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The Reinforcing Effect of Rubber Modification with Nitroso Derivatives

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ABSTRACT

The use of nitroso derivatives in rubber compounds leads to a reinforcing effect with important practical implications. The mechanism of action of these promoters is explained on the basis of the theory according to which the reinforcing effect is due to the strain-crystallization process. This process is dependent on various factors, one of them being the presence of a network based on weak "rubber...carbon black" bonds. The properties of crude and cured blends on natural rubber, polyisoprene, and modified polyisoprene are compared. When nitroso derivatives are used, the active sites on the polymer chain are probably the nitroxyl radicals formed during the modification process. According to the mechanism proposed by the authors in previous papers, the formation of nitroxyl radicals is accompanied by changes of macromolecular characteristics which permit us to explain the reinforcement as well as the modification of viscoelastic and physical-mechanical properties of crude and cured compounds. On the basis of assumptions made on the whole set of reactions regarding both polymer modification with nitroso derivatives and that of rubber compounds, one can explain not only some of the properties but also the conditions in which modi-

fication should be made in order to obtain an optimal reinforcing effect.

INTRODUCTION

The idea of obtaining a reinforcing effect in rubber compounds is rather old, and its aim is to obtain vulcanizates with improved physical characteristics. In the early 1940s it was discovered that mixing natural rubber with carbon black at elevated temperatures with long heating times yields homogeneous compounds as well as a better reinforcing effect in the vulcanizates. The same improvements in properties at substantially shorter mixing times at lower temperatures were obtained by the addition of a nitroso derivative [1].

With the growth of the synthetic polyisoprene industry, interest in nitroso derivatives increased, such compounds now being used especially in order to improve the properties of green compounds. Although synthetic *cis*-polyisoprene rubber is largely similar to natural rubber, it cannot be substituted in many tire compounds because of the lower green strength of rubber compounds based on synthetic polyisoprene as compared with those based on natural rubber (NR). This is why the percentage of synthetic polyisoprene in radial and heavy duty tires is low. Green strength is defined as the difference between stress at break (σ_b) and stress at yield (σ_y) for unvulcanized rubber compounds [2]. A rubber with good green strength has $\sigma_b > \sigma_y$, and the greater this difference, the better the green strength. Compounds based on natural rubber have $\sigma_b - \sigma_y > 0$, while those based on synthetic polyisoprene have $\sigma_b - \sigma_y \cong 0$ or even < 0 .

There are several ways of improving this property, one of them being the modification of polyisoprene rubber with nitroso derivatives (see Fig. 1) [2]. The modification can be performed by using various nitroso derivatives either at the end of the polymerization reaction or during compounding [3].

RESULTS AND DISCUSSION

Marei has shown that compounds based on NR exhibit strain-induced crystallization at room temperature. The crystalline phase content is higher at higher extensions and lower temperatures. In the absence of strain, the crystalline phase content, if present, is low, so the compound can be worked easily. During radial tire manufacture the compound is subject to strain which induces crystallization and, in consequence, a reinforcing effect is obtained. In compounds based on synthetic rubber the crystalline phase appears at lower temperatures [4], which is why at the temperatures used in

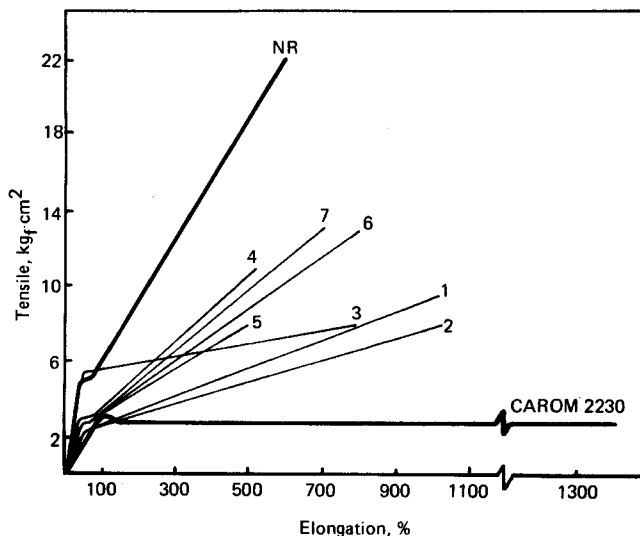


FIG. 1. Stress-strain curves for natural rubber (NR), synthetic polyisoprene (CAROM 2230), and polyisoprene modified at the end of the polymerization process with different amounts of *p*-nitrosodiphenylamine (PNDFA).

tire manufacture the compounds "flow" and $\sigma_b < \sigma_y$. The compounds may also be reinforced by adding crystallizable polymers (e.g., gutta-percha, polyethylene, polypropylene, *trans*-polybutadiene, etc.) [5]. At room temperature all these polymers are crystalline (see Table 1), so if they are distributed homogeneously in rubber, the compound obtained has a good green strength. Such compounds are difficult to obtain because mixing has to be carried out at relatively high temperature, (above the melting point). For *trans*-polybutadiene there is a dependence between microstructure and the melting point of the crystalline phase, and thus it is possible to obtain a polymer similar to natural rubber in respect of its green strength. A too high content of the crystalline phase has a reinforcing effect, even in those stages of tire manufacture in which the compound must flow.

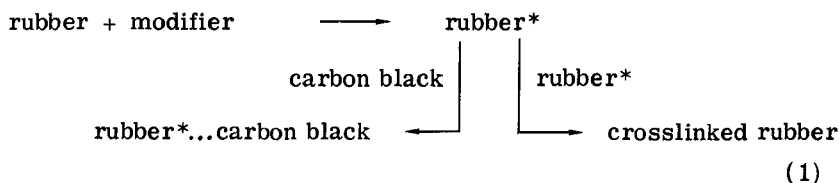
To explain the difference between the green strength of compounds based on natural rubber and those based on synthetic polyisoprene, some physical-chemical properties (e.g., molecular weight of sol fraction, gel content, MWD, content of oligomers, composition of acetic extract) were studied. On the other hand, natural rubber has a greater conformational regularity (all the monomer units are head-to-tail while in synthetic polyisoprene head-head and tail-tail additions are also present, which result in a higher crystallization rate [6]).

TABLE 1. Physical Properties of Some Crystalline Polymers [6]

Polymer	T _g , °C	Melting point of crystalline phase, °C
Natural rubber	-71	25-35
Gutta-percha	-71	60-70
Polyethylene	-90	130
Polypropylene	-35	-
trans-Polypentenamer (80% trans)	-	15-20

Marei [7] showed, based on x-ray studies, that one of the most important factors causing crystallization is the existence of a weak network which was identified in green compounds based on natural rubber and also in polyisoprene modified with nitroso derivatives.

To explain the formation of this weak network in the case of polyisoprene modified with nitroso derivatives, the general scheme of vulcanizate reinforcement is accepted. According to this, in the polymer reaction with a modifier, active sites (*) in the polymer chain are formed which, in turn, can interact with the active sites located on the surface of carbon black particles [1].



In the absence of carbon black there is no reinforcing effect, as seen from Table 2 where the mechanical characteristics of raw rubber are given.

It can be seen that all types of rubber have very low values of tensile strength at break. When carbon black is present, these values increase for NR and modified polyisoprene (MIR). The higher values for MIR sustain the assumption of active site formation in the polymer chain by reaction of the polymer with the nitroso compound. The green strength depends on the carbon black content in the compound. The higher the carbon black content in the compound, the greater the green strength because the number of weak bonds between rubber and carbon black is increased. On the other hand, this higher number of weak bonds leads to "hard" compounds (Mooney viscosity increases

and elasticity decreases). The same behavior was observed for compounds in which carbon black was absent [8].

By modification with nitroso compounds, some physical-mechanical properties of vulcanizates are altered, e.g., the tensile and elongation at break diminish. The latter property shows the same variation with increasing carbon black content (see Table 2) [2].

The mechanism of weak bond formation ("rubber*...carbon black") is a good explanation of the changes of properties of green compounds at low nitroso compound concentrations. The dependence of the green strength of polyisoprene compounds on the amount of nitroso derivative shows a maximum [9]. At the same time, changes of the properties of vulcanizates show some alterations of macromolecular chains during the modification process. To explain these experimental results it is necessary to elucidate the nature of active sites as well as their formation in the polymer chain.

On the basis of experimental data obtained in the modification process of polyisoprene with p-nitrosodiphenylamine (PNDFa), we have proposed a mechanism for this reaction [10].

EPR data show that modification is a very complex radical process. In the course of this process, two types of radicals are formed: nitroxyl and peroxy radicals (see Figs. 2-4) [11, 12]. Nitroxyl radicals are formed in the early stages of the process via polyisoprene macroradical trapping by PNDFa. The consumption of nitroxyl radicals is a complex process which can lead to stable peroxy radicals, and in some circumstances they can be trapped in the network of the crosslinked polymer [12].

The molecular weight of the sol fraction decreases in the course of modification (see Fig. 5). For a gel-free polymer of low molecular weight, the increase of gel content is low, while for one with a high gel content and a high molecular weight the increase is large. The changes of the molecular weight of the sol fraction, of gel content, and of MWD (see Figs. 5-7), led to the idea that the modification of IR with PNDFa is a complex process of scission and recombination reactions which depend on PNDFa content and on polymer macrostructure (see Figs. 5-7). At low PNDFa concentrations the scission reactions are predominant. The reaction products of these scissions can react either with each other or with the polymer chain to give branched or even crosslinked polymers. The greater the PNDFa, the more probably these reactions will occur. Consequently, the viscosity of the sol fraction decreases. At the same time, the recombination reactions occur more frequently, so the amount of branched and crosslinked polymer increases [3].

From changes in the EPR signal of the nitroxyl radical and that of the inherent viscosity of the sol fraction it was concluded that the molecular weight of the polymer diminishes both in the course of radical formation and during their consumption (see Fig. 8) [12].

By using EPR, UV, and VIS spectroscopy, it was observed that the modification process can be accelerated by radical initiators (see Fig. 9) [13].

TABLE 2. Physical-Mechanical Properties of Various Polyisoprene Samples

Property	Sample					
	Natural rubber SMR-20		Isoprene rubber CAROM-2230		Modified isoprene rubber MIR-1	
	I	II	I	II	I	II
<u>Properties of Raw Rubber</u>						
Tensile strength at break, σ_b , kg_f/cm^2	1.75		0.5		0.8	
Tensile strength at yield, σ_y , kg_f/cm^2	2.12		1.9		1.2	
Elongation, %	30		30		30	
Green strength, $\sigma_b - \sigma_y$, kg_f/cm^2	-0.37		-1.4		-0.4	
<u>Properties of Unvulcanized Compound</u>						
Mooney viscosity, ML (1 + 4), 100°C	61.3	87.3	69.6	84	55	95
Tensile strength at break, σ_b , kg_f/cm^2	11.4	23.75	4.7	4.3	5.44	16
Tensile strength at yield, σ_y , kg_f/cm^2	2.4	5.13	4.5	3.68	3.29	4.3

Green strength, $\sigma_b - \sigma_y$, kg_f/cm^2 9.0 18.62 0.2 0.62 2.15 11.7
 Elongation, % 682 420 1000 1000 862 550

Properties of Vulcanized Compound

300% Modulus, kg_f/cm^2 92 106 85 125 66 134
 Tensile strength at break, σ_b , kg_f/cm^2 272 287 252 258 215 219
 Elongation, % 400 500 560 470 520 415
 Permanent set, % 12 16 16 12 16 12
 Shore hardness 61 64 57 67 53 62

	Rubber	Carbon black HAF	Stearic acid	Zinc oxide	Vulcacite CZ	Sulfur
I, phr	100	35	2.0	5.0	0.7	2.25
II, phr	100	50	2.0	5.0	0.8	2.0

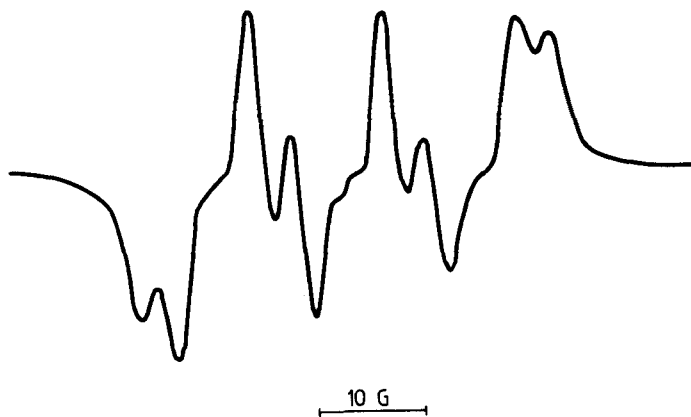


FIG. 2. EPR spectra of nitroxyl radicals formed in the course of modification of polyisoprene with *p*-nitrosodiphenylamine (PNDFA).

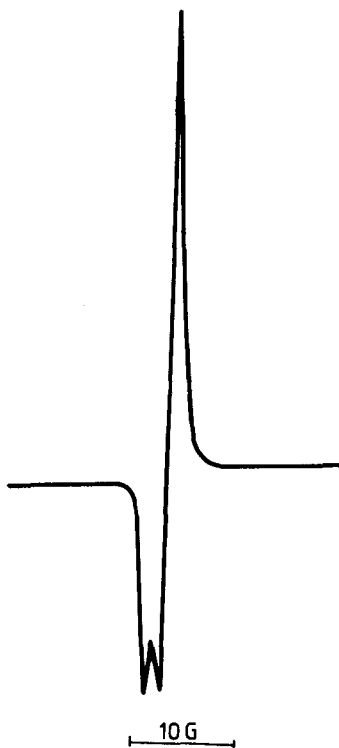


FIG. 3. EPR spectra of peroxy radicals formed at the end of polyisoprene modification with *p*-nitrosodiphenylamine (PNDFA).

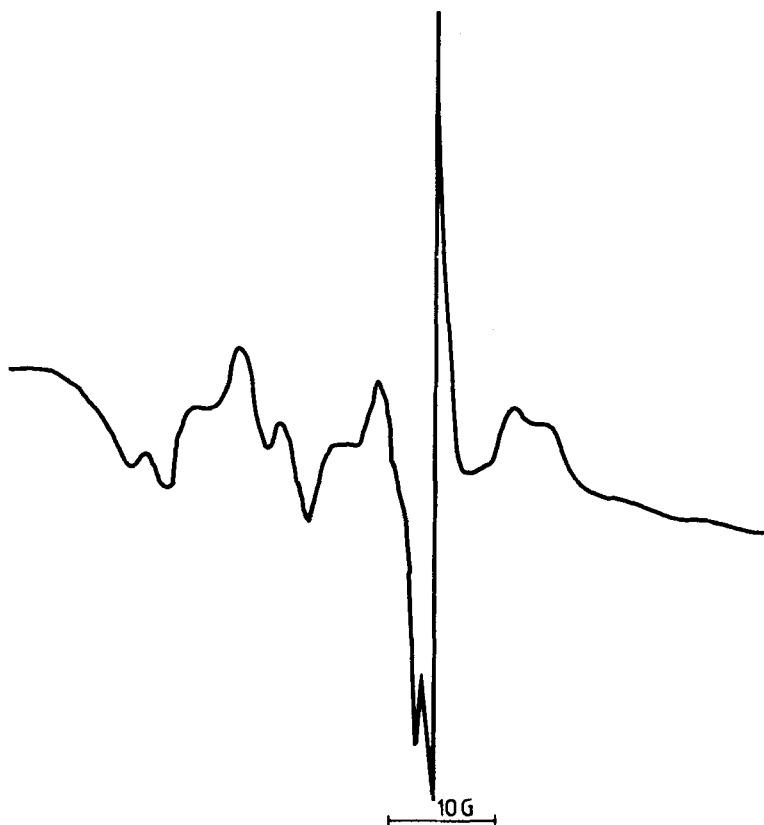


FIG. 4. EPR spectra of the reaction mass which contains nitroxyl and peroxy radicals.

Some long-life radicals can offer useful information about the nature of the radical process. Thus, by studying the EPR spectra of different long-life radicals both in polyisoprene and in a mixture of polyisoprene with PNDFA, it was observed that the rate of consumption of radicals is higher in the latter system. This proves that in the presence of PNDFA more radicals are formed which are able to deactivate the long-life radicals [11, 14].

By raising the temperature, both the formation of nitroxyl radicals from PNDFA and their consumption are accelerated (see Fig. 10) [13].

At a higher molecular weight of the fraction, the bound PNDFA content decreases (see Table 3) [9]. Such a dependence suggests that PNDFA is not randomly bonded along the polymer chain but preponderantly at its ends.

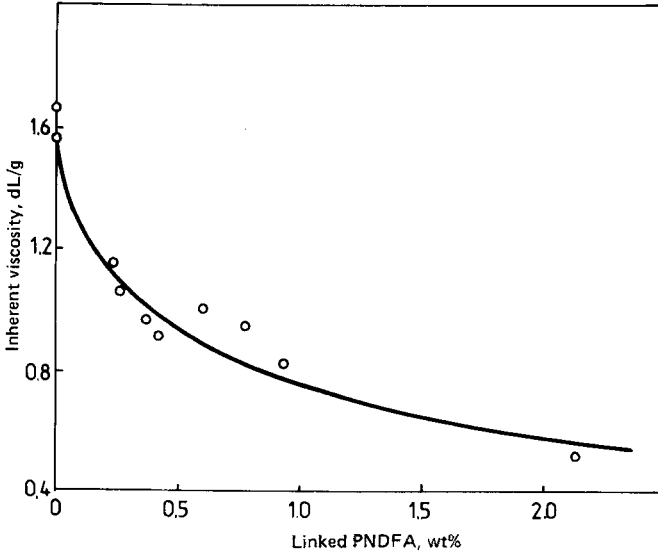


FIG. 5. Variation of inherent viscosity of the sol fraction of modified polyisoprene with PNDF A.

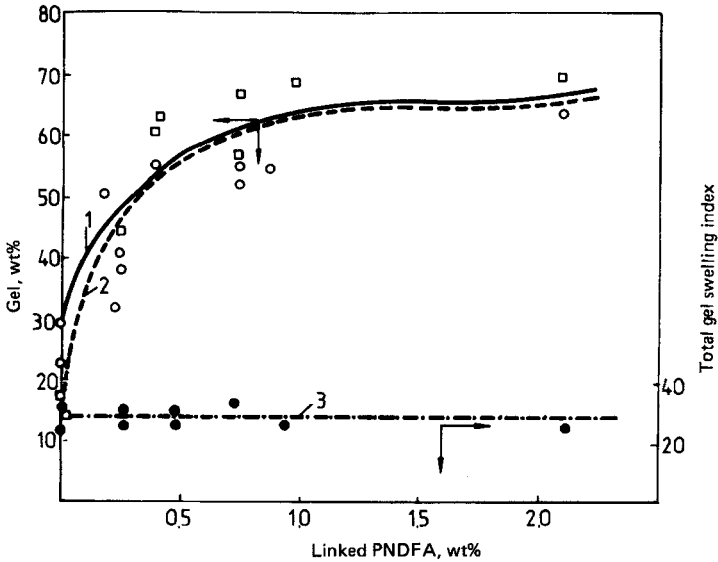


FIG. 6. Variation of gel content of polyisoprene modified with various amounts of PNDF A.

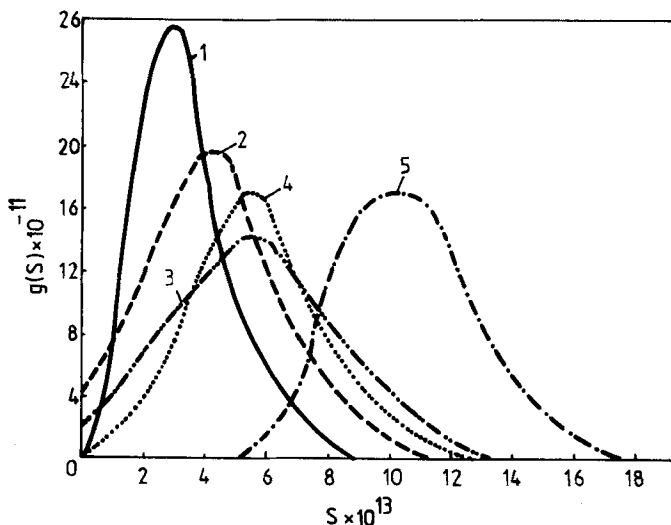


FIG. 7. MWD of the sol fraction of polyisoprene modified with various amounts of PNDFA. 1) 0.2% PNDFA, $\eta_{inh} = 1.16$ dL/g; 2) 0.4% PNDFA, $\eta_{inh} = 0.99$ dL/g; 3) 0.6% PNDFA, $\eta_{inh} = 0.90$ dL/g; 4) 0.8% PNDFA, $\eta_{inh} = 0.83$ dL/g; 5) polyisoprene, $\eta_{inh} = 1.93$ dL/g.

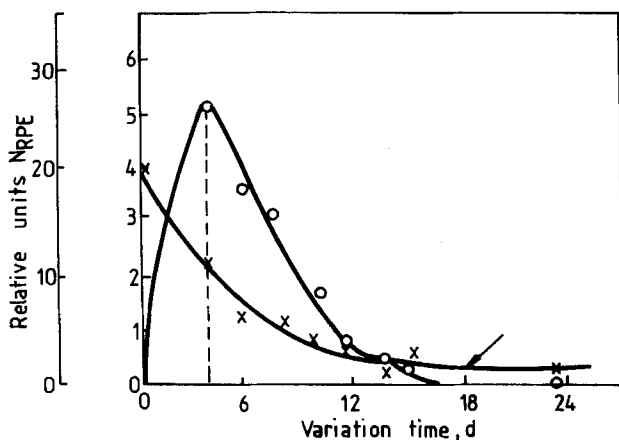


FIG. 8. Variation of EPR signal of nitroxyl radicals (in conventional units) and of inherent viscosity of polyisoprene with linked PNDFA. Solvent, toluene; concentration of polymer, 10%; concentration of PNDFA, 1.5%.

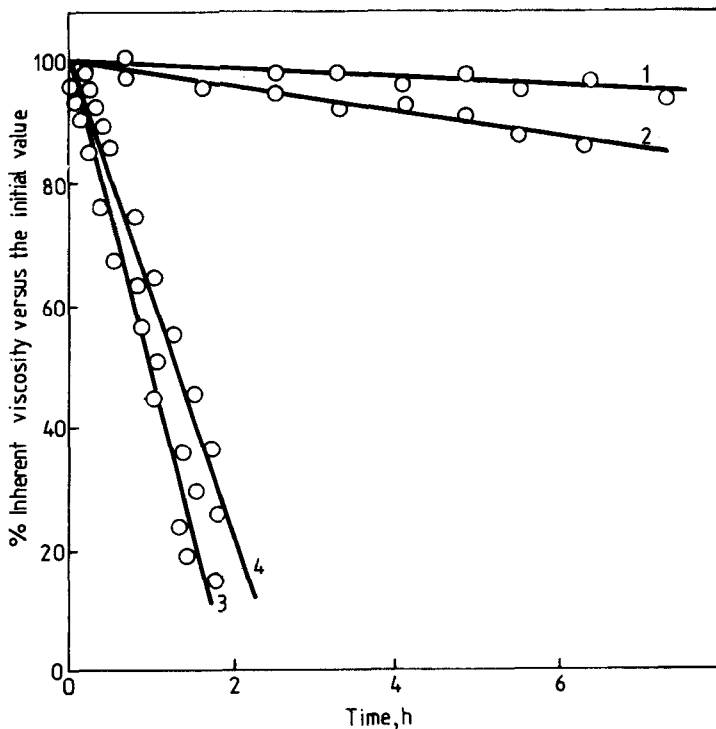


FIG. 9. Variation of inherent viscosity of polyisoprene in CHCl_3 at 40°C . 1) 0.8% polyisoprene; 2) 0.8% polyisoprene + 0.08% PNDFA; 3) 0.8% polyisoprene + 0.4% Perkadox K16; 4) 0.8% polyisoprene + 0.4% Perkadox K16 + 0.08% PNDFA.

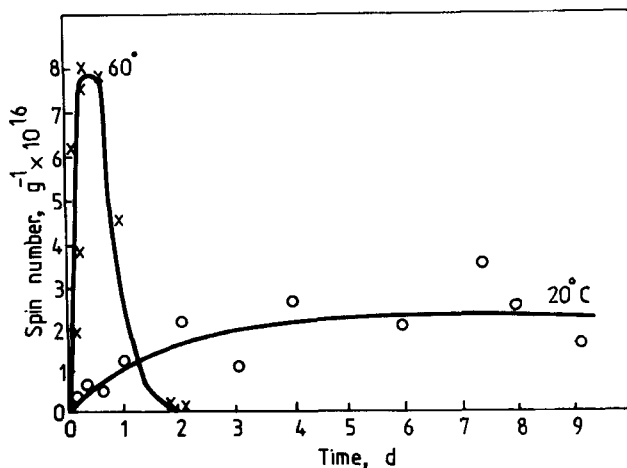


FIG. 10. Effect of temperature on EPR signal intensity in polyisoprene modification with PNDFA. Solvent, toluene; concentration of polymer, 10%; concentration of PNDFA, 1.5%.

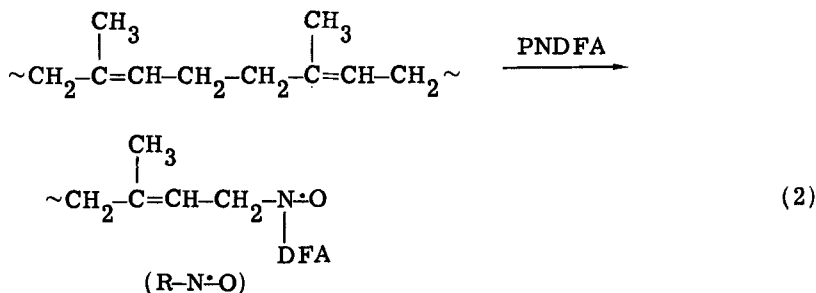
TABLE 3. The Changes of Bound PNDFA Content in Various Fractions of Polyisoprene with 0.35% Modifier [15]

Weight of fraction, %	$[\eta]$, dL/g	Linked PNDFA, %
2.6	0.4	6.0
1.9	0.76	0.34
6.1	1.16	0.13
11.6	1.98	0.07
12.8	4.10	0.02
49.8	4.21	0.01
15.9	4.22	0

The IR and NMR spectra of the reaction products can be explained by making the assumption that scission takes place at the single bond between two methylene groups while the double bond remains unaffected (see Figs. 11 and 12) [12].

The reactions which probably occur in the modification of IR with PNDFA are described below.

1) The formation of nitroxyl radicals via cleavage of the single bond between two methylene groups, followed by fast trapping of these radicals by PNDFA which acts like a "spin-trap:"



This reaction is favored by any factor which facilitates the breaking of the polymer chain (e.g., temperature, light, radical initiators, etc.);

2) Consumption of nitroxyl radicals. The nitroxyl radicals can act like radical initiators as the molecular weight decreases in the course of their consumption. By analogy with Ref. 14, the consumption of nitroxyl radicals follows the next route:

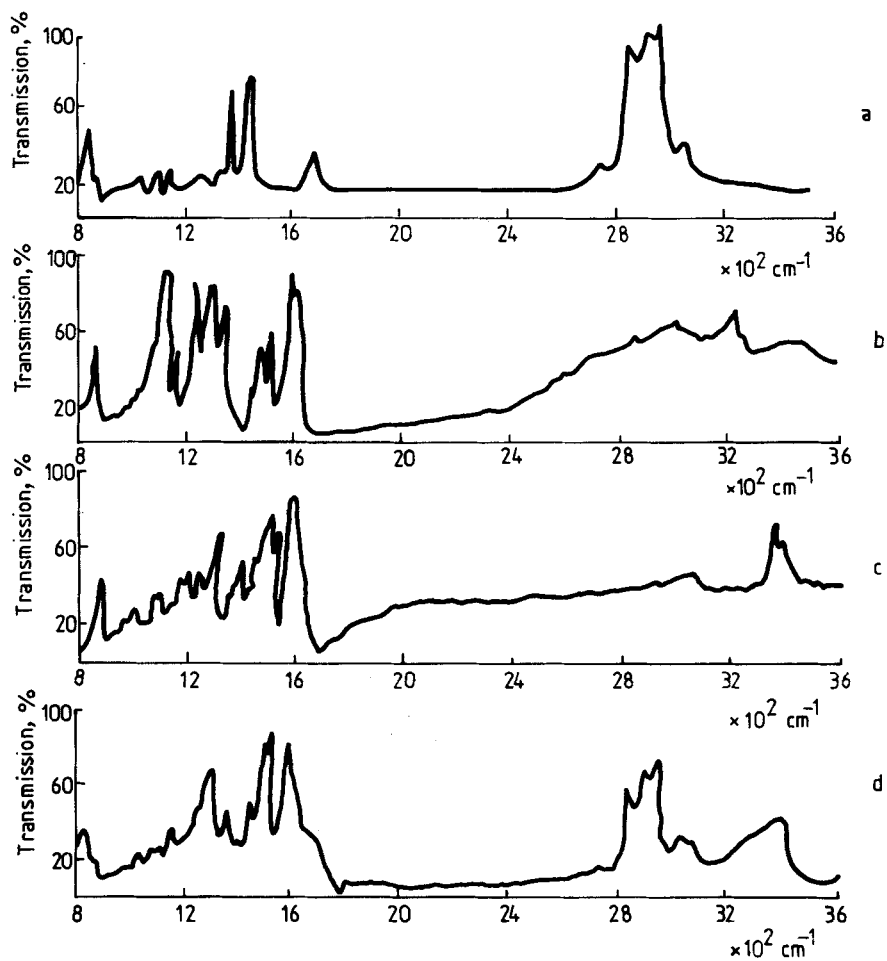


FIG. 11. Infrared spectra of polyisoprene (a), p-nitrosodiphenylamine (b), diphenylamine (c), and modified polyisoprene (1 mol PNDA/6 mol monomer units) (d).

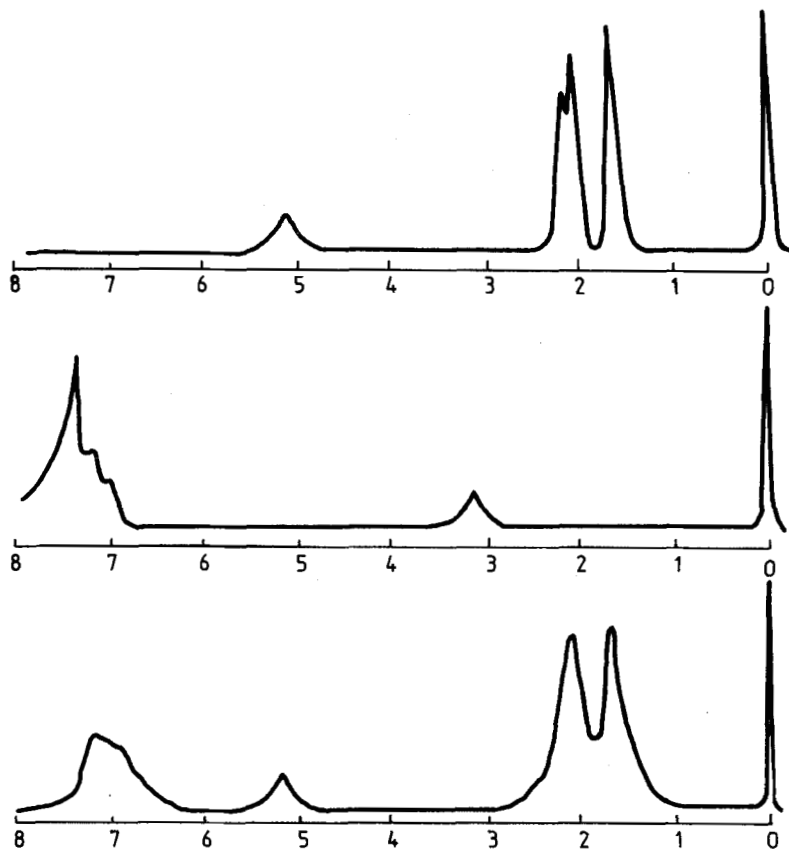
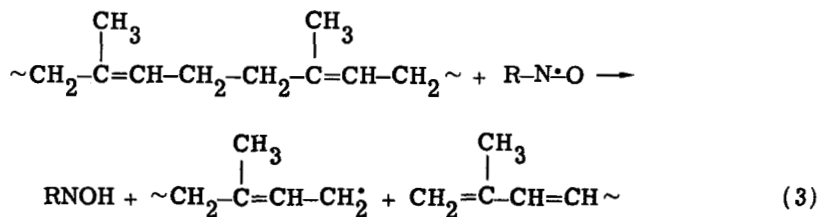
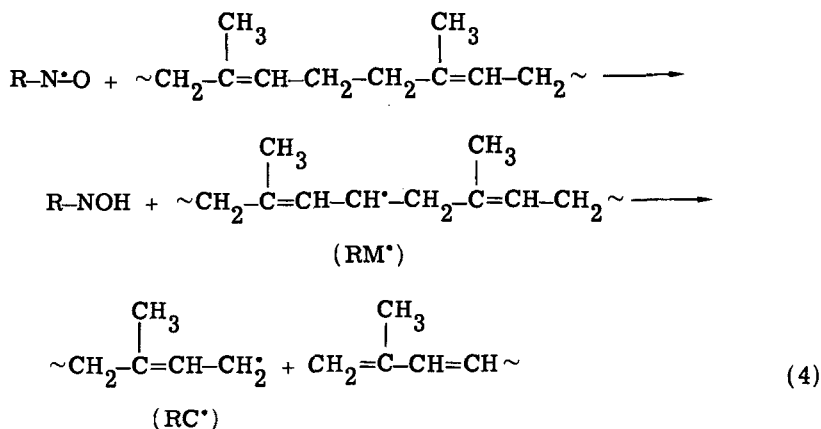


FIG. 12. NMR spectra of polyisoprene (a), p-nitrosodiphenyl-
ine (b), and modified polyisoprene (1 mol PNDFA/6 mol mono-
r units) (c).



Under some experimental conditions this reaction can occur in
steps, the first step being hydrogen abstraction from another

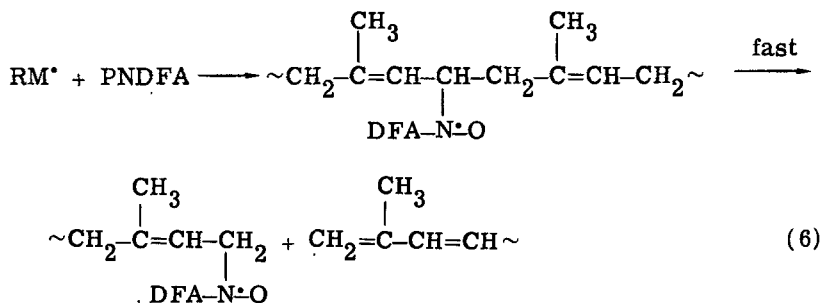
macromolecule and the second step the consumption of the macro-radical RM^{\bullet} formed in the first step:



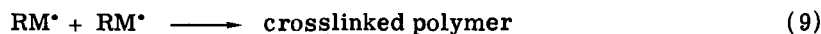
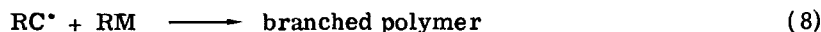
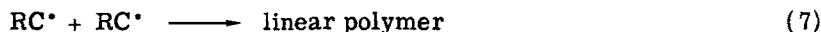
3) Reformation of nitroxyl radicals in the presence of PNDFA:



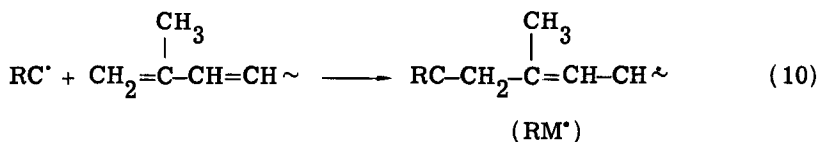
The radical formed by the reaction between RM^{\bullet} and PNDFA is very unstable. This radical disproportionates immediately after its formation:



4) Disappearance of alkyl radicals, in the absence of PNDFA, with the formation of branched and crosslinked polymers:



The consumption of alkyl radicals can also occur by the reaction of this radical with a dienic compound formed in Reaction (6). This is supported by the absence of such compounds in the reaction products even at relatively high PNDFA content:

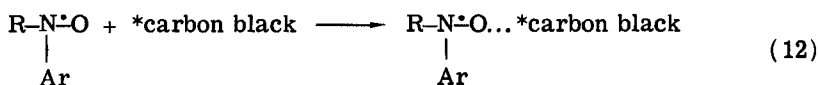


If the modification reaction is carried out in the presence of atmospheric oxygen, the alkyl radicals react with O₂ to give peroxy radicals. These peroxy radicals could be stable when they are trapped in the crosslinked network.



Several mechanisms have been proposed for the reaction of polymers with nitroso compounds, leading to different types of active sites which are responsible for the formation of weak "rubber...carbon black" bonds.

Sullivan [1], in studying the modification of some elastomers with various nitroso derivatives, noticed the formation of nitroxyl radicals in milling operations. These radicals disappear during storage, but they reform, up to the initial concentration, when the compound is milled again. The radicals also disappear in the presence of carbon black. These nitroxyl radicals interact with the active site (*) located on the carbon black surface to give that weak bond, "rubber...carbon black:"



which are responsible for reinforcing effect as well as for the improved physical-mechanical properties.

According to Kavun's mechanism, the same type of active site is proposed; namely, the nitroxyl radicals located along the polymer chain [15]. These two mechanisms of nitroso compound action cannot explain either the dependence of green strength on the amount of nitroso derivatives or the alteration of the physical-mechanical properties of vulcanizates, since they do not account for chain-scission reactions.

TABLE 4. Physical-Chemical and Physical-Mechanical Properties of Green and Cured Compounds

Property	Sample		
	MIR-1	MIR-2	CAROM 2230
<u>Physical-Chemical Properties of Polymers</u>			
Inherent viscosity of sol fraction, dL/g	2.85	3.30	3.68
Gel content, %	22	21	30
Swelling index of gel	39	39	20
PNDFA content, %	0.9	0.5	-
<u>Physical-Mechanical Properties of Green Compound^a</u>			
Mooney viscosity, ML (1 + 4), 100°C	73	95	84
Tensile strength at break, σ_b , kg _f /cm ²	8.85	16	4.30
Tensile strength at yield, σ_y , kg _f /cm ²	3.38	4.3	3.68
Elongation, %	705	550	1000
Green strength, $\sigma_b - \sigma_y$, kg _f /cm ²	5.47	11.7	0.62
<u>Physical-Mechanical Properties of Cured Compounds^a</u>			
300% Modulus, kg _f /cm ²	115	134	125
Tensile strength at break, kg _f /cm ²	192	219	258
Elongation, %	453	415	470
Permanent set, %	12	12	12
Shore hardness	66	62	67

^aRubber, 100 phr; carbon black HAF, 50 phr; stearic acid, 2.0 phr; ZnO, 5.0 phr; Vulcacit CZ, 0.8 phr; sulfur, 2.0 phr.

On the basis of the mechanism proposed by us for the modification process of polyisoprene with PNDFA and of the reinforcing effect of modifiers, it was concluded that the green strength depends both on the molecular weight of the polymer and on the amount of weak "rubber ...carbon black" bonds. The physical-mechanical properties of vulcanizates depend only on the molecular weight. This mechanism satisfactorily explains the values of the characteristics presented in Table 4. It can be seen that the green strength is lower at higher amounts of PNDFA, while the properties of vulcanizates diminish by raising the amount of PNDFA.

Although some properties of vulcanizates are altered by modification with nitroso compounds, this modified rubber with improved green-strength can replace natural rubber in some compositions used in radial tire building.

In conclusion, in the present paper, by using our experimental data as well as those of other authors, it was possible to explain the complex process of reinforcement with nitroso compounds. Thus, some aspects of a process with important practical applications were clarified.

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