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Rad.C-2 Comparative Studies on Sulfur, Peroxide, and Radiation Vulcanization of EPDM Rubber.

M.M. Abdel-Aziz, *A.A. Basfar and *S. Mofti
National Center for Radiation Research and Technology, AEA, Nasr City, P.O.Box 29, Cairo, Egypt.
**Institute of Atomic Energy, KACST, P.O.Box 6086, Riyadh-11442, Saudi Arabia.*

ABSTRACT

The temperature and concentration dependence of the vulcanization characteristics and mechanical properties of EPDM rubber containing various concentrations of peroxide compounds was studied. The peroxides used are Luperox Di, Luperox 500-40 KE, Peroximon DC SC and Peroximon DC 40 KE. The optimum cure parameters for the different types of peroxides indicated that Luperox Di, relatively, give the best properties among the studied peroxides. The mechanical properties of EPDM containing different concentrations of Luperox Di and vulcanized at different temperatures were compared with those of either radiation or sulfur-cured EPDM. The modulus stress and tensile strength of the Luperox Di-cured EPDM were found to increase with either increasing the temperature of vulcanization and/ or concentration of the peroxide. Moreover, the tensile strength values are much higher than those of the sulfur-cured samples, except for those with low concentration of peroxide and vulcanized at relatively low temperature. A comparable result to those of the chemically vulcanized samples was attained by the radiation-vulcanized samples containing 1 phr of crosslinking agent and irradiated to 150 kGy.

Key words: Radiation crosslinking / EPDM / Mechanical properties / Peroxides / sulfur vulcanization.

INTRODUCTION

The selection of cure systems, i.e. vulcanizing agents and accelerators, is the most important task in rubber compounding. Unless a suitable vulcanizing agent in the proper concentration is used, a compound will not develop its optimum properties and adequate processability [1-4]. Sulfur is by far the most widely used vulcanizing agent. Sulfur vulcanization occurs only in unsaturated rubbers. Whereas, either Peroxides or ionizing radiation occur in the crosslinking of saturated, as well as unsaturated rubbers. They are also applied in sulfur curable rubber, such as NR, NBR, EPDM and SBR, where high heat stability and/or low compression set are demanded. In addition, they are especially helpful when sulfur vulcanization is undesirable, e.g. for cable covers (because sulfur free compounds are necessary to avoid copper corrosion), gaskets, heat stable spring components, like motor mounts, building profiles, and the like. The uses of ionizing radiation or organic peroxide leads to vulcanization of simple structure with physically and chemically stable C-C crosslinks[5]. Organic peroxides as crosslinking agents for elastomer offers superiors heat-aging properties when compared to sulfur vulcanized elastomer. However, the susceptibility of organic peroxides to induce premature crosslinking, i.e. scorch, during processing is a major concern in the rubber industry. In conventional methods of compounding, such as milling, internal mixing or extrusion, scorch occurs when the time-temperature relationship results in a condition, where the peroxide undergoes thermal decomposition, initiating the polymer crosslinking reaction. Excessive scorching (crosslinking) may cause the loss of the entire batch or plugging the equipment. Therefore, the

the most favorable approaches of avoiding scorch is to use an organic peroxide that is characterized by having a higher half-life temperature, i.e. the temperature at which 50% of the peroxide decomposes in a given time interval. Although crosslinking can often be produced by purely chemical means, radiation has considerable advantages and sometimes these can not be readily achieved in other ways. That is to say the wide range of temperatures at which the reactions can be induced, with little dependence on temperature of irradiation, etc.

In this study, the effect of four selected peroxide compounds, their concentrations and temperature dependence of the vulcanization characteristics and mechanical properties of EPDM formulations was studied. A comparison of the mechanical properties of EPDM rubber, vulcanized by peroxides, sulfur or ionizing radiation was also carried out.

EXPERIMENTAL

Materials

Ethylene-propylene diene monomer rubber (EPDM-Kelton 720, from DSM Elastomers, Europe B. V.), density ≅ 0.86 g/cm^3 and ethylene/propylene ratio ≅ 72/28 was used in this study. The name and the specifications of the used peroxides are listed in Table 1 and its formulations are presented in Table 2.

Table 1. Type and Specifications of the Peroxides Used.

No.	Chemical Name	Commercial Name	Half-life Temperature °C	
			1 hour	10 hour
1.	Di-t-butyl peroxide	Luperox DI	149	126
2.	2,5-dimethyl-2,5-di (t-butyl peroxide) hexane.	Luperox 500-40 KE*	138	119
3.	Dicumyl peroxide	Peroximon DC SC	135	115
4.	40% active, Dicumyl peroxide.	Peroximon DC 40 KE*	135	115

*40% active peroxide with 60% clay.

Table 2. EPDM Rubber-Peroxide Formulations

Component		Quantity, phr
EPDM (Kelton - 720)	...	100
IPPD (Anti-oxidant)	...	0.5
TMQ (Anti-ozonant)	...	0.5
N 550 Carbon Black	...	50
Sunpar Oil 2280	...	5
Organic peroxides	...	Variable

Zn diacrylate (SR-633) and Modified pentaerthitol triacrylate (SR-444) from Cary Vally Chemical Company, France, were used as radiation crosslinking compounds. In addition, HAF-carbon black and fumed hydrophobic silica type R-972 with particle size of 16 nm and surface area of 113 M^2/g, were used as fillers and reinforcing compounds. The formulation for the sulfur- vulcanized samples includes: 100 phr of EPDM (Kelton 720), 80 phr of Carbon black - N 550, 50 phr of Carbon black - N 762, 110 phr of Oil 2280, 5 phr of ZnO, 0.5 phr of Stearic acid, 1..5 phr of TETRON- A, 2.0 phr of ZDBC, 0.6 phr of TMTD, 0.66 phr of sulfur; and vulcanized at 150 °C for 30 minutes.

TECHNIQUES

Preparation and irradiation of different rubber compounds

Compounding, sheeting and vulcanizing of the different rubber compounds were in accordance with ASTM standards as follows: D-1485 methods for rubber sampling and sample preparation. Compounding of materials was in accordance with D-3182 for mixing standard compounds and preparing standard vulcanized sheets. Five batches from each formulation were prepared and five samples from each batch were tested. Compounding was done using Brabender Plasti-Corder PL2000 and mixer type 350S. The mixer head temperature was maintained at 60°C for at least 5 minutes before mixing. The unloaded rotor speed of the mixer was 64 rpm. The average time for mixing was about 13 minutes. After compounding, rheometric properties and vulcanization characteristics were measured using Monsanto-Oscillating disk curemeter model ODR2000E in accordance with test method D-2084. The remaining compound was sheeted out to about 2-mm thickness after shrinkage has taken place. After 24 h., vulcanized sheets were prepared using PHI hydraulic hot press model Q236H at 150°C under 150-kg/cm^2 pressure and for specified times determined before by the Monsanto curemeter.. 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 for the radiation-vulcanized samples. 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. Dumbbells shaped specimens were cut down from sheets using a steel die of standard width (6mm) and length (20mm). The measurements of mechanical properties were carried out using an Instron tensile testing machine model 4505, USA.

RESULTS AND DISCUSSIONS

A popular method of evaluating the cross-linking efficiency of peroxides is the Monsanto ODR, which records shear modulus (torque) as a function of time during the crosslinking of a polymer. This modulus is proportional to the extent of crosslinking and is a representation of the cure reaction. The cure characterization, namely t_2, S_{min}, t_{90}, S_{90} and peak rate of the EPDM formulations containing peroxide type Luperox Di is presented in Figs. 1-5. The parameters determined from the rheographs of the respective compounds are presented in these figures as a function of temperature. Where, t_2 is the scorch time, time corresponding to two units above minimum torque. ASTM defines scorch time as the time to incipient crosslinking under specified isothermal condition [6]

of vulcanization). At this point, the stock also loses its plastic quality, thus preventing the stock from being processed further [7, 8]. S_{min} is the minimum torque in kg-cm, which relates to the flow of rubber compound during mixing (its viscosity). Whereas, t_{90} and S_{90} are the time and torque, respectively, corresponding to the optimum cure, the time to 90% of the maximum torque in kg-cm. In addition, the peak rate is corresponding to the change of torque with time at the peak, in kg-cm/min., i.e. rate of the reaction.

From these figures, it can be noticed that the values of t_2, S_{min} and t_{90} for the different formulations steadily decreased as either the temperature or the concentration of the peroxide is increased. In contrast, the values of the torque (S_{90}) and the peak rate increased with increasing of either temperature or the concentration of the peroxide. Besides, the values of S_{90} show maximums, which also depend on concentration of the peroxide as well as the temperature of vulcanization.

It can be predicted from the presented data that the formulations containing 4 phr from Luperox Di and vulcanization at 170°C for 30 minutes may give the best mechanical properties (S_{90} = 88 kg-cm and scorch time = 2 min.).

Similarly, the dependence of the vulcanization parameters of the EPDM rubber, at different temperatures ranging from 150 190 °C, on the type and concentrations of the other peroxides were studied, based on data deduced from rheometric measurements for these formulations. These peroxides namely Luperco 130 XL 45, Peroximon DC SC and Peroximon DC40KE. The optimum cure parameters for the different types of peroxides deduced from the corresponding rheographs are calculated and presented in Table 3. From this table, it can be concluded that the samples containing Luperox Di, relatively, give the best properties followed by that containing peroximon DC SC.

The number of crosslinks formed depends on the concentration of the peroxide, its activity and the reaction time. It is termed as the degree of vulcanization or crosslink density, which is presented here by

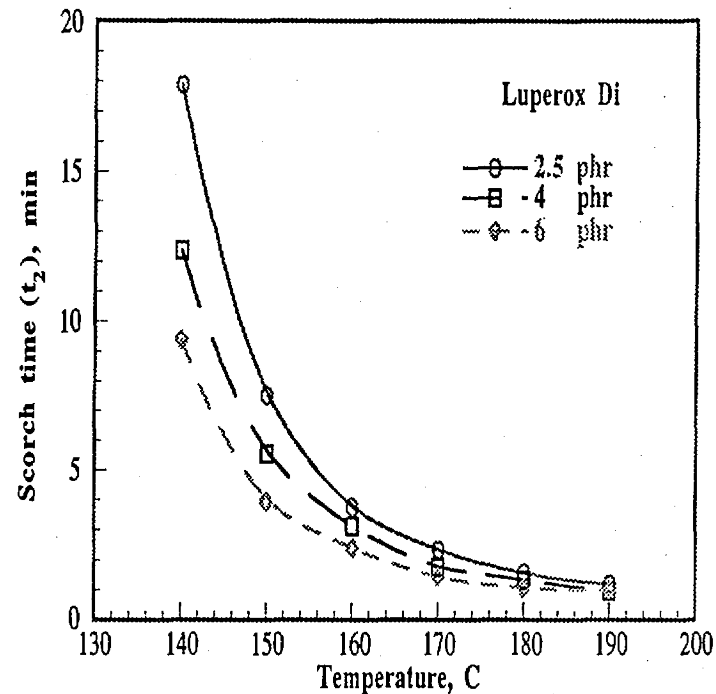

Fig. 1 : The change of the scorch time (t_2) with temperature for EPDM compounds containing different concentrations of peroxide type Luperox Di

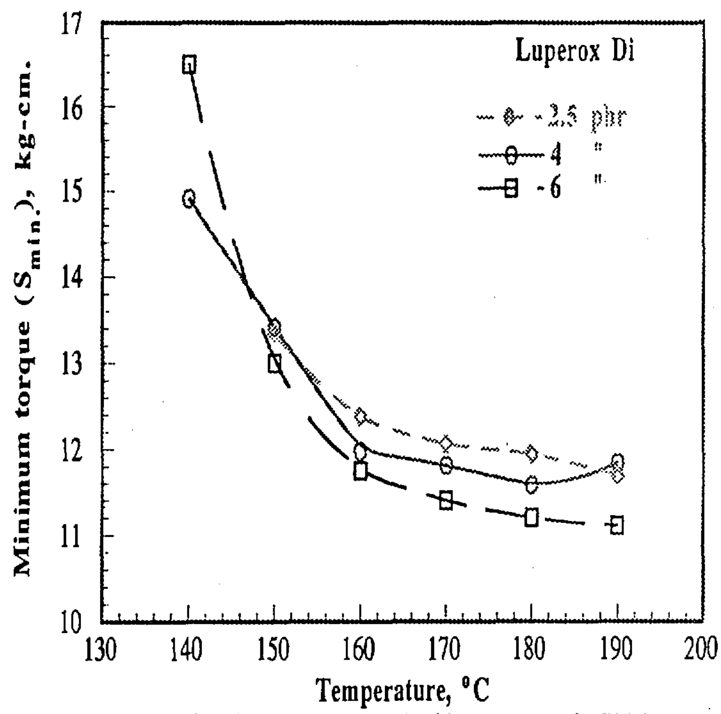

Fig. 2 : The change of minimum torque ($S_{min.}$) with temperature for EPDM compounds containing different concentrations of peroxide type Luperox Di

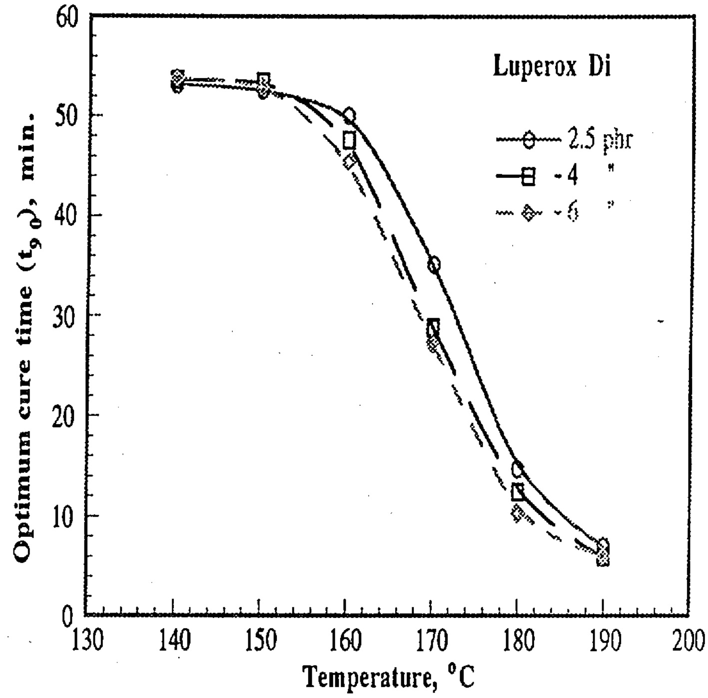

Fig. 3: The change of the optimum cure time (t_{90}) with temperature for EPDM compounds containing different concentrations of peroxide type Luperox Di

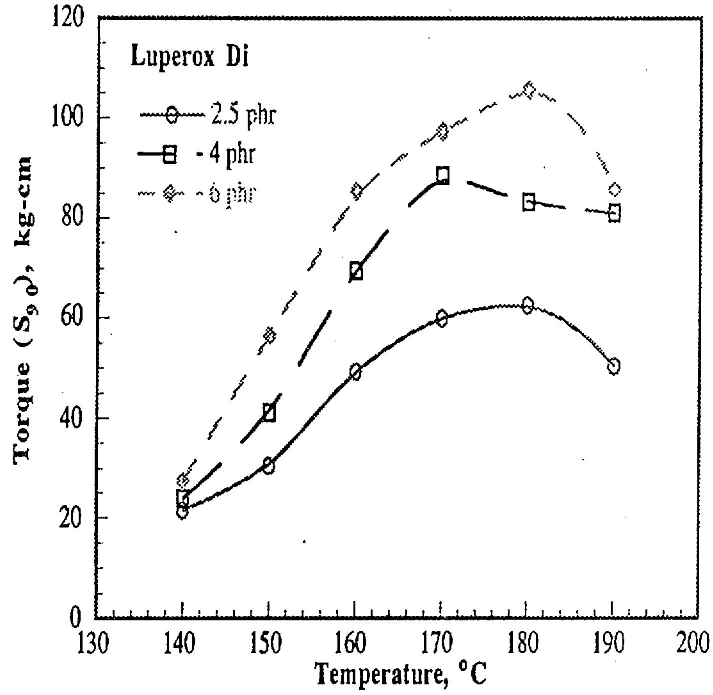

Fig.4: The change of the optimum torque (S_{90}) with temperature for EPDM compounds containing different concentrations of peroxide type Luperox Di

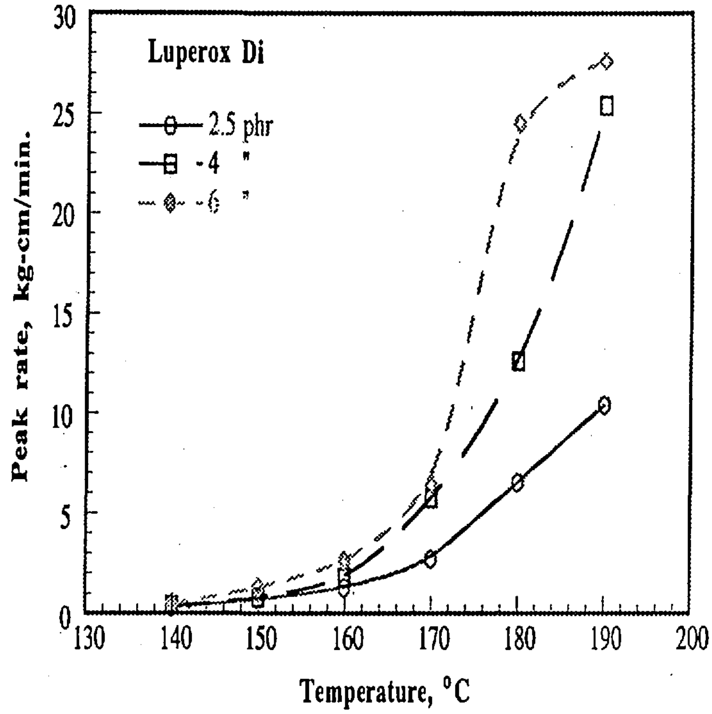

Fig. 5 :The change of the peak rate with temperature for EPDM compounds containing different concentrations of peroxide type Luperox Di

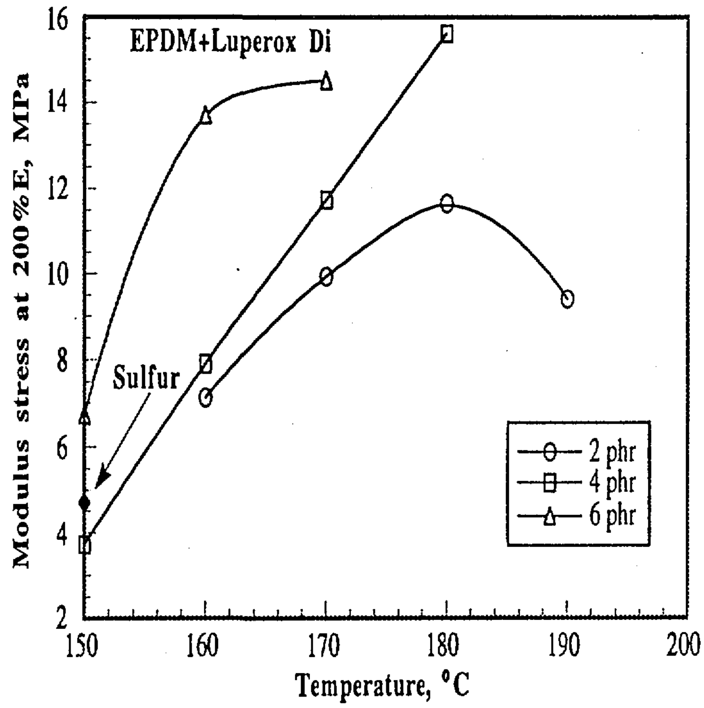

Fig. 6 :Temperature dependence of the Modulus stress at 200%E. of EPDM rubber containing different concentrations of peroxide type Luperox Di

the maximum torque (S_{90}). Depending on the choice of the chemicals of vulcanization, the start of vulcanization (scorch) of a rubber compound can be rapid or slow (t_2).

Table 3: The Optimum Cure Parameters for EPDM Enhanced With Different Types of Peroxides.

Parameter	# 1 Luperox Di	# 2 Luperco 130xL45	# 3 Peroximon DC SC	# 4 Peroximon DC40KE
1. Concentration of Peroxide, phr.	4	6	6	8
2. Optimum time for cure (t_{90}), min.	30	25	22	26
3. Temperature, °C.	170	180	160	160
4. Scorch time (t_2), min.	2	1	1.8	1.9
5. Torque at optimum cure, (S_{90}), kg-cm.	88	70	81	64

In a compression molding process, it is necessary for the rubber compound to maintain a more or less prolonged flow ($S_{min.}$) in order to fill all cavity spaces and for all entrapped air to escape. The tightening caused by crosslinking by which an undesirable deformation is prevented is opposed by the softening caused by the heat of vulcanization. A rapid vulcanization initiation is undesirable in most cases, as it interferes with safe processing of the compounds and ultimately is the cause of vulcanization already occurring during mixing and processing, which in turn can no longer be extruded or calendered[9].

In the under cure phase, most technological properties of rubber are not yet fully developed. It is therefore, usually necessary to vulcanize to optimum cure stage (maximum stress values). Since all technological properties do not reach their optimum value simultaneously, it is necessary to compromise with a high over and under cure.

Mechanical Properties of EPDM

The mechanical properties were measured for the samples containing different concentrations of Luperox Di and vulcanized at different temperatures. The obtained data are presented in Figs. 6-8. Besides, these data are compared with those of the sulfur-cured EPDM. From these figures, it can be observed that the values of modulus stress at 200% E, as well as the ultimate tensile strength increase with either increasing the temperature of vulcanization and/or the concentration of the added peroxide. However, this increase with temperature shows maxims in most cases and after that the tensile strength declined.

Moreover, the tensile strength values are much higher than those of the sulfur-cured samples, except for those, with low concentration of peroxides, i.e. 2-4 phr, and vulcanized at relatively low temperature, i.e. 150°C. In contrast, the values of the ultimate elongation decreased with either increasing the peroxide content and/or temperature of vulcanization. Meanwhile, all these values of E% are less than those for the sulfur-cured EPDM samples. Consequently, it appears that the formulation of EPDM containing 6 phr of Luperox Di and vulcanized at 160°C gives the best tensile properties, but this on the expense of its elasticity. However, a formulation combining good tensile strength with suitable elasticity is desired.

Hence, other trials to improve the elongation of these formulations were carried out. A modified formulation based on that of ASTM D3568-86 was developed. This formulation containing: EPDM (100 phr), carbon black-N762 (80 phr), ZnO (5 phr), Stearic acid (1 phr), oil-2280 (50 phr), TMTD (1 phr), MPT (0.5 phr).Luperox Di (6 phr) and vulcanized at 160°C for 60 minutes. The vulcanization condition was based on the data deduced from the rheometric measurements for this formulation.

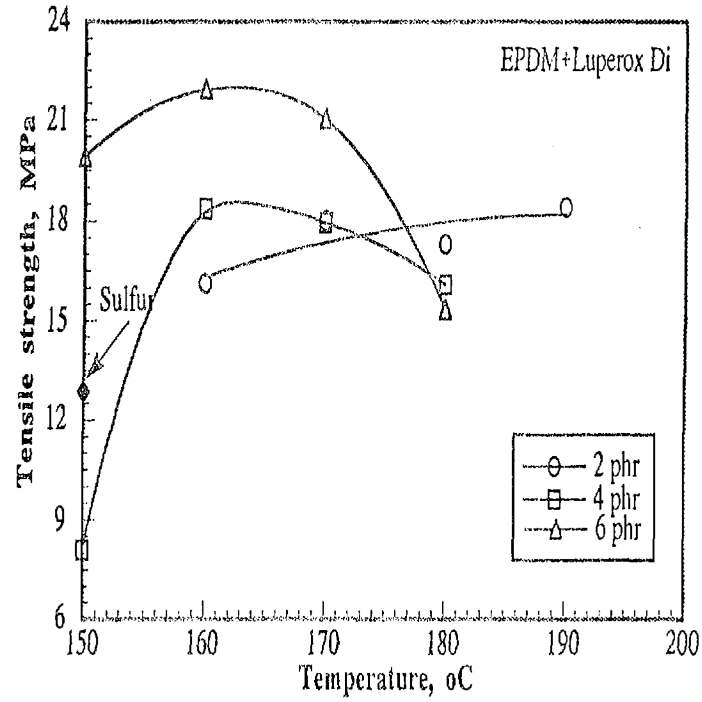

Fig. 7: Temperature dependence of the tensile strength of EPDM rubber containing different concentration of peroxide type Luperox Di

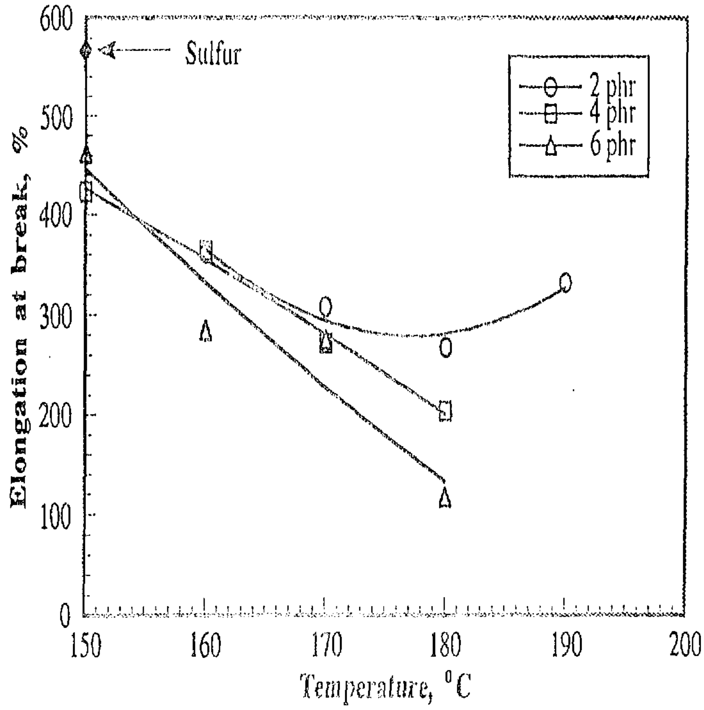

Fig. 8: Temperature dependence of the elongation of break of EPDM rubber containing different concentrations of peroxide type Luperox Di

The mechanical properties, namely TS and E% of the latter formulation were 16 MPa and 561%, respectively, which are, relatively, the best compared with those of the other samples including the sulfur-cured sample. Hence, the latter modified formulation for EPDM will be considered for optimum cure conditions and mechanical properties and to be used as a reference for the comparison with radiation developed formulations.

Mechanical Properties of Radiation-Vulcanized EPDM Rubber

The irradiation dose dependence of the TS and E% of EPDM rubber either filled with HAF-carbon black or ultra-fine silica type Aerosil 972 at the same concentration, i.e. 45 phr, and enhanced with 2 phr of either the coagent SR-633 or SR-444 are presented in Figs 9 and 10, respectively. It has been noticed that, in case of the coagent type SR-633, crosslinking did not occur at an irradiation dose less than 40 kGy. While in the case of the trifunctional monomer, i.e. SR-444, crosslinking was already detected at irradiation dose as low as 20 kGy. In addition, the TS increased with the increase of irradiation dose and reached their maximum values at 80 100 kGy, in case of the samples enhanced with the coagent SR-444, and at 150 kGy for the samples enhanced with the coagent SR-633, beyond which the TS decreased. This behavior may be attributed to the increased crosslinking brought about by irradiation resulting in improvement in TS values.

However, at comparatively higher irradiation doses, the increase in network formation accompanied by expected degradation as well as the reduced ability of macromolecules for orientation and ordering lead to a decrease in the tensile strength [10, 11]. In addition, the values of the E% are steadily decreased with increasing irradiation dose (Fig. 10). The magnitudes of E% of the samples containing the coagent SR-444 are lower than those of the samples containing the coagent SR-633 at all irradiation doses. Besides, similar E% values to those of the chemically vulcanized samples were attained for the irradiated samples containing the coagents SR-444 and SR-633 at 80 kGy and 150 kGy, respectively.

CONCLUSION

The optimum cure parameters of EPDM containing different concentrations of different peroxide compounds at different temperatures were deduced using Monsanto rheometer. The samples containing the peroxide type Luperox Di, relatively, give the best properties followed by that containing Peroximon DC SC. The tensile strength values of the Luperox Di cured EPDM are much higher than those of the sulfur cured samples, but this on the expense of the elasticity. Th radiation- modified formulations of the EPDM rubber compounds have superior mechanical properties compared to those of the chemically vulcanized compounds.

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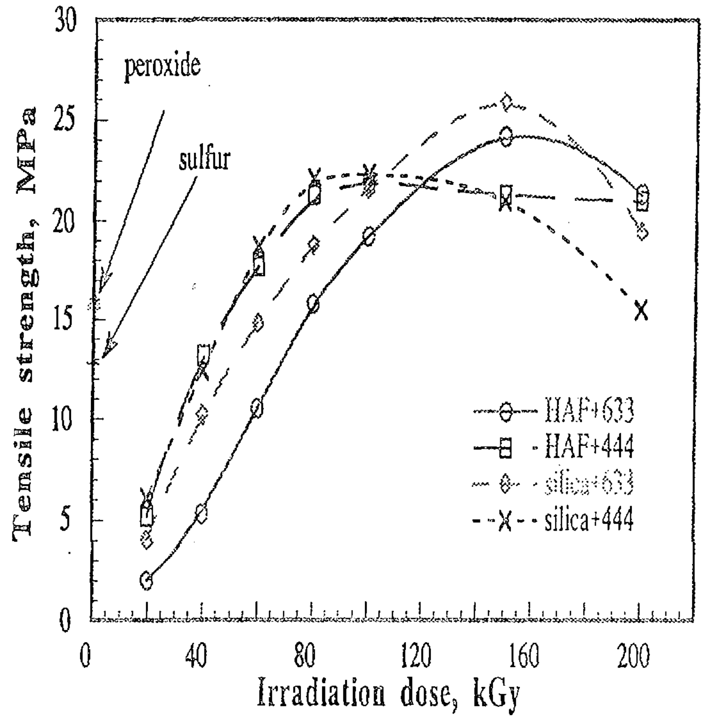

Fig. 9: Irradiation dose dependence of the tensile strength of EPDM rubber filled with 45 phr of either HAF-carbon black or silica type A-972 and enhanced with 2 phr of either the coagent SR-444 or SR-633

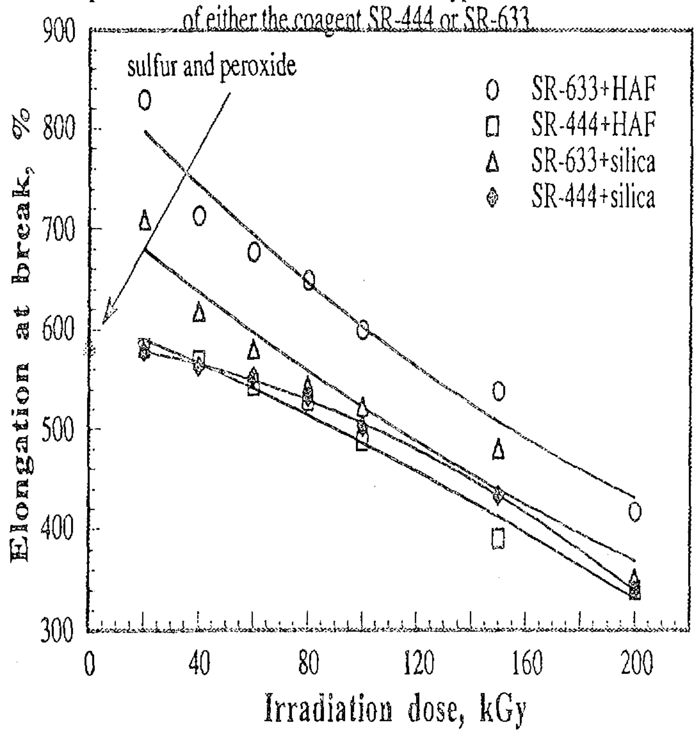

Fig. 10: Irradiation dose dependence of the elongation at break of EPDM rubber filled with 45 phr of either HAFcarbon blackorSilicatype 972 and enhancedwith 2 phr of either the coagent SR-633 or SR-444

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