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Rad.C-11 Improvement of Some Physical Properties of Loaded Nitrile Rubber Vulcanized By Ionizing Radiation.

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ABSTRACT

The effect of four-selected polyfunctional compounds namely, trimethylacrylic ester, trimethylol propane trimethacrylate, zinc diacrylate and modified pentaerthitol triacrylate, as crosslinking agents, on the mechanical properties of radiation vulcanized nitrile rubber was studied. The effect of incorporation of either HAF-carbon black or fumed silica, as filler and reinforcing agents, on its mechanical properties was also studied. The coagent namely, trimethylacrylic ester, was found to produce a set of optimum mechanical properties, i.e. moderate crosslink density, good tensile strength and elasticity at low irradiation doses, i.e. 40 kGy.

Key words: Radiation crosslinking / NBR / Mechanical properties / Coagents / Fillers.

INTRODUCTION

The radiation-induced vulcanization of rubbers is the process of crosslinking of flexible macromolecules. Under real conditions, this process is complicated not only by degradation, but also by other specific reactions, such as cyclization and cis-trans isomerization of double bonds. The contributions of these reactions are determined by many factors: the nature of the initial polymer, the presence of additives, the temperature, etc. In practice, radiation- vulcanized rubber mixes are most often multi-component mixtures containing fillers, antioxidants, sensitizers, etc. Fillers usually have a certain sensitizing effect. In filled rubber systems, ionizing radiation lead to the formation of a three-dimensional network not only in the polymer itself, but also between the elastomer molecules and the filler particles. The sensitizers of radiation-induced structerization are usually polyfunctional compounds that reduce the absorbed dose needed for crosslinking. The appropriate choice of sensitizers makes it possible to control the density and type of the network and thus to attain the optimum properties of crosslinked polymers by using low absorbed irradiation doses [1-5].

Nitrile rubber is the most commonly used polymer in oil field equipment, where very severe service conditions include high temperatures and pressures as well as exposure to corrosive fluid, oils and gasses. However, it has inferior resistance to ozone; sunlight; and natural aging; and poor resistance to oxygenated solvents. Products formulated with a highly acrylonirile content nitrile rubber using fumed silica of high surface area show high tensile and abrasion resistance and low water swell [6].

In this work, the effect of γ-irradiation on the mechanical properties of NBR rubber in presence of different sensitizes, namely SR-350, SR-444, SR-517 and SR- 633, in addition to either HAF-carbon black or silica fillers, and other additives were studied.

EXPERIMENTAL

1. Materials

Acrylonitrile   3307 NS) from Bayer Co. Germany was used. Its acrylonirile content and density are 34% and 0.99 g/cm^3, respectively. HAF-carbon black and fumed silica namely, Aerosil A-130 were used as filler and reinforcing materials. Silica produced by a thermal method is frequently called fumed silica. The Degussa Company in Germany developed the original process and the product marketed under the brand name Aerosil. The polyfunctional compounds namely, trimethylacrylic ester (SR-517), trimethylol propane trimethacrylate (SR-350), zinc diacrylate (SR-633) and modified pentaerthitol triacrylate (SR-444) were used as crosslinking agents. The compounds IPPD (1 phr), TMQ (1 phr), tetrene and paraffin wax (0.5 phr) were used as antioxidants and antiozonants. The nomenclature and specifications of these compounds are listed in Table 1.

Table 1: The nomenclature and specifications of the used compounds

No.	Trade name	menclature and specifications
1	SR-517	Trimethacrylic ester, brown liquid, specific gravity=1.06
2	SR-350	Trimethylol propane trimethacrylate, specific gravity=1.06, Molecular weight = 388
3	SR- 633	Zinc triacrylate, yellowish powder, specific gravity=1.6.
4	SR- 444	Modified pentaerthitol diacrylate, specific gravity=1.16, liquid Viscosity = 300- 700
5	IPPD	N-isopropyl-N-phenyl-p-phenylene diamine
6	TMQ	Trimethyl quinoline
7	Tetrene	Tetraethylene tetramine
8	HAF-carbon black	Particle Size Index = 27, surface area =83 m^2/g and Iodine Adsorption = 82 g/kg.
10	Aerosil- 130	Hydrophilic silicon dioxide, 16 nm particle size, 2.2 g/cm^3 density and 340 m^2/g surface area.

2. Techniques

Preparation of Samples and Irradiation:

The NBR formulations were prepared separately using Plasti-corder PL2000, from Brabender Co., Germany, fitted with a mixer type 350S. The mixing time was 12 minutes at 70°C and 64-rpm speed, followed by rubber milling at the same temperature. A hot press was applied to make sheets with a thickness of about 2-mm at 100° C for 5 minutes under 150-kg/cm^2 pressure. The irradiation was carried out in nitrogen atmosphere and dose rate at about 13 kGy/h using irradiator type Gamma cell 220 from Nordion International Inc., Canada.

Mechanical properties

The mechanical properties were measured in accordance with ASTM D-412. Five samples from each formulation were tested. Dumbbells shaped specimens were cut from sheets using a steel die of standard width (6mm) and length (20mm). The measurements of the mechanical properties were carried out using an Instron tensile testing machine model 4045, USA.

RESULTS AND DISCUSSION

Effect of Coagents on the Mechanical Properties of Irradiated NBR Loaded with Fumed Silica:

The mechanical properties, namely modulus stress at 200% elongation (σ200), tensile strength (TS) and elongation at break (E%) for NBR samples were measured and are presented in Figs. 1-3, respectively. These NBR samples are containing 4 parts of the selected polyfunctional compounds per 100 parts of the rubber (4 phr), in addition of 45 phr of silica type A-130, 1 phr of tetrene, antioxidants and irradiated to different doses ranging from 20 to 200 kGy.

From Fig. 1, it can be seen that the σ200 increased linearly with irradiation dose and the rate of increase depends on the type of coagent added. In addition, from the change in TS with irradiation dose presented in Fig. 2, it can be seen that the maximum TS was attained at irradiation dose ranging between 60 and 100 kGy. In contrast, the elongation at break presented in Fig. 3 decreased steadily with irradiation dose showing average values of elongation ranging between 500-600%, in presence of the coagents, at irradiation dose of about 60 kGy. Whereas, a corresponding value of E% was attained at 100 kGy in absence of any coagent. These values of elongation at break were attained, almost, at the same crosslink density as measured by σ200. In addition, the samples filled with silica, in absence of coagent, showed the highest TS and E% at the same range of irradiation dose, i.e. 60 100 kGy. This may be explained as: the primary particles of fumed silica are spherical and during manufacture coagulate immediately after formation into chains [7] and these eventually form agglomerates. In addition, the fumed silica particles (A-130) have silanol groups both on and below their surface, whereas on the inside (and partially on the surfaces), Si-O-Si bonds have formed [8]. These silanol Si-OH groups endeavor to interact via hydrogen bonds to form a three-dimensional chain structure. These hydrogen bonds are relatively weak and break up as soon as high shear forces are applied, i.e. during mixing and processing of the rubber formulation. These opened chains of silica in addition to the existence of -OH group on their surfaces promote the formation of three-dimensional network via radiation crosslinking. Consequently, with a relatively lower crosslink density of the rubber, the presence of the silica filler may lead to a synergistic effect in improving the tensile strength as well as elongation % of the rubber samples. This synergistic effect increased positively with irradiation dose up to 100 kGy, as the crosslink density increased to the optimum value. In contrast, at high irradiation doses, the increased crosslink density and the perspective predominant degradation can effect negatively on the role of the fumed silica as well as the mechanical properties. Whereas, in the case of incorporating the crosslinking compounds, the crosslink density increased at a higher rate than in its absence with increasing the irradiation dose. This may hinder the role played by the silica chains and the entanglement in improving the mechanical properties, especially the elongation at break and tensile strength. The addition of silica to a compound rapidly increases its viscosity. Silica-to-silica attraction is high, with the result that large aggregates are formed, impeding flow, and the mix becomes very stiff. The additives chosen in this situation for plasticization can be soluble zinc compounds or materials, such as tetrene.

Effect of Coagents on the Mechanical Properties of Irradiated NBR Loaded with HAF-Carbon black

The mechanical properties of NBR formulations containing 45 phr of HAF-carbon black in absence and in presence of 4 phr of the same selected coagents, antioxidants, and irradiated to different irradiation doses ranging from 20-200 kGy, were measured. The σ200, the TS and E% as a function of irradiation doses for these formulations are presented in Figs. 4-6, respectively. From these figures, it can be seen that, the σ200 increased linearly with increasing the irradiation dose (Figs. 4). The efficiency of the coagents in increasing the modulus stress, i.e. crosslink density, with irradiation dose can be presented as follows: SR-444 > SR-350 > SR-517 > SR-633 > control. In addition, the rate of increase of the modulus stress per unit dose of irradiation for these formulations, calculated from Fig. 4, and ordered according to the previous consequences are: 0.32, 0.18, 0.16, 0.13 and 0.11 MPa/kGy, respectively. The tensile

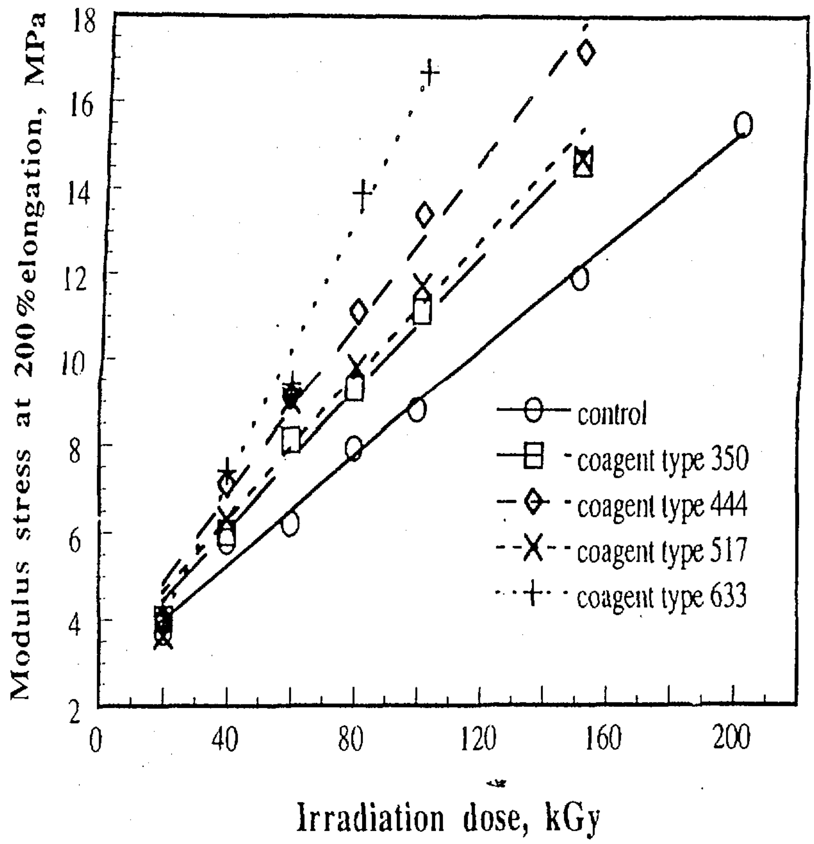

Fig. 1: Irradiation dose dependence of the modulus stress at 200%E. of the NBR rubber containing 45 pphr of silica type130 and 4 pphr of different coagents

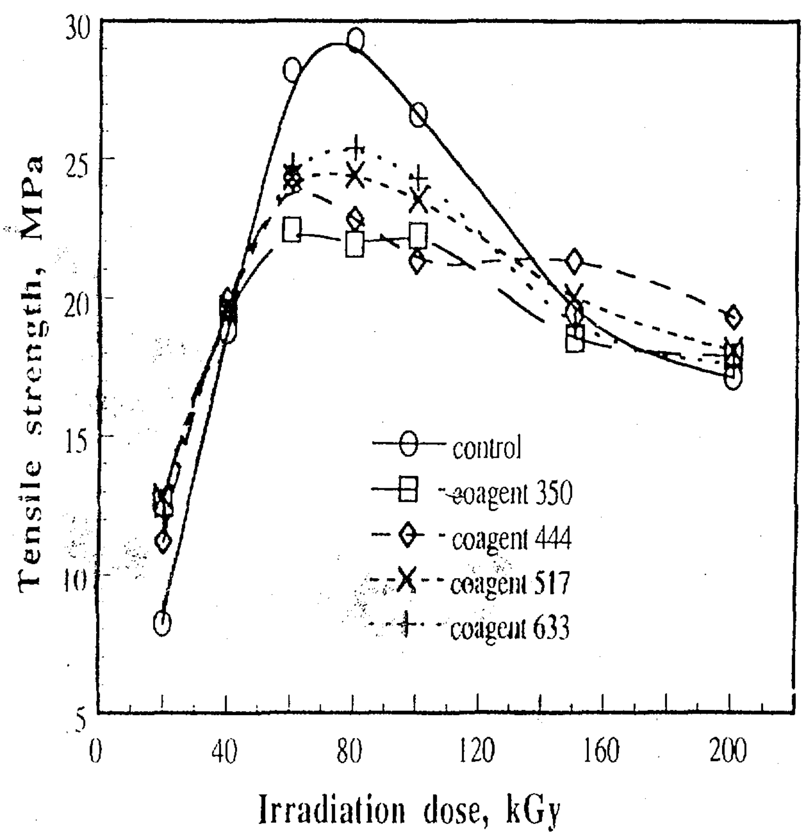

Fig. 2: Irradiation dose dependence of the tensile strength of the NBR rubber containing 45 pphr of silica type130 and 4 pphr of different coagents.

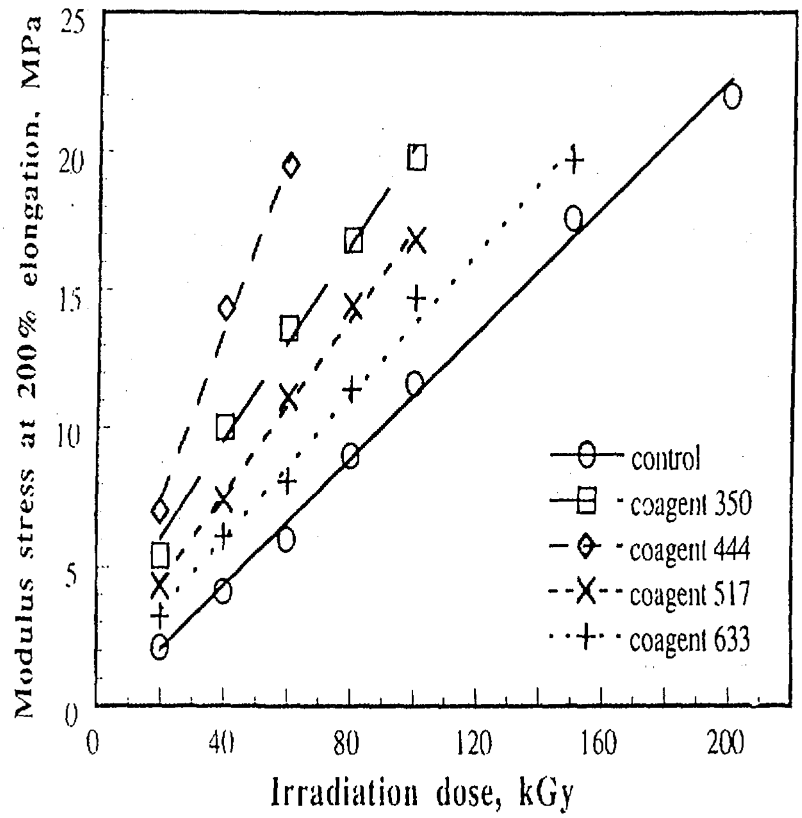

Fig. 3: Irradiation dose dependence of the modulus stress at 200%E. of the NBR rubber containing 45 pphr of HAF- carbon black and 4 pphr of different coagents.

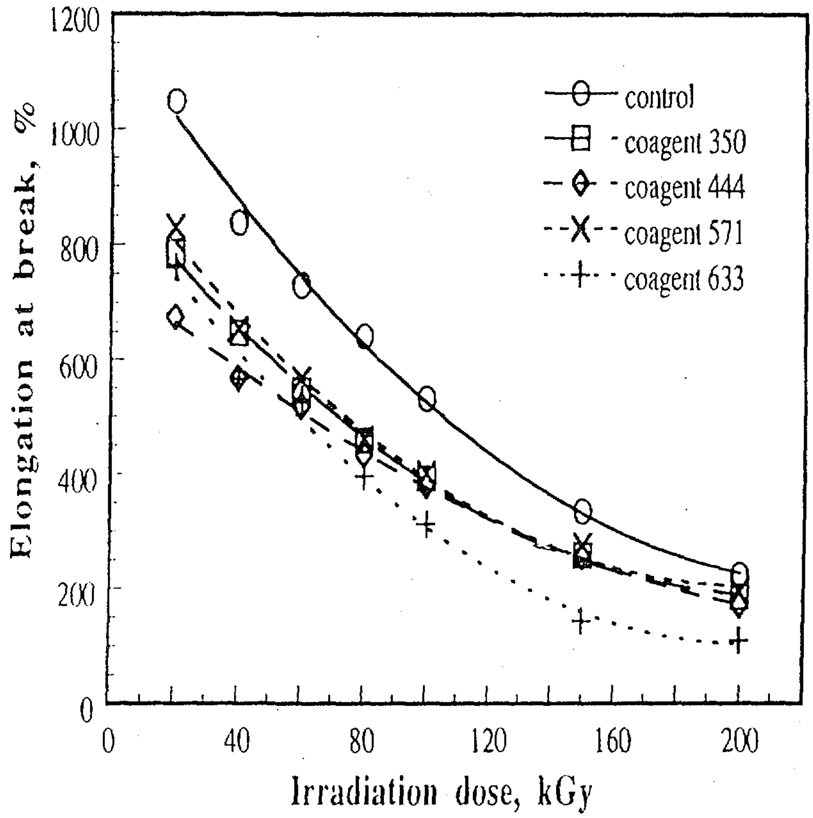

Fig. 4: Irradiation dose dependence of the elongation at break of the NBR rubber containing 45 pphr of silica type130 and 4 pphr of different coagents

strength of the samples of the formulations containing the different coagents (Fig. 5) increased with irradiation dose (with different rates) up to about 100 kGy and then decreased with rate depending on the type of the coagent added. The effect of coagents in improving the tensile strength of these formulations is outstanding, compared to that of the control sample, especially, at the low irradiation dose, i.e. 20 kGy. The gap in this effect diminishes as the irradiation dose increased up to about 80 kGy. At higher irradiation doses, the tensile strength of the samples containing the coagents decreased more than in its absence. The rate of increase or decrease in the TS depends on the type of the added crosslinking agent. The noticeable difference in the TS at low irradiation doses may be related to the different affinity of rubber and the different coagents to the irradiation dose. At higher irradiation doses, the effect of radiation degradation is predominant and its effect is more pronounced in presence of the coagents. The irradiation dose dependence of the E% of these formulations is presented in Fig. 6. It can be seen that the E% steadily decreased at different rates with irradiation dose up to about 100 kGy and then decreased with a lower rate. The order of decrease of E% for the different formulations is as follows: SR-444 > SR-350 > SR-517 > SR-633 > control. Moreover, the difference in the E% for the different samples is noticeable at low irradiation doses and becomes narrower as the irradiation dose increased. This may be attributed to the difference in the efficiency of the coagent compounds in enhancing the samples at low irradiation doses. Whereas, both crosslinking and degradation processes are taking place at higher rate at high irradiation doses, especially in the presence of the coagents as mentioned before.

In radiation-cured vulcanizates, rubber molecules adsorbed on the filler surface form a transition layer between the filler and the rubber. In this case the, formation of this layer is due to the effect of secondary electrons, the quantity of which is different because they pass through a material of non-uniform density. A high density of three-dimensional network characterizes the layer and the higher the content and the larger the specific surface area of the filler, the greater is the volume fraction of he rubber bonded to it [9]. This may explain the superior TS of the NBR samples filled with the ultra-fine silica if compared with those of the NBR samples filled with the HAF-carbon black at the same level of concentration and irradiation dose.

In a future work, the coagent type SR-517 was selected to study the effect of various coagent concentrations on the physical, mechanical and thermal properties of the filled NBR at different irradiation doses. This selection is based on the effect of this coagent in producing a set of optimum mechanical properties, i.e. moderate crosslink density, good tensile strength, as well as elasticity, at low irradiation dose, i.e. 40 kGy.

CONCLUSIONS

Four-selected polyfunctional compounds namely, trimethylacrylic ester, trimethylol propane trimethacrylate, zinc diacrylate and modified pentaerthitol triacrylate, as crosslinking agents, were tested for improving the mechanical properties of radiation vulcanized nitrile rubber. Ultra-fine particle silica gives the utmost reinforcement in rubbers if compared with HAF-carbon black filler. Products formulated with a high acrylonirile content nitrile rubber using a fumed silica of high surface area show high tensile and elongation. Incorporation of the different coagents resulted in an improvement in the mechanical properties of NBR rubber, filled either with HAF-black or fumed silica, if compared with the control samples, especially at low irradiation doses and their effect are more pronounced in case of HAF-carbon black than in case of silica.. The coagent type SR-517 showed moderate crosslink density, good tensile strength, as well as elasticity, at low irradiation dose, i.e. 40 kGy.

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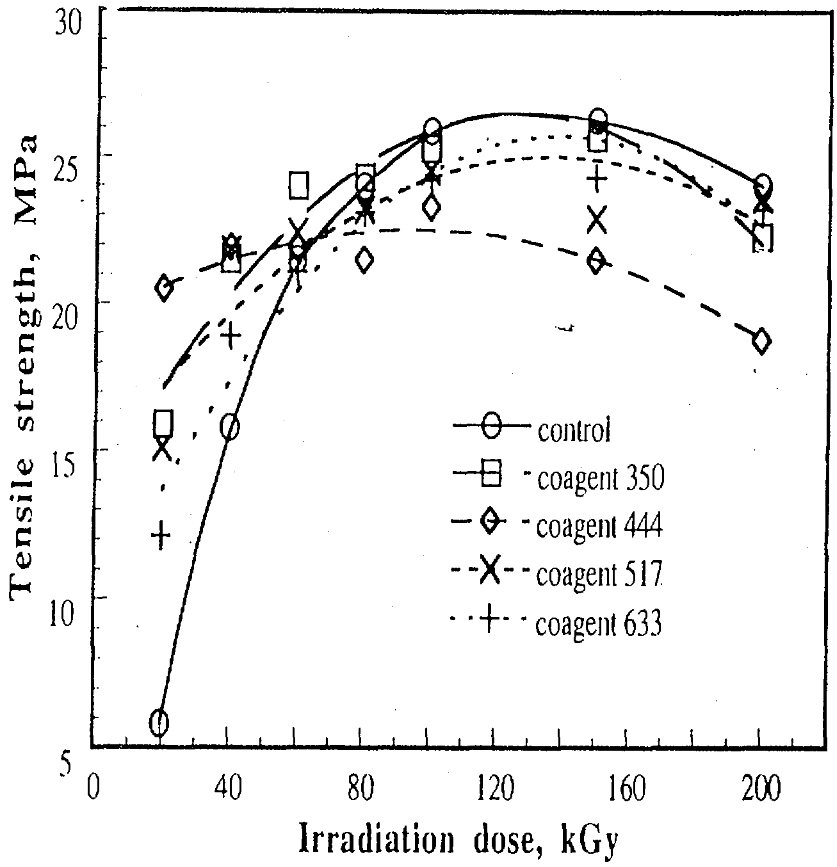

Fig. 5: Irradiation dose dependence of the tensile strength of the NBR rubber containing 45 pphr of HAF-carbon black and 4 pphr of different coagents.

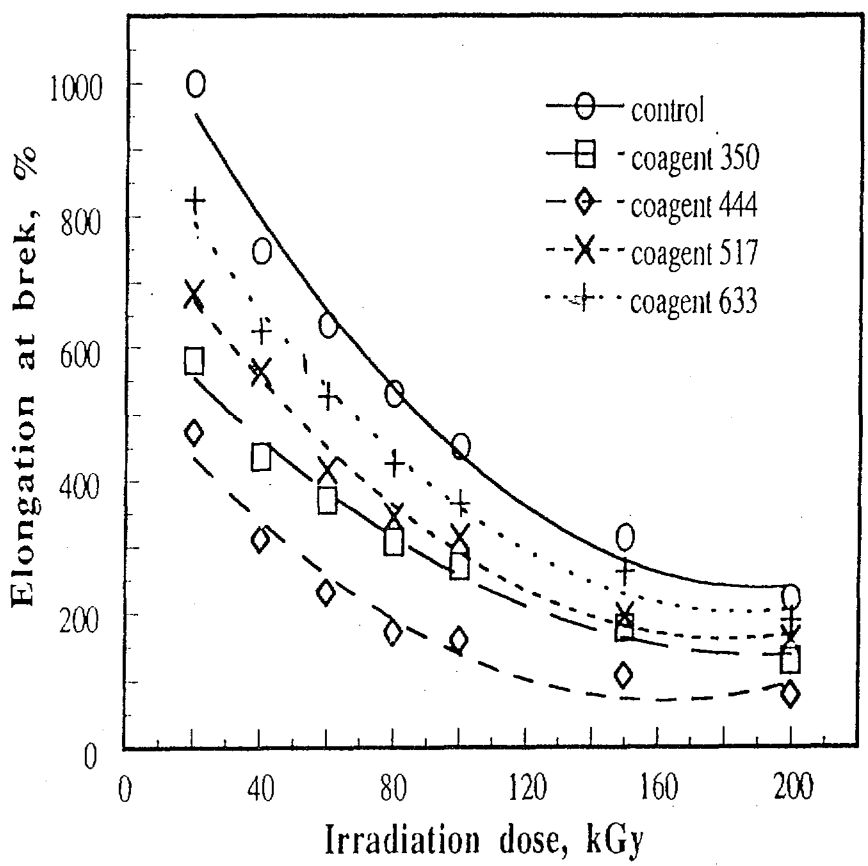

Fig. 6: Irradiation dose dependence of the elongation at break of the NBR rubber containing 45 pphr of HAF-carbon black and 4 pphr of different coagents

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