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Diene Rubber Modification Using Thiol-Type Derivatives

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ABSTRACT

Thiol-containing antioxidants such as 4-(mercaptoacetamido)-diphenylamine (MADA) undergo ready addition of –SH groups to the double bonds in diene rubbers in the presence of initiators. The reaction is a radical chain process leading to rubbers with improved thermooxidative resistance. The modification reaction has been carried out on high cis-polyisoprene and polybutadiene, and conditions under which the physicochemical properties (e.g., inherent viscosity, gel content, and microstructure) are less affected have been found. An oxygen absorption test and DSC were used as rapid methods for evaluation of thermooxidative stability of modified rubbers. The superiority of rubbers with MADA chemically attached (ranging from 1 to 4 phr) was shown by a circulating air oven test and by an extraction process which simulates the aggressive environments experienced by many rubbers under practical conditions. The results obtained show that a small degree of modification (1 phr MADA) is large enough to provide good thermooxidative stability without alteration of the molecular characteristics of the parent rubbers. At higher degrees, cis-trans isomerization can occur.

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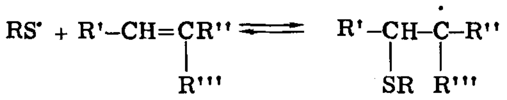
INTRODUCTION

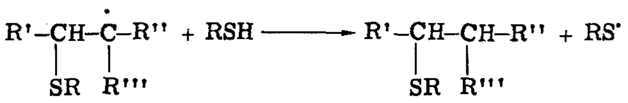
Because of double bond reactivity in diene homopolymers and their technological importance, these rubbers are very attractive materials for chemical modification [1]. By using such a reaction, one can modify the physicochemical and physicomechanical properties of polymers. The type of product obtained depends on the conditions under which the reaction is carried out. An example of a modification reaction is the functionalization of diene rubbers (polyisoprene and polybutadiene) with antioxidant groups. This is a well-known way to obtain chemically attached antioxidants to polymeric chains which are highly resistant to removal from their polymeric substrate than are conventional ones [2-10]. Under certain conditions, for instance, high temperatures and contact with lubricating oils or detergents, the ability to remain in substrates they are meant to protect is more important than their intrinsic activity. This requirement is important for rubber articles with a high surface-area to volume ratio [4].

Chemical attachment of antioxidant groups can be made by addition of thiols to olefinic double bonds of polydienes [9, 11-14]. The reaction is a radical chain process described by Meyer and co-workers [15]:

$$\text{Initiator}^{\bullet} + RSH \longrightarrow RS^{\bullet} + \text{InitiatorH} \qquad (1)$$



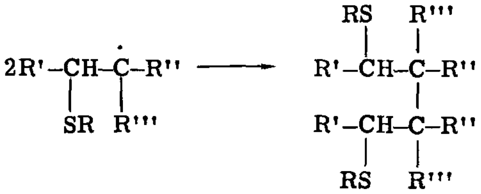
$$RS^{\bullet} + R'{-}CH{=}\underset{\substack{|\\ R'''}}{C}R'' \rightleftharpoons R'{-}\underset{\substack{|\\ SR}}{CH}{-}\overset{\bullet}{\underset{\substack{|\\ R'''}}{C}}{-}R'' \qquad (2)$$



$$R'{-}\underset{\substack{|\\ SR}}{CH}{-}\overset{\bullet}{\underset{\substack{|\\ R'''}}{C}}{-}R'' + RSH \longrightarrow R'{-}\underset{\substack{|\\ SR}}{CH}{-}\underset{\substack{|\\ R'''}}{CH}{-}R'' + RS^{\bullet} \qquad (3)$$

where R may be alkyl, aryl, acyl, etc. radicals which may contain other substituents such as hydroxyl, carboxyl, ester, etc. R', R'', and R''' are portions of the polymeric molecule attached to doubly bonded carbon atoms of the original polymer:

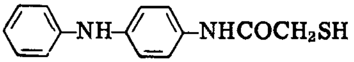
$$2RS^{\bullet} \longrightarrow RS{-}SR \qquad (4)$$



$$2R'{-}\underset{\substack{|\\ SR}}{CH}{-}\overset{\bullet}{\underset{\substack{|\\ R'''}}{C}}{-}R'' \longrightarrow \begin{array}{c} RS \quad R''' \\ | \qquad | \\ R'{-}CH{-}C{-}R'' \\ \qquad | \\ R'{-}CH{-}C{-}R'' \\ | \qquad | \\ RS \quad R''' \end{array} \qquad (5)$$

By using various mercaptans, Weinstein [12, 16] obtained rubbers with chemically attached antioxidant groups that showed improved thermooxidative resistance.

The present study describes the experimental results obtained by radical addition of 4-(mercaptoacetamido)diphenylamine (MADA) to the double bonds in polyisoprene (IR) and polybutadiene (BR) with high cis-1,4 contents:



(MADA)

EXPERIMENTAL

The polymers used were prepared by solution polymerization in the presence of a Ziegler-Natta type catalyst. After the polymerization was stopped, 1% of the antioxidant 2,6-ditertbutyl-4-methylphenol was added.

MADA was synthesized by amidation of 4-aminodiphenylamine with thioglycolic acid according to the procedure of Weinstein [12].

The addition of MADA to polymers was carried out in solution in benzene at 70°C for 10 h with AIBN as the initiator and in the absence of oxygen.

The reaction conditions, the physicochemical characteristics of modified polymers, the induction period values for oxidation, as well as the temperature of the exotherm maximum (DSC) are shown in Table 1.

Figure 1 shows the dependence of the inherent viscosity of modified elastomers versus MADA concentration with the AIBN/MADA ratio kept constant at a value of 0.1. Under the conditions used, the changes of the inherent viscosity and of the gel content were of negligible importance. This creates the possibility of modifying these rubbers without altering the properties mentioned above.

The thermooxidative stability of modified polymers was evaluated by isothermal oxygen absorption at 130°C and by DSC. Figures 2 and 3 show the oxygen absorption curves of polybutadiene and polyisoprene, respectively, when they were modified with various amounts of MADA. For both rubbers the thermooxidative resistance increases with increasing MADA concentration, and is more pronounced for polybutadiene (Fig. 4). For example, the induction period values were more than 720 min compared to 50 min for the unmodified parent polymer.

The DSC data, presented in Figs. 5 and 6, show the same dependence on thermooxidative resistance of modified polymers with MADA concentration.

A circulating air oven test (in which there is a continuous change of atmosphere over the surface of the polymer) was used to prove the higher stability of modified polymers. By measuring the inherent vis-

TABLE 1. Modification Conditions and Physicochemical Characteristics of Modified Polymers[a]

Polymer	Modification conditions		η_{inh}, dL/g	Gel content, %	Induction period $\tau_{130°C}$, min	T_{max} (DSC) °C
	MADA, phr	AIBN, phr				
PBM_0	-	-	2.37	Trace	50	160
PBM_1	1	0.1	2.23	"	250	189
PBM_2	2	0.2	2.20	"	455	209
PBM_3	4	0.4	2.24	"	>720	230
MPI_0	-	-	3.20	14[b]	25	167
MPI_1	1	0.1	2.85	8[b]	175	207
MPI_2	2	0.2	2.55	14[b]	300	213
MPI_3	4	0.4	2.50	10[b]	365	228

[a] Temperature, 70°C; time, 10 h.

[b] These values represent the tight gel content.

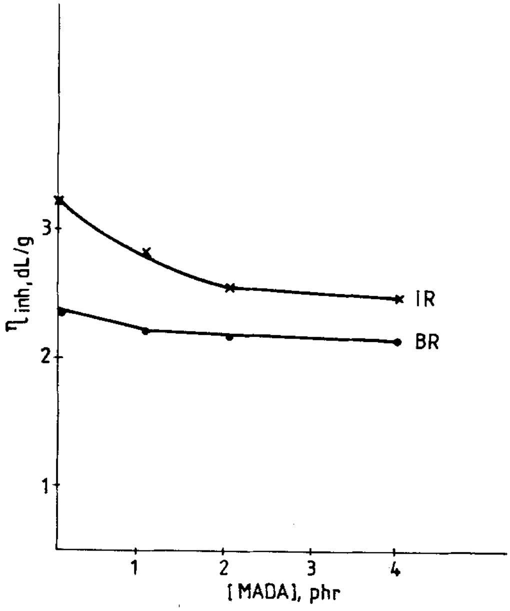


FIG. 1. Inherent viscosity of modified elastomers (IR and BR) versus MADA concentration. Temperature, 70°C; [AIBN]/[MADA] = 0.1; time, 8 h.

cosity and gel content at different time intervals (4 and 8 h, respectively), it was observed that there is a small change of these for modified polymers, while the change is very dramatic for the parent polymers (Figs. 7-10). As expected, the predominant reaction was crosslinking for polybutadiene and scission for polyisoprene.

Chemically attached antioxidants avoid major disadvantages of conventional antioxidants; their loss by volatilization, extraction, and cleansing with solvents, detergents, and oils [4, 7].

It is known that such traditional tests as the oxygen absorption test and the air oven test predict the intrinsic antioxidant activity very well but that they are quite inadequate for evaluation under the aggressive conditions experienced by rubbers in many practical applications [4]. The antioxidant losses from polymers subjected to aggressive conditions are well simulated by extraction processes [2]. Therefore, the modified polymers were Soxhlet extracted with an azeotropic mixture consisting of 1,1,1-trichloroethane (60 mL), acetone (110 mL), and methanol (42 mL) [9] for 5 h under nitrogen, after which the induction period was measured. As shown in Fig 11, the extracted modified polymer keeps its high thermooxidative stability while the polymer with MADA incorporated conventionally loses it on extraction. The

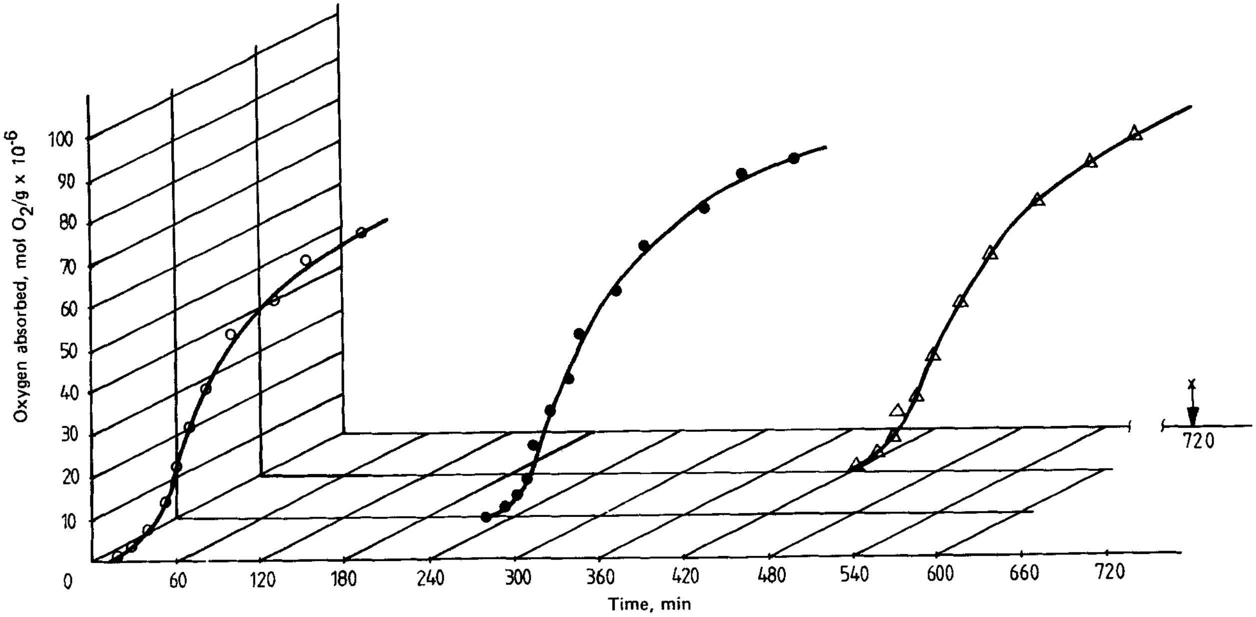


FIG. 2. Oxygen absorption at 130°C of modified polybutadiene: (○) control, no MADA; (●) 1 phr MADA; (△) 2 phr MADA; (×) 4 phr MADA.

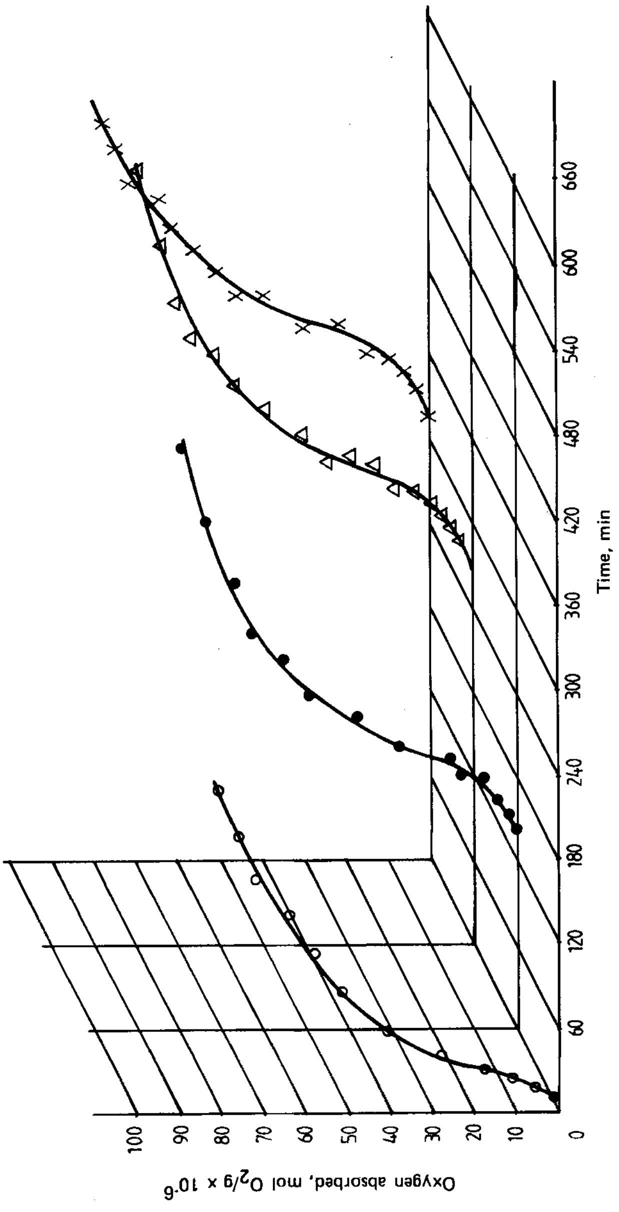


FIG. 3. Oxygen absorption at 130°C of modified polyisoprene: (○) Control, no MADA; (●) 1 phr MADA; (△) 2 phr MADA; (×) 4 phr MADA.

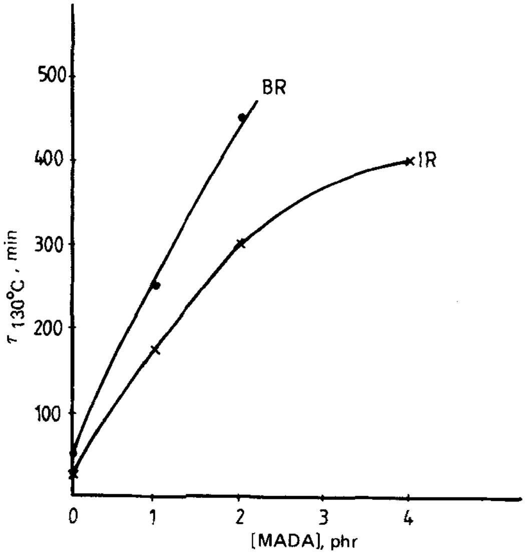


FIG. 4. Variation of induction period of modified rubbers with MADA concentration.

difference between the oxygen absorption curves of a modified polymer before and after solvent extraction can be explained by the fact that the addition of MADA is normally not run to 100% conversion. Unattached MADA is not harmful since it is a good antioxidant in its own right.

The experimental results show that the molecular characteristics measured vary insignificantly with increasing MADA concentration while the stabilities of modified polymers are strongly affected by it. A concentration of 1 phr MADA is preferred because at higher values a change in the cis/trans ratio is observed. This change is probably due to cis/trans isomerization which can take place in the presence of thiyl radicals [17-19] (see the equations on page 536).

Table 2 presents the content of cis-1,4 and trans-1,4 for polybutadiene modified with various concentrations of MADA.

The high thermooxidative stability of modified rubbers studied in the present paper can be attributed to three factors [4, 6]:

1. "Molecular dispersion" of the antioxidants in the polymer substrate by chemical attachment of these to the polymer chain.

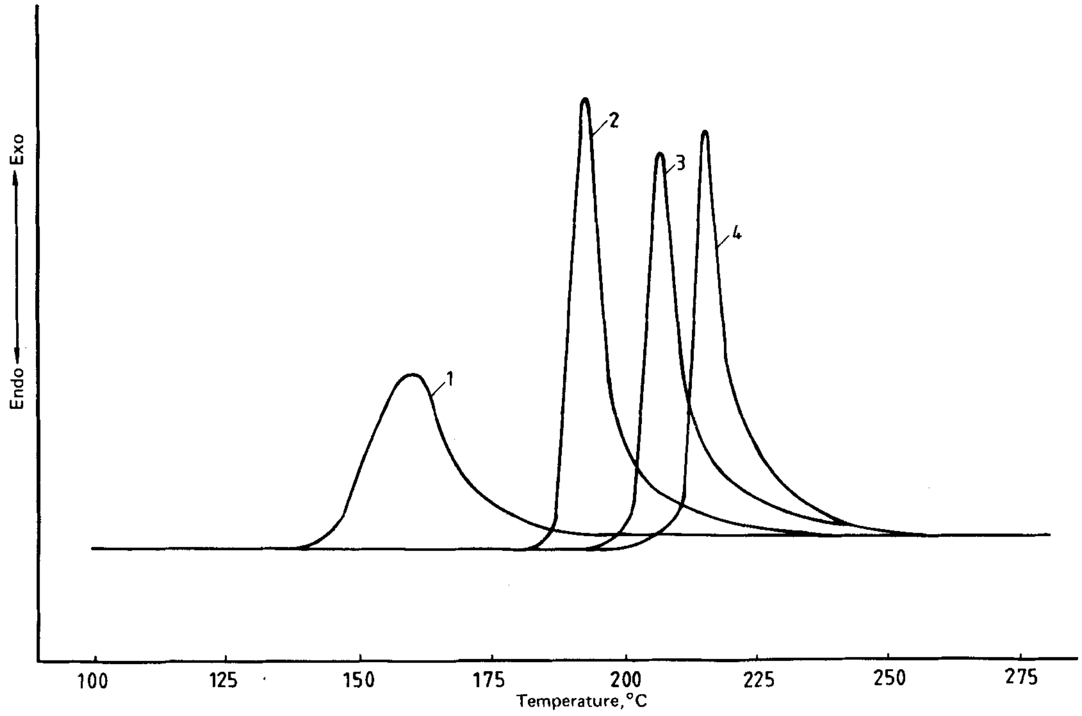


FIG. 5. DSC curves of modified polybutadiene with various MADA content; heating rate, 10°C/min: (1) 0 phr MADA, (2) 1 phr MADA, (3) 2 phr MADA, (4) 4 phr MADA.

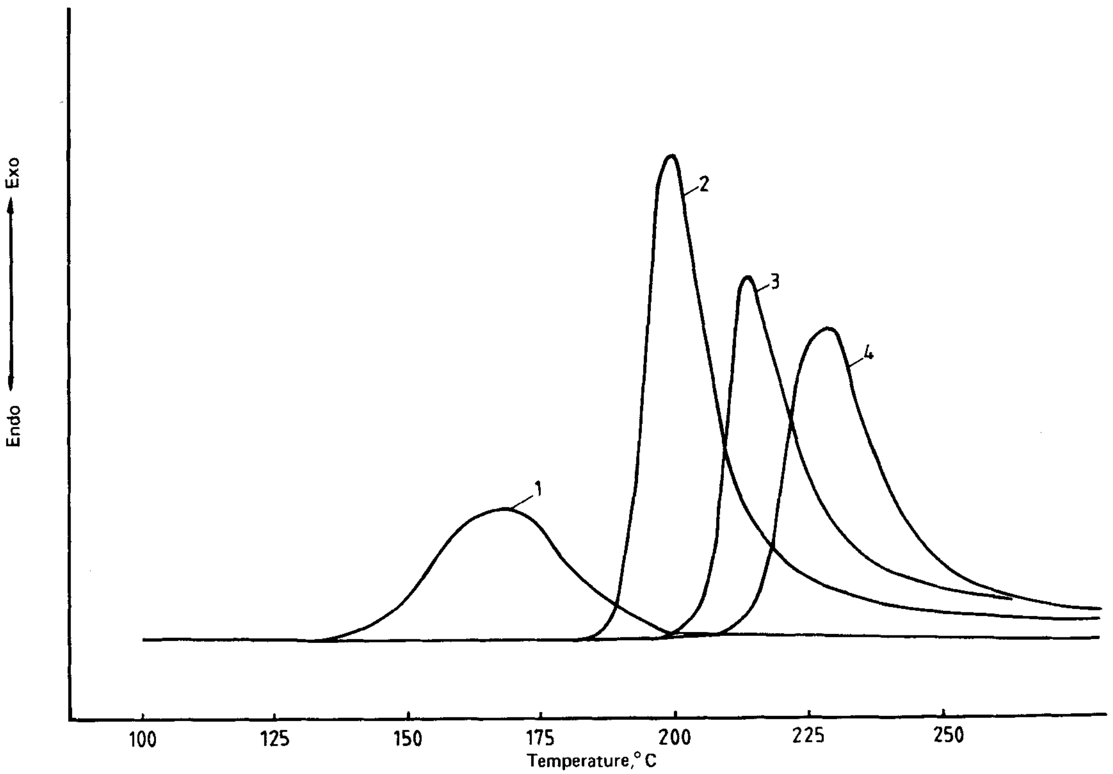


FIG. 6. DSC curves of modified polyisoprene with various MADA content; heating rate, 10°C/min: (1) 0 phr MADA, (2) 1 phr MADA, (3) 2 phr MADA, (4) 4 phr MADA.

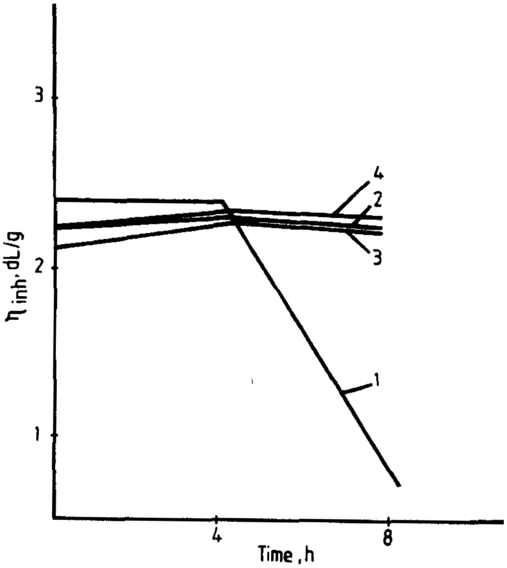


FIG. 7. Inherent viscosity of modified polybutadiene versus aging time in circulating air oven (temperature, 100°C; air velocity, 70 m^3/h): (1) 0 phr MADA, (2) 1 phr MADA, (3) 2 phr MADA, (4) 4 phr MADA.

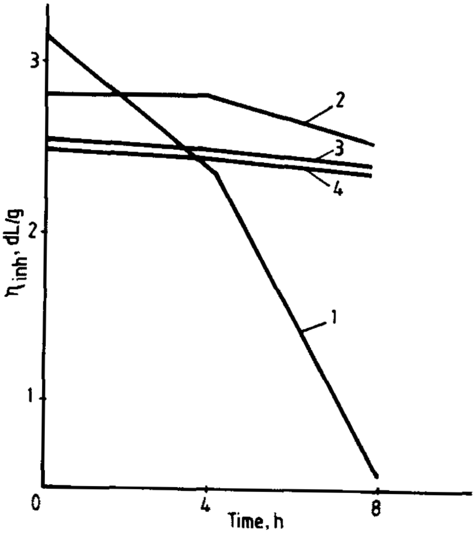


FIG. 8. Inherent viscosity of modified polyisoprene versus aging time in circulating air oven (temperature, 100°C; air velocity, 70 m^3/h): (1) 0 phr MADA, (2) 1 phr MADA, (3) 2 phr MADA, (4) 4 phr MADA.

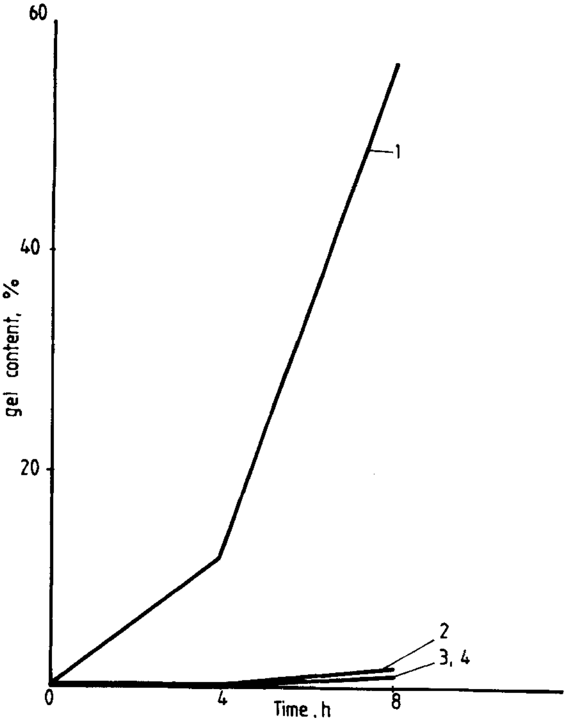
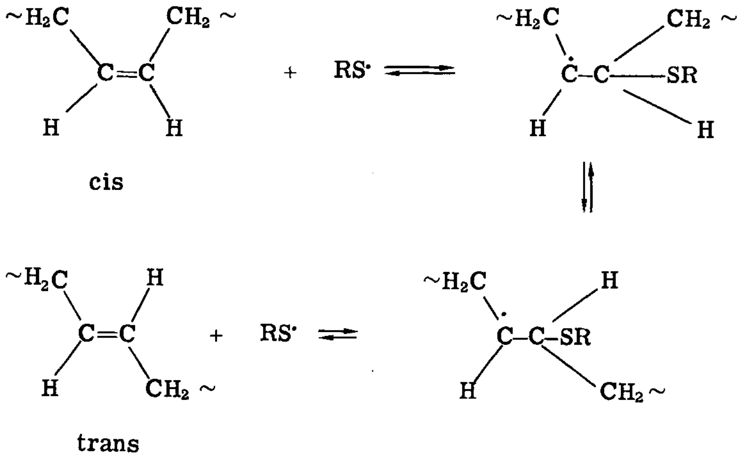


FIG. 9. Gel content of modified polybutadiene versus aging time in circulating air oven (temperature, 100°C; air velocity, 70 m^3/h): (1) 0 phr MADA, (2) 1 phr MADA, (3) 2 phr MADA, (4) 4 phr MADA.



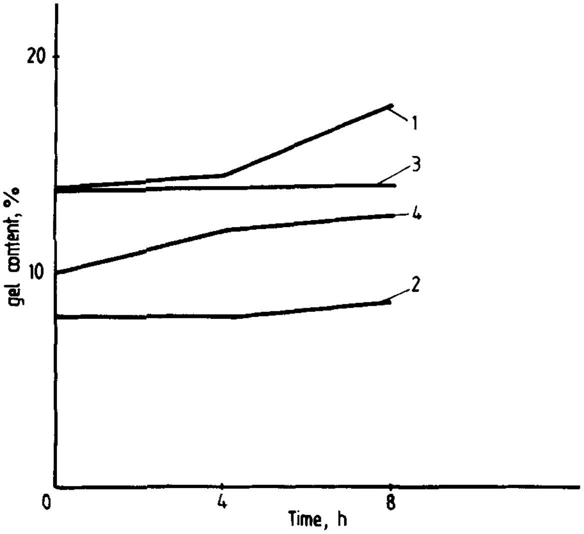


FIG. 10. Gel content of modified polyisoprene versus aging time in circulating air oven (temperature, 100°C; air velocity, 70 m^3/h): (1) 0 phr MADA, (2) 1 phr MADA, (3) 2 phr MADA, (4) 4 phr MADA.

TABLE 2. cis and trans Content of Modified Polybutadiene as a Function of MADA Concentration

Polymer	MADA, phr	cis-1,4, %	trans-1,4, %
PBM$_0$	-	86.5	12.0
PBM$_1$	1	85.0	12.6
PBM$_2$	2	77.5	20.0
PBM$_3$	4	67.5	28.0

2. Immobilization of the antioxidant within the polymer matrix, thus avoiding its physical loss.

3. Autosynergistic interaction of the peroxydolytic sulfur moiety with the electron donor chain-breaking function (arylamine).

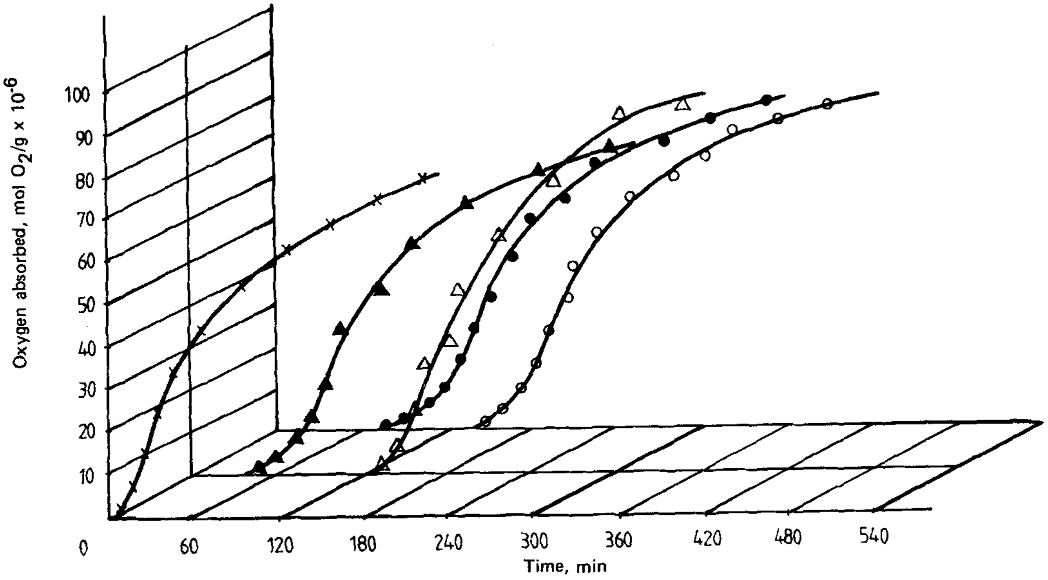


FIG. 11. Oxygen absorption at 130°C of modified polyisoprene: (×) control, no MADA; (▲) 1 phr MADA-A (extracted); (△) 1 phr MADA-A (unextracted); (○) 1 phr MADA-B (unextracted); (●) 1 phr MADA-B (extracted).

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