

# Radiation Vulcanization of Hydrogenated Acrylonitrile Butadiene Rubber (HNBR)

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## SYNOPSIS

Raw polymer and compound of hydrogenated acrylonitrile butadiene rubber (HNBR) were subjected to  $\gamma$ -ray irradiation. Crosslinking was found to be the main chemical reaction induced by irradiation; the ratio of chain scission to crosslinking as well as the dose at which gelation occurred were determined from gel content measurements to be 0.41 and 3.8 Mrad, respectively. The excellent hot-air and oil-resistant properties should be retained because no formation of double bonds or changing of the nitrile groups were observed within the optimum dose range. Desired mechanical properties of the vulcanizate may be conveniently obtained by controlling the radiation dose. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Hydrogenated acrylonitrile butadiene rubber (HNBR) is a high-performance elastomer obtained by selective hydrogenation of the carbon-carbon double bonds of nitrile rubber. Depending on the acrylonitrile content and degree of saturation, HNBR has a unique set of properties which are expected to overcome the weaknesses of acrylonitrile butadiene rubber (NBR) and fluorocarbon elastomers (FKM). These include outstanding mechanical properties, good resistance to wear, good resistance to technical oils and fluids containing chemically aggressive additives as well as fuels including "sour gasoline," and excellent resistance to hot air, thus meeting many of the most stringent application requirements.<sup>1-4</sup>

Partly unsaturated products resulting from incomplete hydrogenation of NBR are suitable for crosslinking with traditional sulfur systems, but saturated polymers given by complete hydrogenation are crosslinkable only with radical donors, such as peroxide, or by high energy irradiation. Studies have shown that properties of peroxide-crosslinked HNBR are inferior to those prepared by sulfur crosslinking; in contrast with that of peroxide

crosslinking, sulfur crosslinking can give higher elongation at break, greater tensile strength, and better dynamic behaviour.<sup>5,6</sup> However, peroxide vulcanization is expected to lead to better resistance to hot air because of the saturated original HNBR used and the carbon-carbon crosslinked bonds yielded.

Radiation crosslinking of elastomers dates back to the end of the 1940s.<sup>7,8</sup> In addition to the general advantages of radiation vulcanization, including that the process can be performed under ambient temperature and closely controlled conditions, no SO<sub>2</sub> gas evolution, and no incineration residue of the rubber goods, radiation crosslinking of HNBR also has an advantage in that there is no limitation on the degree of hydrogenation. Thus it may provide products with the benefits of both sulfur crosslinking and peroxide crosslinking. The object of this work is to investigate the crosslinking behaviour of HNBR by means of  $\gamma$ -ray irradiation and to identify the relationship between properties and the vulcanization process.

## EXPERIMENTAL

### Raw Polymer and Compound

The saturated raw polymer of HNBR, Terban 1706 (provided by Bayer Co., Ger.), was chosen for this study. Its properties are shown in Table I.

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**Table I Raw Polymer Properties of HNBR**

Acrylonitrile (ACN) content (%)	34
Mooney viscosity (ML <sub>144</sub> , 100°C)	68
Density (g/cm <sup>3</sup> )	0.95
Residual double bonds content (%)	< 1

The compound was composed of TB-1706, 100 phr; carbon black, 60 phr; antioxidant, 2 phr; plasticizer, 10 phr; and stearic acid, 1 phr.

### Irradiation

Except for the samples prepared for Fourier transform infrared (FTIR) spectroscopy measurements, irradiation of 60 × 40 × 2 mm<sup>3</sup> compounding sheets was performed using a 10,000 Ci Co.-60 source under room temperature. The dose rate used was 180 Gy/min.

### Instruments and Measurements

FTIR spectra of raw polymer films (casting from THF solution) were recorded on an FTS-7 spectrometer (Bio-Rad, Digilab Division).

Gel contents of irradiated samples were determined by solvent (THF) extraction at the boil for 24 h. The results were justified using an unirradiated sample extracted under the same conditions to exclude the effect of fillers.

Thermomechanical analysis (TMA) measured the penetration of an indenting needle into the sample under the action of a constant force of 200 g; the heating rate was 10°C/min.

Dynamic mechanical analyses (DMA) were carried out on a METRAVIB Viscoanalyser at a temperature range of -100°C to 180°C. Speed of temperature variation was 5°C/min., and the frequency given was 7.8 Hz.

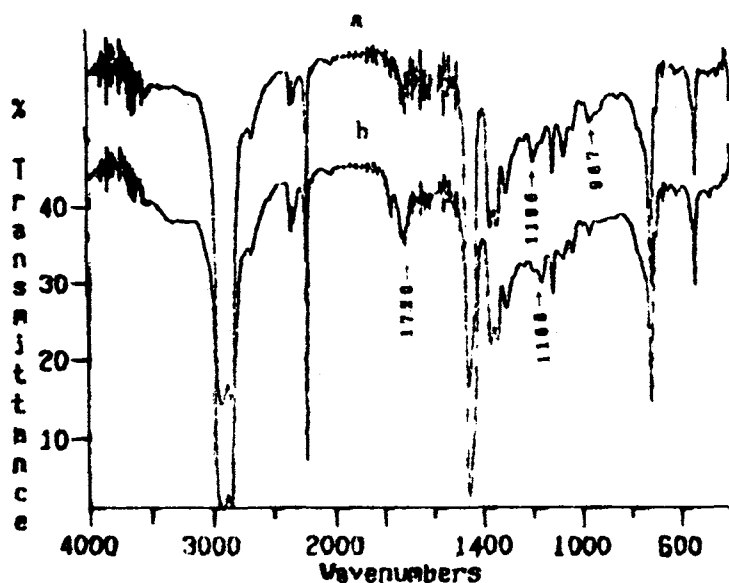
Tensile strength and elongation at break were measured on an Instron-1121 tensile testing machine at a strain rate of 100 mm/min.

## RESULTS AND DISCUSSION

### Chemical Reactions in Raw Polymer Induced by Irradiation

Figure 1 gives the FTIR spectra of HNBR (raw polymer) before and after irradiation. The radiation dose chosen was the optimum dose under which the desired mechanical properties of the vulcanizate can be obtained. From these spectra, the following irradiation-induced chemical reactions were observed:

- (1) New absorption peaks appeared at about 1720 cm<sup>-1</sup> and beyond 3200 cm<sup>-1</sup>, indicating that the sample was slightly oxidized during irradiation. In practice, antioxidants are usually added to rubber products; therefore,



**Figure 1** FTIR spectra of HNBR film (a) before irradiation and (b) after irradiation to 17.2 Mrad.

the effect of oxygen may be reduced to the extent that useful properties may not be affected.

- (2) The absorption intensities at  $967\text{ cm}^{-1}$  and  $1070\text{ cm}^{-1}$ , which are responsible for the small degree of unsaturation ( $< 1\%$ ) in the original polymer, decrease after irradiation. No other types of double bonds were measured in the dose range studied ( $< 30\text{ Mrad}$ ), although studies have shown that double bonds usually form when a saturated polymer is subjected to irradiation.<sup>7</sup> This result may assure us that the hot air resistance property of the vulcanizate will not be decreased due to radiation-induced formation of double bonds.
- (3) The absorption band at about  $1196\text{ cm}^{-1}$  decreases, whereas the band at  $1165\text{ cm}^{-1}$  increases with the increasing radiation dose. These bands are ascribed to the coupled  $V(\text{C}-\text{C})$  vibration of branching points; therefore the alterations of these bands with radiation may give evidence of radiation-induced crosslinking, which is of great practical importance in affecting the mechanical properties of the products.
- (4)  $-\text{C}\equiv\text{N}$  groups, indicated by a sharp absorption peak at  $2236\text{ cm}^{-1}$ , remain unchanged under the dosage studied.

### Radiation Crosslinking Behavior of the Compound

When a polymer which is radiation-crosslinkable is subjected to irradiation, some of the initial molecules are linked together to form an infinite network which is insoluble and is referred to as the gel fraction, while another fraction of molecules remains soluble. The relative amount of sol and gel fraction can be determined experimentally; the result of such a determination can provide useful information on crosslinking and chain scission efficiencies. Figure 2 shows the gel fraction of irradiated HNBR compound as a function of radiation dose. As expected, the gel content increases with the dose, indicating that there are more macromolecules crosslinked with increasing radiation dose. It is our experience that more than 70% gel content can be achieved, producing radiation-crosslinked products satisfactory for applications such as wire, cable, tubes, etc., if the dose is higher than 14 Mrad.

It is considered that both crosslinking and degradation may occur simultaneously in the same polymer, the characteristics ultimately depending on the process which predominates under the irradiation condition. The ratio of crosslinking to chain scission probabilities can be derived from the sol fraction.<sup>9</sup> Assuming that both crosslinking and degradation are proportional to dose:

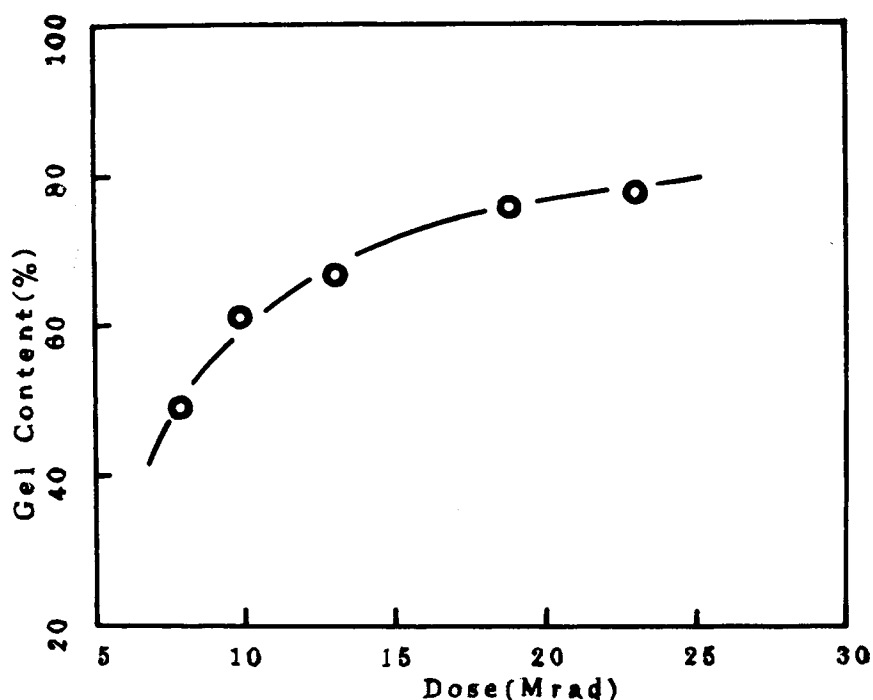


Figure 2 Relationship between gel content and radiation dose.

$$q = q_0 R \quad (1)$$

$$p = p_0 R \quad (2)$$

where  $q_0$  and  $p_0$  are the probabilities of crosslinking and degradation, respectively. The ratio of degradation to crosslinking remains constant with dose and is  $p_0/q_0$ . Presuming that the molecular weight distribution in the polymer is random, and that crosslinking and chain scission occur randomly, the Charlesby and Pinner equation is applicable,

$$(s + s^{1/2}) = p_0/q_0 + (2 - p_0/q_0)Rg/R \quad (3)$$

where  $s$  is sol fraction,  $Rg$  is the dose (in Mrad) to gel point, and  $R$  is the adsorbed radiation dose. Equation (3) describes a straight line if  $(s + s^{1/2})$  is plotted versus  $1/R$ . Such a plot based on our experiment is illustrated in Figure 3. From this illustration the following equation is derived:

$$(s + s^{1/2}) = 0.41 + 6.24/R \text{ (efficiency is 0.99)} \quad (4)$$

The value of  $p_0/q_0$  given by the intercept is 0.41, almost the same as the value for the saturated polymer, polyethylene ( $p_0/q_0$  is 0.35), but higher than that of unsaturated rubber, such as natural rubber ( $p_0/q_0$  is 0.14). This result may be reasonable considering that the HNBR studied is almost saturated.

From equation (4), the dose for gelation  $Rg$  was also calculated to be 3.9 Mrad, which is believed to be closely related to the initial molecular weight and additives.

### Relaxation Behavior of Vulcanizate

The storage modulus  $E'$  and the loss  $\tan \delta$  as a function of temperature, given by dynamic mechanical thermal analyses, are plotted in Figures 4 and 5, respectively. From these we can see that two relaxation peaks exist, referred to as  $\alpha$ , the sharp one at about  $-25^\circ\text{C}$ , and  $\beta$ , the broad one from  $50$  to  $150^\circ\text{C}$ . The former, assigned to the motion of chain segments (e.g., glass transition), is shifted to slightly higher temperature and reduced in magnitude with increasing radiation dose, because crosslinking provides a barrier to segmental thermal motion. In reference to our TMA analysis (for details see the following section), the  $\beta$ -relaxation is considered to be the viscous flow of whole macromolecules (the softening temperature determined is about  $85^\circ\text{C}$ ). The magnitude of this relaxation shows a remarkable reduction under irradiation and leads to a broader plateau at higher dosage. Three-dimensional networks resulting from radiation crosslinking restrain the chain motion, therefore the material cannot flow

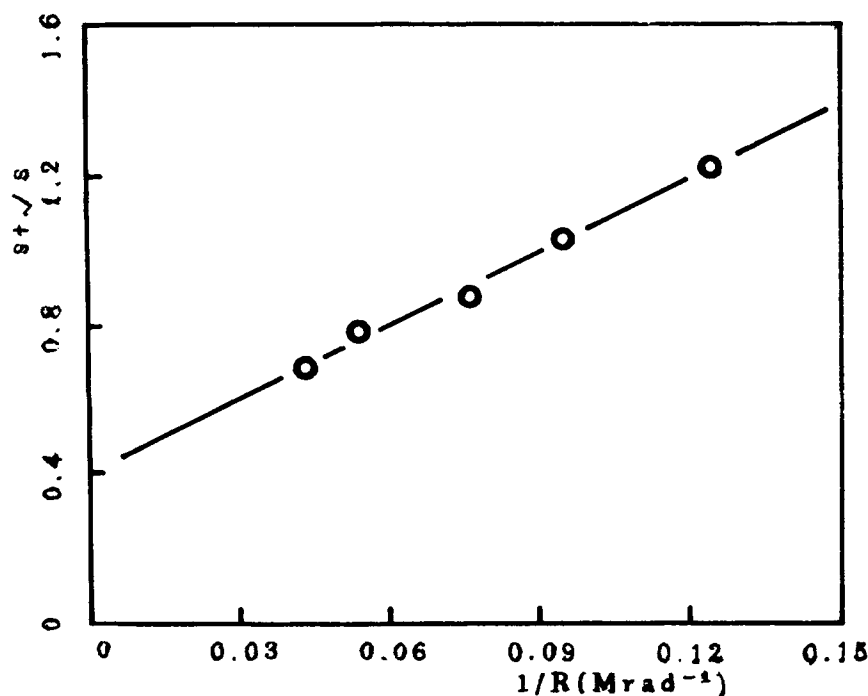


Figure 3 Charlesby-Pinner function for radiation cured of HNBR compound.

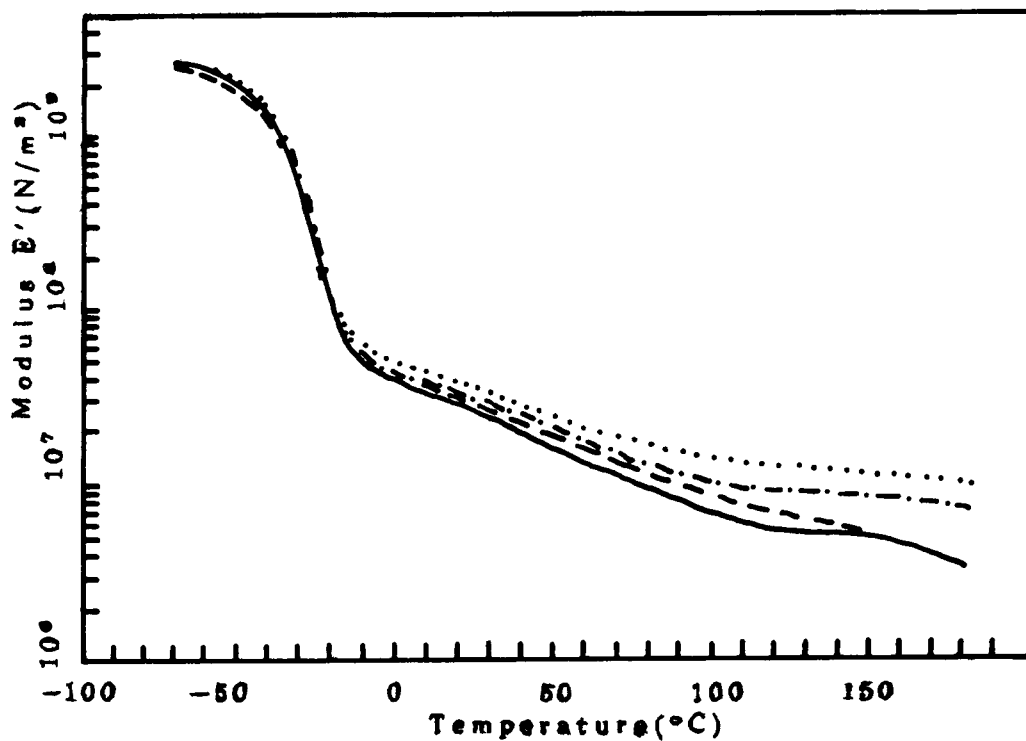


Figure 4 Temperature dependence of storage modulus  $E'$  for HNBR vulcanizate. Dose: — 0; --- 8.0 Mrad; - · - · 17.2 Mrad; · · · · 35.0 Mrad.

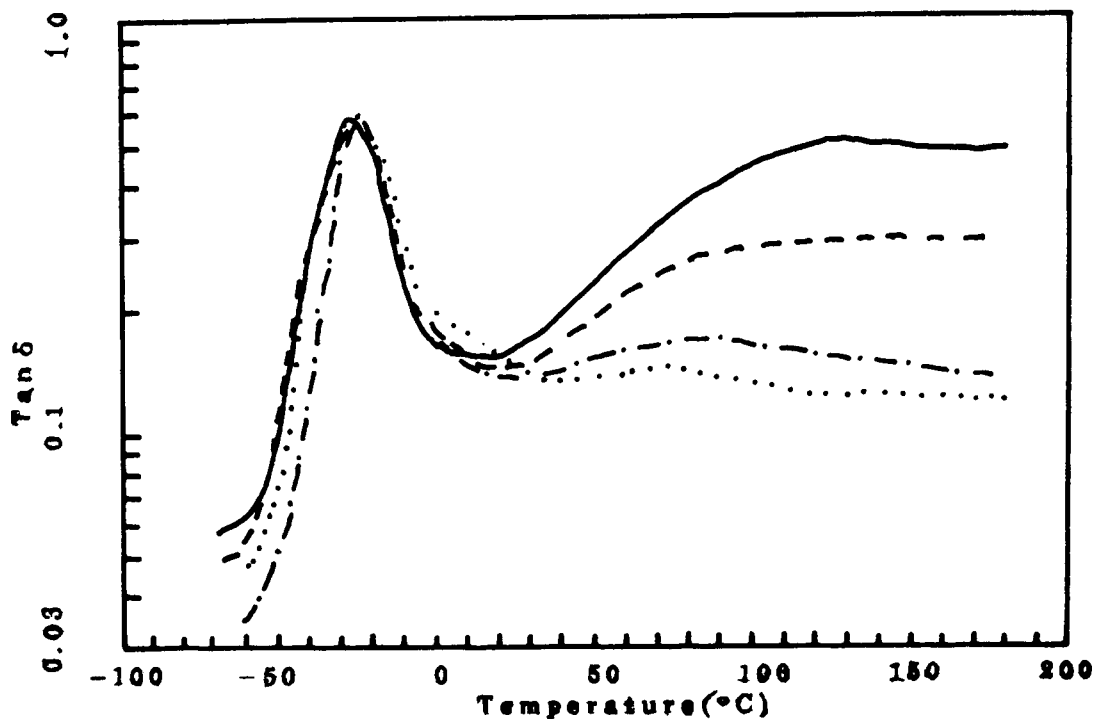


Figure 5 Temperature dependence of loss tan  $\delta$  for HNBR vulcanizate. Dose: — 0; --- 8.0 Mrad; - · - · 17.2 Mrad; · · · · 35.0 Mrad.

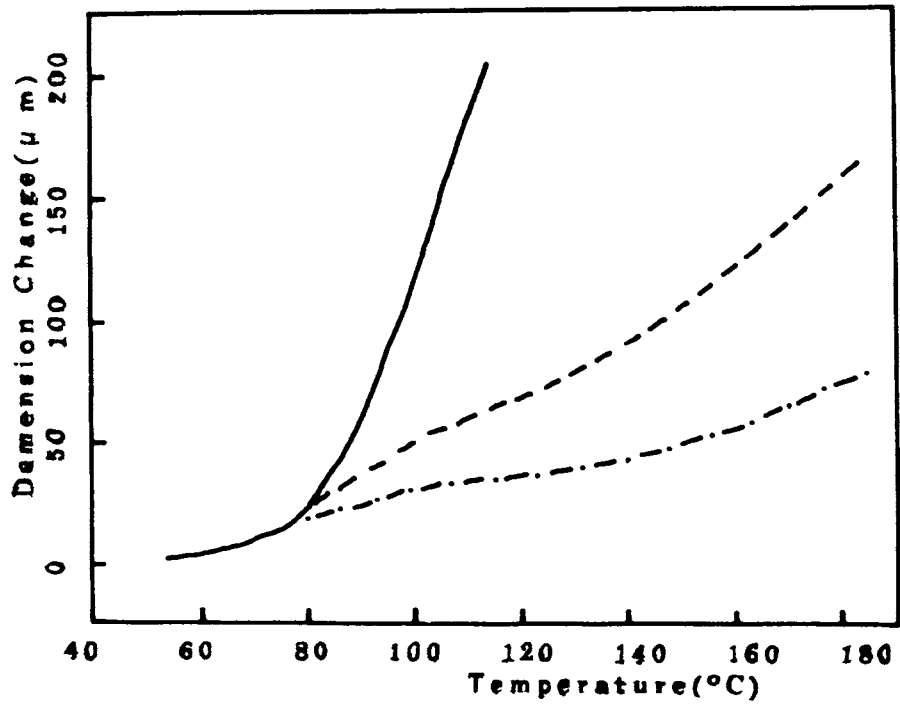


Figure 6 TMA curves of HNBR vulcanizate. Dose: — 0; --- 8.0 Mrad; - · - · 17.2 Mrad.

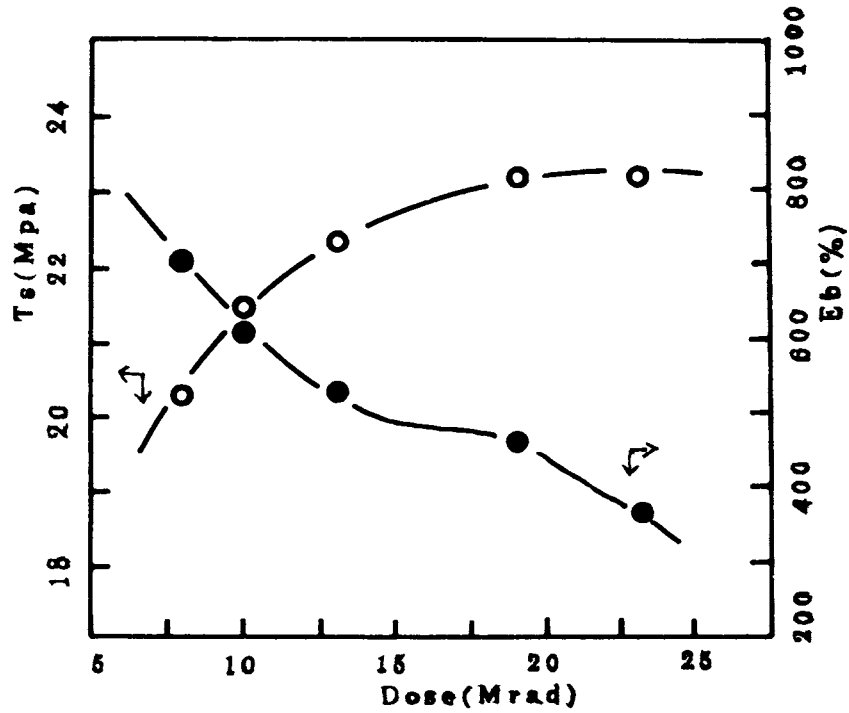


Figure 7 Mechanical properties of radiation-cured HNBR compound. ○ Tensile strength ( $T_s$ ), ● Elongation at break ( $E_b$ ).

even at higher temperature but performs like a crosslinked elastomer.

No effect of irradiation on the modulus is observed at the lower temperature range (below the glass transition temperature). In contrast, the modulus at higher temperature increases with increasing dose. Because increasing radiation dose results in increasing crosslinking density, this result is consistent with the general conclusion that elastic modulus of an elastomer above  $T_g$  is determined by the crosslinking density.

### Thermomechanical and Mechanical Properties

Temperature dependencies of dimensional change with radiation dosage are shown in Figure 6. For uncured material, the curve shows a transition point at about 85°C, which is considered to be the softening temperature of the rubber. After irradiation to certain doses, the transition disappeared; the deformation of the material is dependent on radiation dose or, in other words, on crosslinking density.

Mechanical properties are usually of the most practical importance in the investigation of radiation vulcanization of rubber. Early studies indicated that the mechanical properties of radiation-cured materials were inferior to those prepared by conventional sulfur vulcanization, but later publications reported that physical strength values for elastomers cured by radiation are equivalent to those prepared by other crosslinking techniques.<sup>10,11</sup> Tensile strength ( $T_s$ ) and elongation at break ( $E_b$ ) data determined by our experiments are shown in Figure

7. As expected, raising the dosage can increase the tensile strength but reduces the value of elongation at break. A good balance between these two parameters for the vulcanizate was found in the dose range from 10 to 20 Mrad. Taking into account the crosslinking degree, the radiation dose for optimum properties may be 14–20 Mrad.

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