.0
Dicumyl peroxide (95%)	3.0
Antirad ^b	4.0

^a CSM 40 from DuPont.

^b The following antirads were used—Recipe 1: Control, no antirad; Recipe 2: brominated acenaphthene (BrAc); Recipe 3: pyrene (Py); Recipe 4: poly(acenaphthene sulfide) (PACsU); Recipe 5: poly(pyrene sulfide) (PPySu).

ucts obtained on cooling were a brittle metallic black mass.

As per the elemental analysis, PACsU has five hydrogen of acenaphthene replaced by sulfur and PPySu has six hydrogen of pyrene replaced by sulfur to give polymeric adducts. Both these compounds are found to be insoluble in all the solvents. In DTA-TG analysis, PACsU was found to decompose at 500°C, whereas PPySu was found to decompose at 550°C in oxidative environment, without melting, with a single exotherm in single-step degradation.

Compounding and Molding

Compounding of CSP was carried out with the necessary ingredients as per the compositions given in Table I. Compounding was done in the open roller mill at room temperature. The test slabs of 15 cm × 15 cm × 0.2 cm were molded using the flywheel-type press at 160°C and 7 tons pressure for optimum cure time determined from the Monsanto Rheo-

meter MDR 90. The cure characteristics data for these vulcanizates are given in Table II.

Specimens for wide-angle X-ray study were cut from the test slabs having dimensions of 1 × 2.5 × 0.2 cm. The dumbbell-shape tensile specimens and 6.5 cm-diameter disc specimens for resistivity measurements were also cut from the test slabs prior to radiation exposure.

Exposure Conditions

All specimens were subjected to γ radiation exposure in Co⁶⁰ at 40°C at a dose rate of 0.5 Mrad/h with a continuous flow of air (10 mL/min). This ensures a fresh environment throughout the exposure for homogeneous degradation.

Testing Procedures

Volume and Surface Resistivity

The volume and surface resistivity measurements were carried out using a Hewlett-Packard high-resistance meter HP 4329a on the disk specimen. The measurements were carried out before as well as after γ irradiation of varying cumulative dosage. Time-domain measurements were carried out over a period of time at various intervals after γ irradiation dose of 20 Mrads.

Wide-Angle X-ray Diffraction Spectroscopy

The wide-angle X-ray diffraction (WAXD) studies were carried out using the test specimen of 1 × 2.5 × 0.2 cm. Specimens were removed from the γ chamber followed by conditioning at room temperature for 1 h before subjecting them to the WAXD studies using a Philips PW 1820 diffractometer. Specimens were carefully inserted back in the γ chamber after each scanning. To quantify the extent of damage caused due to γ radiation, the same specimen was used, assuming that there would be very

Table II Rheometric Data for CSP Vulcanizates

Recipe No.	Minimum Torque (dN m)	Maximum Torque (dN m)	Induction Time (min)	Scorch Time (min)	Optimum Cure Time (min)
1	10	68	1.5	2.5	20.0
2	9	66	1.4	2.5	19.5
3	8	66	1.6	2.6	20.0
4	10	67	1.5	2.4	19.5
5	9	67	1.6	2.5	19.5

little effect of X-rays on the specimen during the WAXD measurements.

Mechanical Properties

Mechanical properties, viz., tensile strength, modulus, elongation at break, and hardness, were measured as per appropriate ASTM procedure.

RESULTS AND DISCUSSION

Surface and Volume Resistivity

The increase in the surface and volume resistivity seen in the time-domain studies on a specimen after irradiation of 2 Mrads [Fig. 2(a) and (b)] indicate that the transient charge species are formed and they

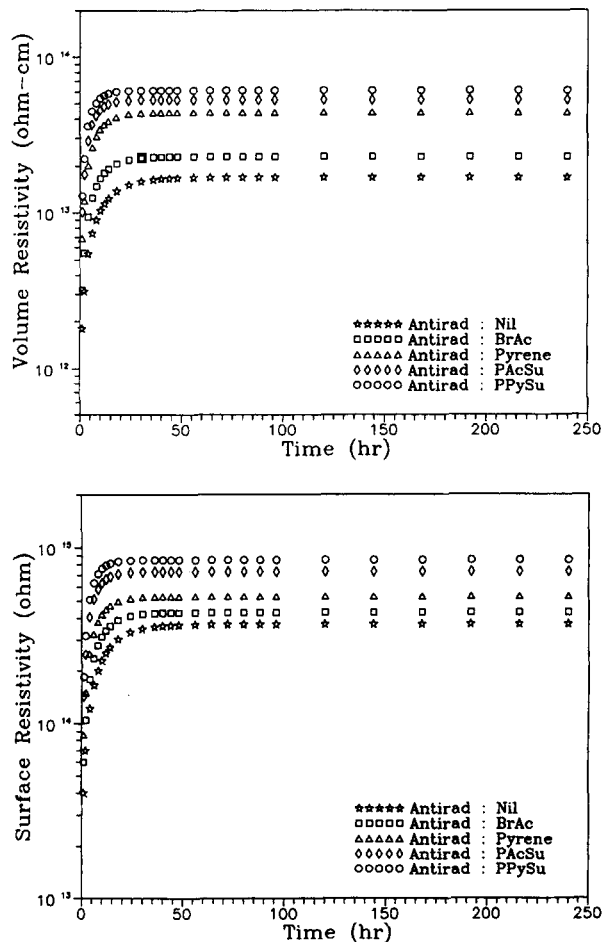


Figure 2 (a) Plots of surface resistivity in time-domain measurements for CSP vulcanizates after exposure for 2.0 Mrad dose in γ radiation. (b) Plots of volume resistivity in time-domain measurements for CSP vulcanizates after exposure for 2.0 Mrad dose in γ radiation.

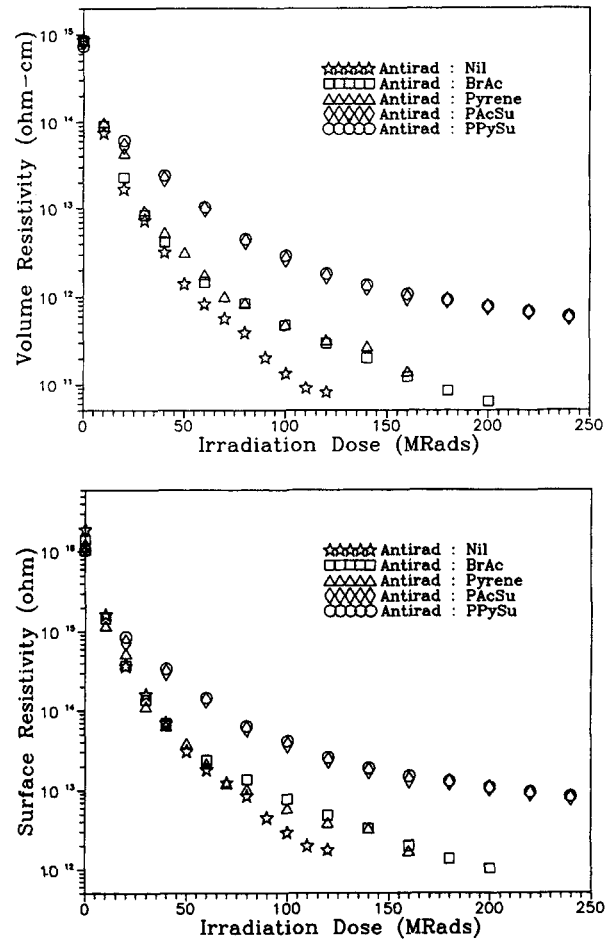


Figure 3 (a) Plots of volume resistivity at different doses of γ radiation for CSP vulcanizates. (b) Plots of surface resistivity at different doses of γ radiation for CSP vulcanizates.

become decayed by a diffusion-controlled recombination mechanism. The exponential increase in the volume and the surface resistivity for all the specimens are analyzed and fit to a first-order kinetic equation. The half-life data computed are as per Table III.

The increase in resistivities is found to be negligible after 24 h; hence, all specimens subjected to the resistivity studies are conditioned at room temperature and 55% relative humidity for 24 h after removal from the γ irradiation, prior to resistivity measurements.

The volume and surface resistivity of the CSP vulcanizates decrease with increase in the exposed dosage of γ irradiation, as shown in Figure 3. The pronounced effect of antirads is clearly seen by comparing the curves representing the control specimen and those with antirads. The curves of volume

resistivity and surface resistivity for each specimen are almost parallel. This is indicative of homogeneous changes in the bulk rather than only a surface phenomenon.

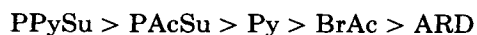
Wide-Angle X-ray Diffraction Spectroscopy

The addition of antirads does not have any pronounced effect on the diffraction pattern of CSP vulcanizates as indicated by Figure 4(a). The WAXD studies on specimens exposed to γ radiation indicate that there are many extra peaks appearing at higher 2θ values. Existing peaks also show an increase in intensity as shown in the representative Figure 4(b)–(d). These data qualitatively corroborate the view that degradation leads to increase in the crystallinity, both long range as well as short range. This can be attributed to the formation of direct cross-links on the backbone chains of CSP during the irradiation of polymer in the radiooxidative environment. Figure 5 shows the increase in the intensity of some of the prominent peaks against the total irradiation dosage. The trends are indicative of the stabilization effect of the antirads in the formulations. However, it is difficult to quantify the data.

Mechanical Properties

It is very clear from Figure 6(a)–(d) that tensile properties, i.e., tensile strength, elongation at break, and modulus at 100% elongation, undergo changes complementary to each other. In all specimens, the tensile strength first increases and then decreases continuously as the ultimate elongation at break continues to decrease. Simultaneously, the modulus and hardness increases as the radiation dosage increases. All these indicate that the material is predominantly undergoing cross-linking. However, it can be seen that the changes in the property are retarded with the addition of antirads and thereby achieve the necessary stability criteria. The stability criteria selected for the present study is 50% change in the tensile properties along with the change in the hardness by 10 units of Shore A, from initial values.¹⁰

The materials with PPySu and PAcSu antirads satisfy the stability criteria for the material up to 200 Mrads, whereas Py in combination with ARD stabilizes CSP up to 100 Mrads. Thus, the stabilizing action of antirads can be presented in the following order:



From the above observations and results, an explanation for the stabilizing action of various antirads used for this study can be given as follows:

The polymeric form of PPySu and PAcSu serves two purposes, viz., (a) it does not allow the material to leach out on the surface and (b) it retains the structural characteristics even when the bond cleavage may take place due to high-energy radiation. The highly aromatic material has localization of the electron possible over a large surface. This helps in stabilizing radicals and/or ions formed during the radiolytic reaction on the material, thus preventing the chain reaction to start. Also, the impinging energy can be absorbed by these polymeric adducts by going to the excited state and relaxing by either heat dissipation or by formation of free radicals and/or ions by the bond cleavage. These free radicals and/or ions are highly stabilized and are not available for further reaction. Thus, these antirads act as very efficient energy scavengers. Because of the very high steric hindrance on the aromatic nuclei of these material, the singlet oxygen is not allowed to react with antirads and thereby prevent the formation of the active free radicals, which is otherwise the case with Py. This is evident from the curves for the mechanical properties where the change in properties is extremely rapid for Py, once the induction period marking the stabilizing action is completed.

CONCLUSIONS

The effect of various antirads studied indicates that the use of a polynuclear aromatic material acts as an energy scavenger and free-radical scavenger in the high-energy radiation environment. Use of antirads in combination with an antioxidant retards

Table III Half-life Data from DC Resistivity Measurements

Recipe No.	Antirad Used	Half-life (h)	
		(a)	(b)
1	Nil	7.3	7.5
2	BrAc	5.4	5.5
3	Py	4.5	4.7
4	PAcSu	3.5	3.6
5	PPySu	3.2	3.2

(a) Computed from volume resistivity (DC) measurements;
(b) computed from surface resistivity (DC) measurements.

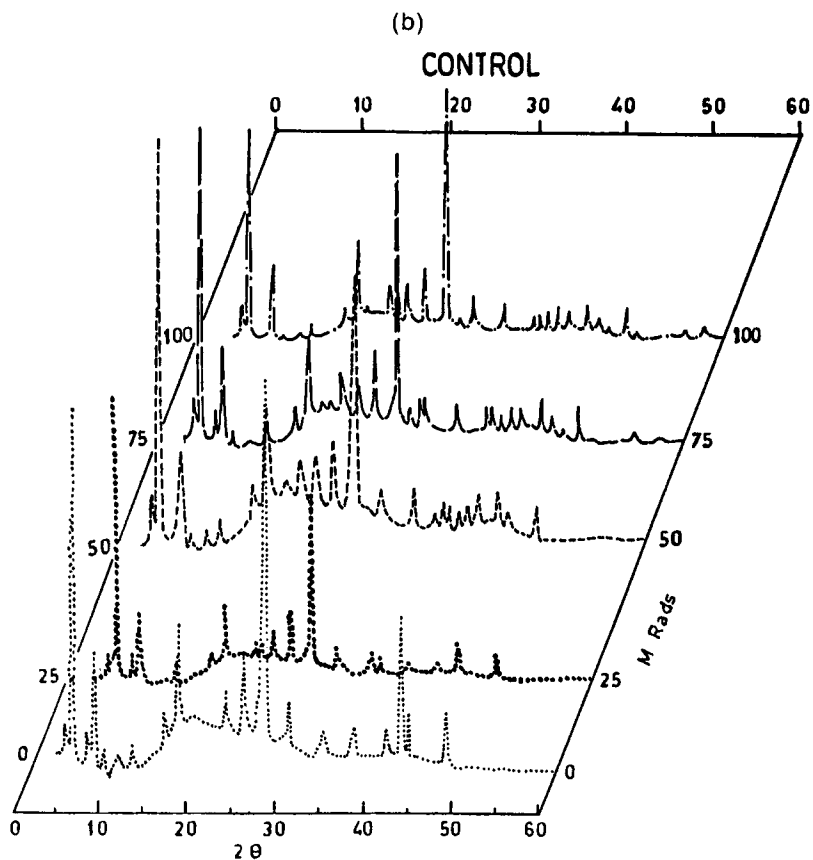
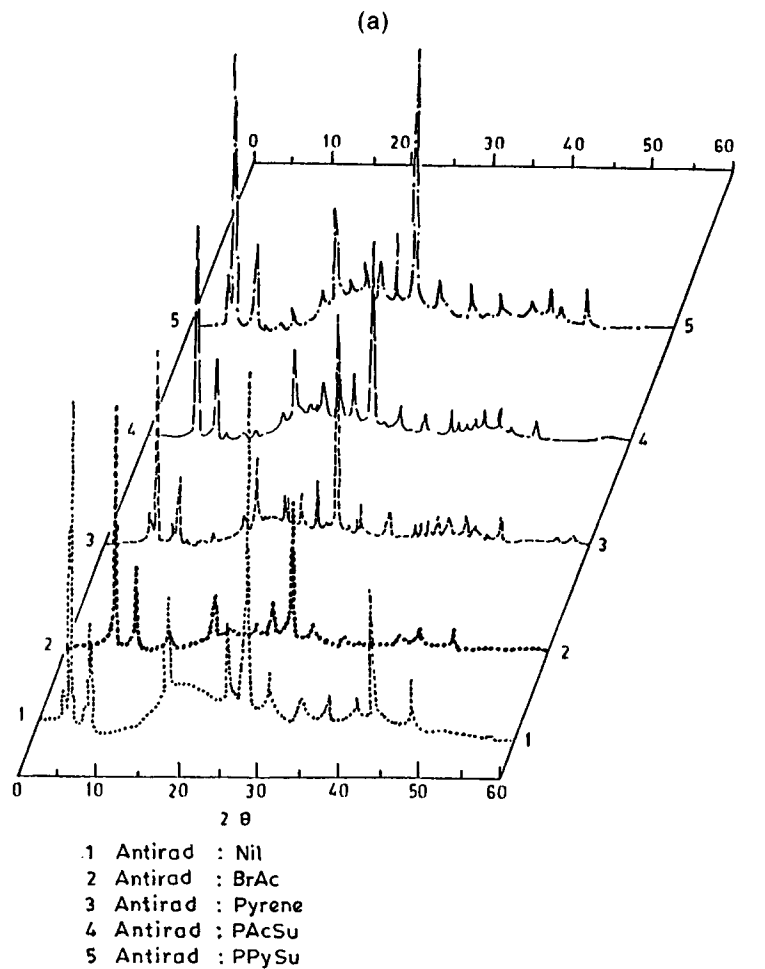


Figure 4 Plots of WAXD spectra of CSP vulcanizates: (a) unirradiated vulcanizates; (b) control specimen at different doses of γ radiation; (c) BrAc specimen at different doses of γ radiation; (d) PPySu specimen at different doses of γ radiation.

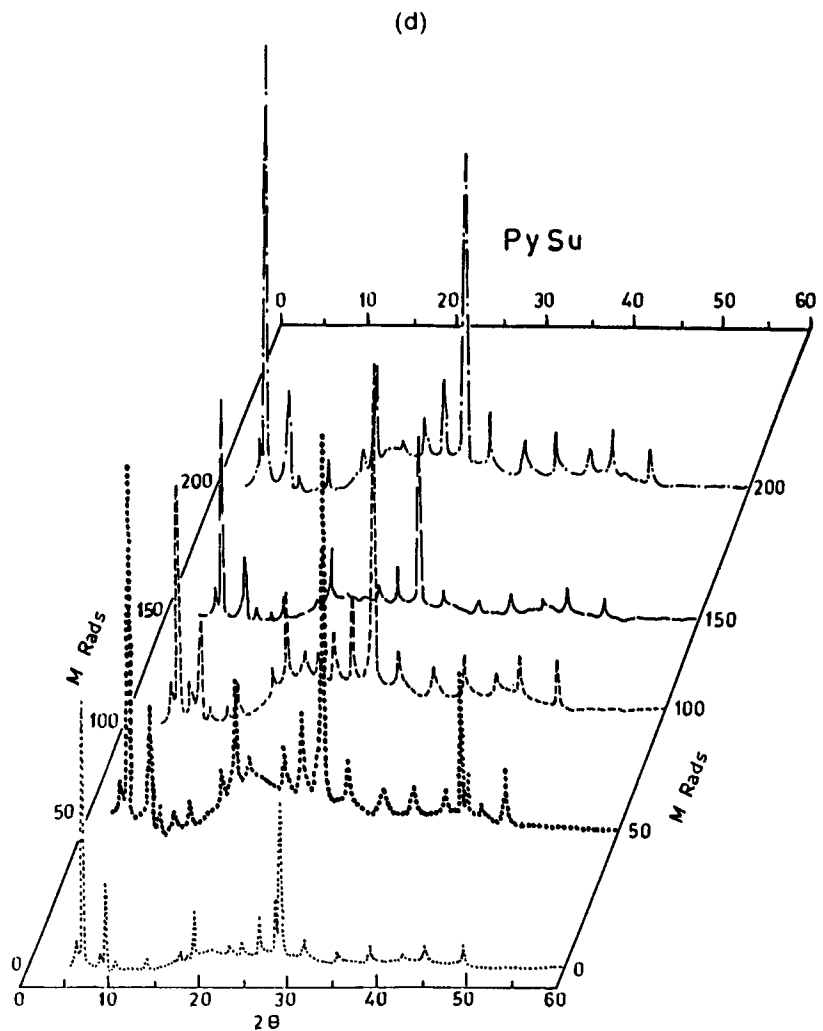
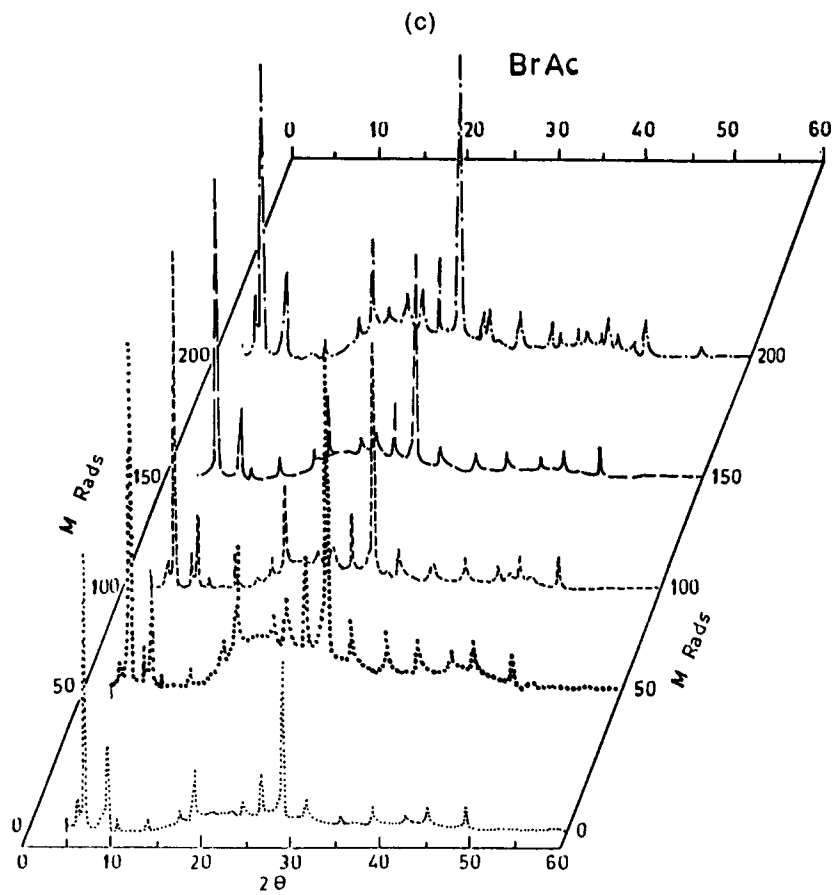


Figure 4 (Continued from the previous page)

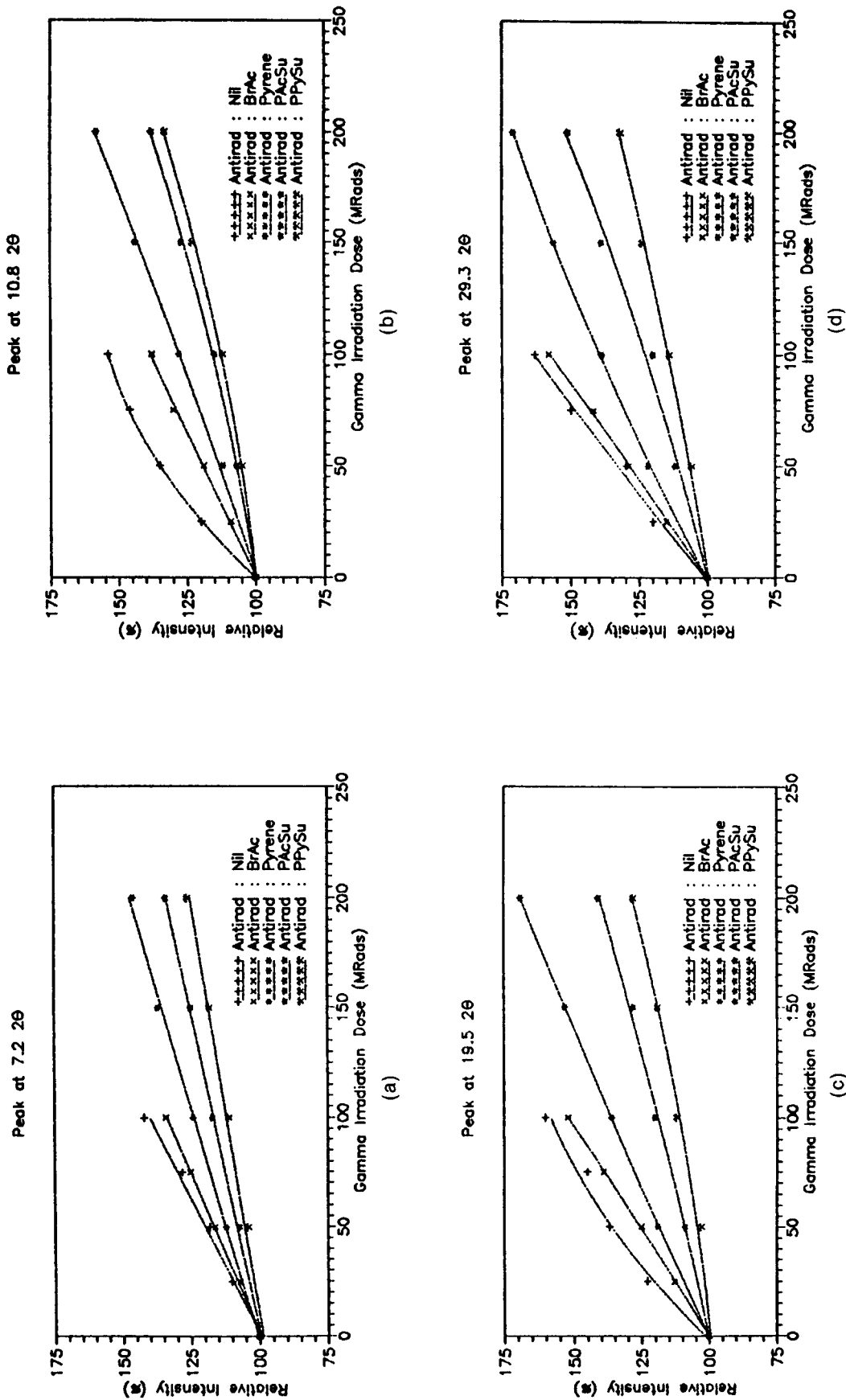


Figure 5 Plots of relative intensity of WAXD peaks at (a) 7.2° 2θ, (b) 10.8° 2θ, (c) 19.5° 2θ, and (d) 29.3° 2θ for CSP vulcanizates containing antirads at different doses of γ radiation. Relative intensities are calculated after normalizing the intensity of peaks with respect to the peak at 25.8° 2θ (corresponding to aluminum silicate added as filler).

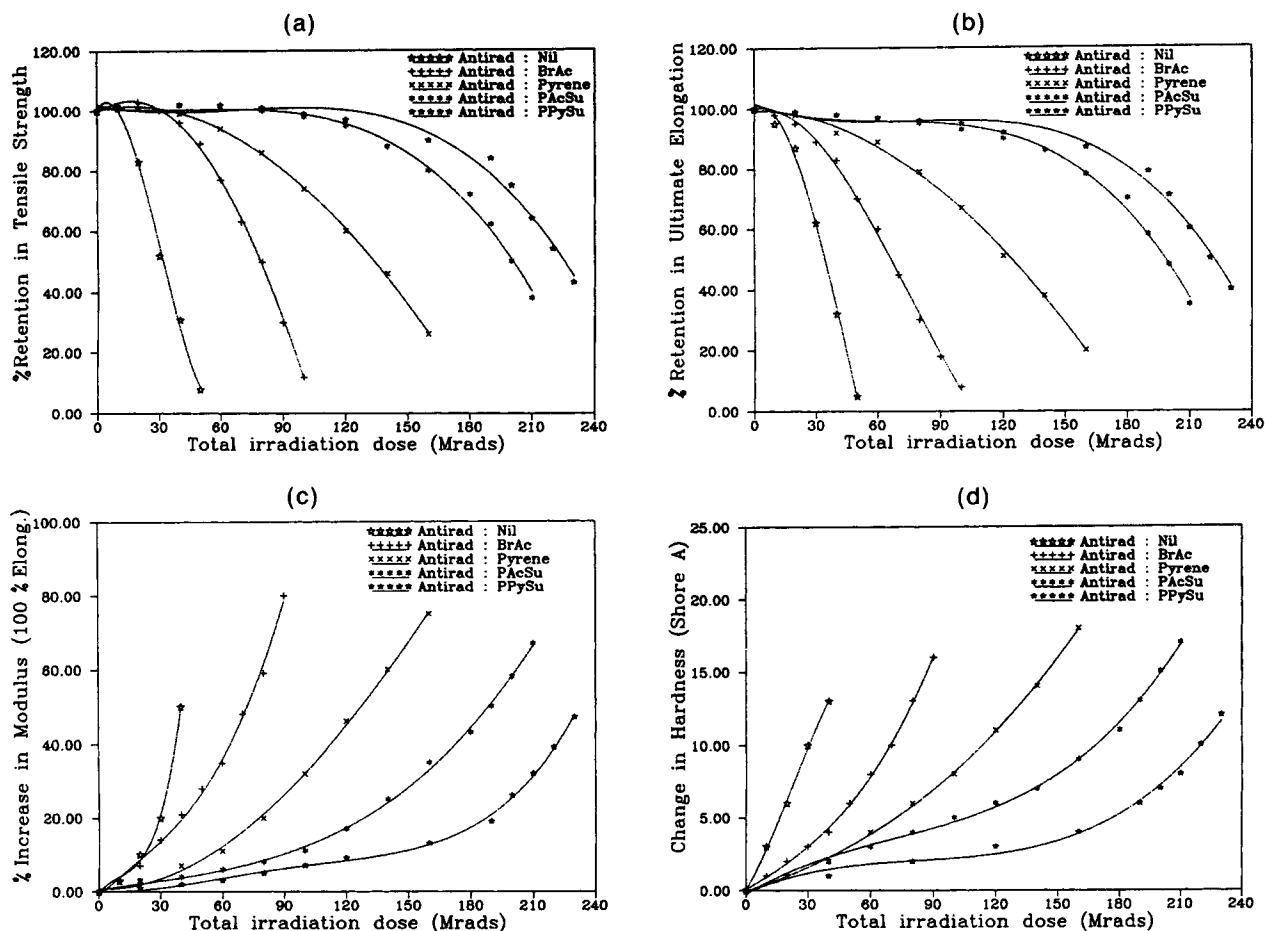


Figure 6 Plots of % retention in mechanical properties at different doses of γ radiation: (a) tensile strength; (b) ultimate elongation at break; (c) modulus at 100% elongation; (d) hardness (Shore A).

the oxidative radiation degradation rate and can also improve the induction period of the deterioration. The use of polymeric polynuclear aromatics like poly(pyrene sulfide) and poly(acenaphthene sulfide) can enhance the stability up to 200 Mrads. The wide-angle X-ray diffraction analysis provides evidence of chlorosulfonated polyethylene undergoing degradation predominantly via cross-linking reactions. The efficiency of antirads evaluated using the resistivity measurements established the following in decreasing order:

brominated acenaphthene < pyrene
 < poly(acenaphthene sulfide)
 < poly(pyrene sulfide)

REFERENCES

1. R. L. Clough and K. T. Gillen, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 2041 (1981).
2. R. L. Clough and K. T. Gillen, *Nucl. Techn.*, **59**, 344 (1982).
3. H. Wilski, E. Duch, H. Leugering, and S. Rosinger, *Coll. Polym. Sci.*, **259**, 818 (1981).
4. R. L. Clough and K. T. Gillen, in *Oxidation Inhibition in Organic Materials*, P. Klemchuck and J. Pospisil, Eds., CRC Press, Boca Raton, FL, 1990, p. 191.
5. R. L. Clough and K. T. Gillen, in *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 1988, Vol. 13, p. 667.
6. L. Novacovic, O. Gal, V. Markovic, and V. T. Stannett, *Radiat. Phys. Chem.*, **26**, 331 (1985).
7. D. J. Carlsson, C. J. B. Dobbin, and D. M. Wiles, in *Polymer Stabilization and Degradation*, P. Klemchuck, Ed., ACS Symposium Series 280, American Chemical Society, Washington, DC, 1985, p. 359.
8. C. S. Shah, M. J. Patni, and M. V. Pandya, *Frontiers of Polymer Research*, P. N. Prasad and J. K. Nigam, Eds., Plenum Press, New York, 1991, p. 565.
9. M. Hagiwara and Y. Morita, *Radiat. Phys. Chem.*, **18**, 701 (1981).
10. IEC standard 541-3.

Received March 29, 1993

Accepted July 30, 1993