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THE EFFECT OF ANTIOXIDANTS ON STYRENE–BUTADIENE RUBBER VULCANIZED BY ALKYLPHENOLFORMALDEHYDE RESIN

A. A. Yehia and E. M. Abdel-Bary

Laboratory of Polymers and Pigments, National Research Centre, Cairo, Egypt

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Abstract—Styrene–butadiene rubber was compounded with various phenolic- and amino-type antioxidants and model compounds, and then vulcanized by a *p*-octylphenolformaldehyde resin. Vulcanization characteristics were evaluated by the Monsanto Oscillating Disc Rheometer and other techniques. It was found that phenolic-type antioxidants have no practical effect on the vulcanization, while amino-type compounds retard it. The retardation effect of the latter depends on the electron density of the nitrogen atom and on the number of hydrogen atoms linked to it.

INTRODUCTION

p-Alkylphenolformaldehyde resins are widely used as vulcanizing agents for natural and synthetic rubbers.(1,2) The vulcanization is accelerated by metal halides ($SnCl_2.H_2O$, $FeCl_3.6H_2O$) or chloro-organic compounds (chlorinated paraffins, chlorosulphonated polyethylene).(3–5) The network structures of phenolformaldehyde vulcanizates are thermally very stable in comparison with sulphur vulcanizates.

It has been established(6) that some rubber compounding ingredients, such as tetramethylthiuram disulphide and antioxidants (derivatives of *p*-phenylenediamine), markedly decrease the rate and the extent of vulcanization of rubber by alkylphenolformaldehyde resin. This was attributed to some sort of low activation energy of interaction between the alkylphenolformaldehyde resin and those ingredients leading to by-products having no vulcanization activity.

The mode of action of alkylphenolformaldehyde resin on the rubber hydrocarbon chains has been discussed.(7,8) The most probable mechanism is that in which both the methylol group and phenolic hydroxyl group are employed, forming chroman ring with the rubber hydrocarbon chains.(9) According to this mechanism, the formation of *o*-methylenequinone during the vulcanization is essential. This product is very active, and can react with compounds containing labile hydrogen.

The purpose of this work is to establish some relationship between the structure of antioxidants and their retardation effect during vulcanization with phenolformaldehyde resin. The system styrene–butadiene copolymer with *p*-octylphenolformaldehyde resin was selected.

MATERIALS AND TECHNIQUES

Materials

(I) The rubber used in all experiments was styrene–butadiene rubber SBR-1502-non-staining, with the following characteristics: raw viscosity (ML/200/4) 48–58; tensile strength (kg/cm^2) minimum 220; elongation at break, minimum 575 per cent; stabilizer (2,6-di-tert-butyl-4-methylphenol)-(Inol) approx. 1·25 phr.

(II) The vulcanizing system was *p*-octylphenolformaldehyde resin (St-137) and neoprene.

(III) The ingredients, the effects of which have been studied, were

1. *p*-phenylenediamine (PPD);
2. N-isopropyl-N′-phenyl-*p*-phenylenediamine (IPPPD);
3. N-cyclohexyl-N′-phenyl-*p*-phenylenediamine (CPPPD);
4. N,N′-diphenyl-*p*-phenylenediamine (DPPPD);
5. sym.-di-1,3-dimethyl butyl-*p*-phenylenediamine (DBPPD);
6. sym.-di-β-naphthyl-*p*-phenylenediamine (DNPPD);
7. 4,4′-dihydroxy diphenyl;
8. 2,2′-methylene-bis-(4-methyl-6-tert-butylphenol) (MBMBP);
9. methylene-bis-dimethyl-4,6-phenol (MBDMP);
10. β-dimethylaminopropriophenone [AK—N—$(CH_3)_2$];
11. β-dimethylaminopropiophenone hydrochloride [AK—N—$(CH_3)_2 \cdot HCl$];
12. β-anilinopropiophenone (KA—NH—C_6H_5);
13. β-morpholinopropionphenone (AK—N—$C_4H_8O \cdot HCl$).

β-Aminoketones employed were synthesized according to Mannich(10) and by exchange reactions(11) and were crystallized from ethyl alcohol. The other components were of the grades customarily used practically.

Techniques

1. The basicity (p*Ka*) of the synthesized compounds was measured by potentiometric titration in ethanol.(12)

2. All rubber mixes were prepared on a two-roll mill 470 mm dia, working distance 300 mm, speed of slow roll 24 rev/min, and gear ratio 1·4. The roller temperature was kept at about 70° during mixing. The compounded rubber was left for at least 6 hr before vulcanization. The vulcanization press was operated at 163 ± 2° under a pressure of about 40 kg/cm^2.

3. The rubber mixes and vulcanizates were tested according to standard methods using:
   (a) Mooney plastometer(13) at 150°.
   (b) The vulcanization characteristics were determined with a Monsanto Oscillating Disc Rheometer(14) at 164°. This Oscillating Rheometer records the development of cross links by automatically plotting the increase in torque in rheometer units vs cure time. The maximum rheometer reading (R_∞) attained denotes the cross link efficiency of the curing system, since the height of torque is proportional to the cross link density for the specific formulation.
   (c) A tensile testing machine for tensile strength, elasticity and elongation at break.(15)

RESULTS AND DISCUSSION

For systematic study of the effect of rubber antioxidants on the vulcanization of SBR by *p*-octylphenolformaldehyde resin, various phenolic and amino antioxidants were incorporated in the rubber mixes. The mix contained 100 g SBR (1502), 10 g neoprene, 1·5 g stearic acid, 5·0 g zinc oxide, 50 g carbon black (HAF), and 8·0 g phenolic resin. To the mix, 0·5 g of antioxidants was added unless indicated otherwise.

TABLE 1. THE EFFECT OF ANTIOXIDANTS ON THE PROPERTIES OF SBR VULCANIZED BY AN ALKYL PHENOL-FORMALDEHYDE RESIN; CURE TIME = 45 min; DOSE OF ANTIOXIDANTS = 0·5 hr

	Physico-mechanical properties			
Antioxidant	Modulus 300% (kg/cm^2)	Tensile strength (kg/cm^2)	Elongation (%)	Permanent set (%)
None	121	240	490	12
MBMBP	110	244	538	11
4,4′-Dihydroxydiphenyl	115	245	510	10
DPPPD	101	228	553	13
CPPPD	94	209	550	14
IPPPD	87	198	560	17
p-Phenylene diamine	51	90	608	25

The extent of vulcanization was evaluated by determining the change in the physico-mechanical properties of the rubber vulcanizates. The results are given in Table 1 from which two distinguishing features can be noted:

1. Rubber vulcanizates containing phenolic antioxidants have physico–mechanical properties of the same level as that of the control. Consequently, no retardation of the vulcanization had taken place.
2. The physico–mechanical properties of rubber vulcanizates containing amino antioxidants are significantly decreased. This decrease depends greatly on the chemical structure of the incorporated antioxidant. Consequently, great retardation of the vulcanization had taken place in the presence of these antioxidants.

It was then interesting to examine the effect of concentration of the amino antioxidants on the physico–mechanical properties. With N-isopropyl-N′-phenyl-*p*-phenylenediamine (IPPPD), increase of its concentration led to decrease of modulus and tensile strength of the rubber vulcanizates and to increase of the elongation at break and permanent set at all times of vulcanization (Fig. 1 and Table 2).

TABLE 2. THE EFFECT OF N-ISOPROPYL-N′-PHENYL-*p*-PHENYLENEDIAMINE CONCENTRATION ON THE PROPERTIES OF SBR VULCANIZED BY ALKYLPHENOLFORMALDEHYDE RESIN AT 163°

	Dose/hr											
	Modulus 300% (kg/cm^2)			Tensile strength (kg/cm^2)			Elongation at break (%)			Permanent set (%)		
Cure time (min)	30	45	60	30	45	60	30	45	60	30	45	60
0·00	117	121	141	226	240	245	508	490	460	14	12	11
0·25	94	105	107	204	207	228	566	540	530	20	14	13
0·50	75	87	90	194	198	197	607	550	505	22	17	16
0·75	67	71	75	157	167	185	590	566	610	24	18	18
1·00	37	51	61	98	128	140	700	590	630	45	33	27
1·50	25	35	30	52	60	56	735	625	670	65	59	63

These results were supported by determining the Mooney plasticity of the green rubber mixes containing the antioxidants MBMBP, MBDMP and *p*-phenylenediamine and its derivatives. The results are illustrated in Fig. 2. The phenolic antioxidants do not retard, but even slightly accelerate the vulcanization; on the other hand, the amino antioxidants (PPD and its derivatives) greatly retard the vulcanization.

The degree of retardation greatly depends on the substituents linked to the nitrogen atom of the amino group. Thus while PPD has the highest retardation effect, the degree of retardation is greatly decreased by substituting one hydrogen atom in each amino group. It is also observed that the aliphatic substituent C_4H_9 retards the vulcanization to a greater extent than aromatic substituents (phenyl and naphthyl). The same conclusion can be derived for N-phenyl-*p*-phenylenediamine in which a hydrogen atom at the NH_2 group is replaced by e.g. isopropyl, cyclohexyl or phenyl radicals. The rate of vulcanization in the presence of *p*-phenylenediamine and its

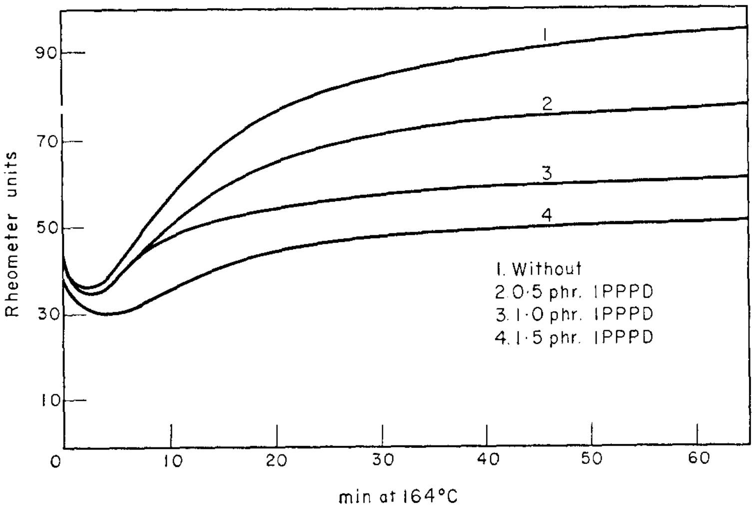

FIG. 1. Effects of various concentrations of N-isopropyl-N′-phenyl-*p*-phenylenediamine on SBR vulcanized by *p*-octylphenolformaldehyde resin.

derivatives can be put in the following order: PPD < IPPPD < CPPPD < DPPPD (Fig. 2).

These results are in good agreement with σ^* Taft values of the substituents, reflecting the electron-donating or withdrawing property of the substituents and indicating their inductive effect and electron density on the amino nitrogen. Table 3 shows that, as the electron density on the nitrogen increases, the extent of vulcanization decreases for a similar number of hydrogen atoms.

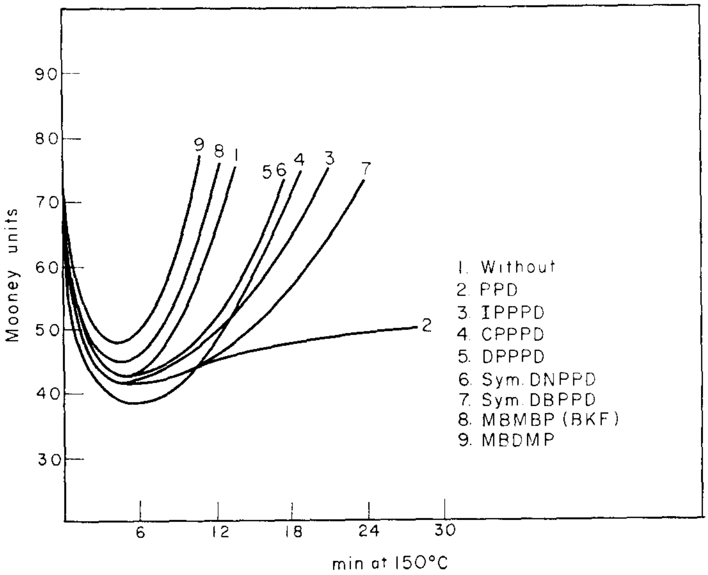

FIG. 2. Effects of various antioxidants on Mooney plasticity of SBR vulcanized by *p*-octylphenolformaldehyde resin.

TABLE 3. EFFECT OF ANTIOXIDANTS OF GENERAL FORMULA C_6H_5—NH—C_6H_5—NHR ON THE PROPERTIES OF SBR VULCANIZED BY ALKYLPHENOLFORMALDEHYDE RESIN (CURE TIME 30 min)

			Properties				
Antioxidant	R	σ_R*	Modulus 300% (kg/cm²)	Tensile strength (kg/cm²)	Elongation (%)	Permanent set (%)	R_∞* at 164°
None	—	—	121	240	490	12	93
IPPPD	—$CH(CH_3)_2$	−0·19	87	198	560	17	78
CPPPD	—C_6H_{11}	−0·15	94	209	550	14	83
DPPPD	—C_6H_5	+0·60	101	228	553	13	86

* R = Maximum rheometer reading.

The investigation of the effect of a labile hydrogen atom and the electron density on the nitrogen atom on the vulcanization of SBR by *p*-octylphenolformaldehyde was carried out by incorporating secondary and tertiary β-aminoketones in rubber mixes. Thus, β-alkyl and arylaminopropiophenones of the general formula $C_6H_5COCH_2$-$CH_2NR_1R_2$ were synthesized and their basicities (p*Ka*) were measured. The physico-mechanical properties of the rubber vulcanizates containing these compounds are given in Table 4 and the Mooney plasticity is illustrated in Fig. 3.

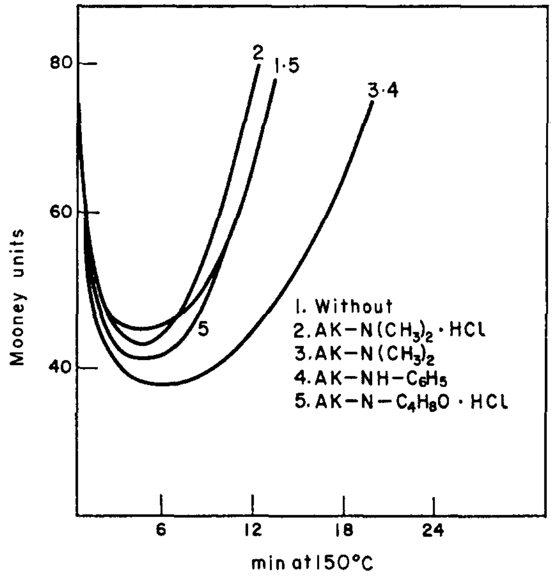

FIG. 3. Effects of β-alkyl and aryl aminopropiophenones and their hydrochloride salts on Mooney plasticity of SBR vulcanized by *p*-octylphenolformaldehyde resin.

From these results, one can infer that both AK—N—$(CH_3)_2$ and AK—NH—C_6H_5 decrease the vulcanization markedly and practically in the same order, in spite of the fact that the former does not contain a labile hydrogen atom. It is also noteworthy that the hydrochloride salt of AK—N—$(CH_3)_2$ has practically no effect. This means that the retardation effect of AK—N—$(CH_3)_2$ is due to the unshared pair of electrons on the nitrogen atom which are blocked in the case of its hydrochloride salt. The unshared electron pair in tertiary aminoketones has, therefore, a specific retarding role in the vulcanization of SBR with phenolic resins.

TABLE 4. THE PHYSICO-MECHANICAL PROPERTIES OF SBR VULCANIZATES CONTAINING SECONDARY AND TERTIARY β-ALKYL (ARYL) AMINOPROPIOPHENONES. CURE TIME 45 min, DOSE 1·6 /hr

Ingredients	p*Ka*	Modulus 300% (kg/cm^2)	Tensile strength (kg/cm^2)	Elongation (%)
None	—	121	240	490
AK—N—$(CH_3)_2$	7·17	71	166	660
AK—N—$(CH_3)_2$.HCl	7·17*	85	230	640
AK—NH—C_6H_5	2·85	78	192	650
AK—NC_4H_8O.HCl	5·50*	77	246	665

* Measured for free base.

The effect of rubber ingredients on the vulcanization characteristics of SBR by alkylphenolformaldehyde resin was evaluated by the Monsanto Oscillating Disk Rheometer. The results are given in Fig. 4. The data are in good agreement with those obtained by the Mooney plastometer and physico-mechanical properties.

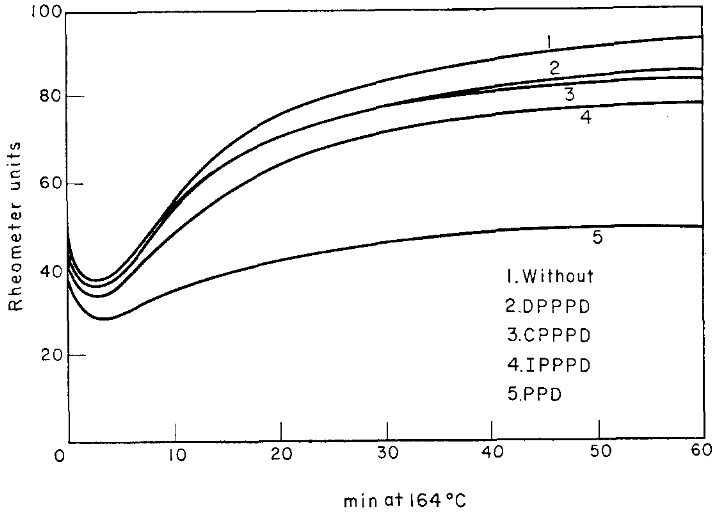

FIG. 4. Effects of various rubber ingredients on SBR vulcanized by *p*-octylphenolformaldehyde resin.

From these results, it can be concluded that phenolic antioxidants do not retard the vulcanization. This may be due to the relative stability of the hydroxyl group, and hence the difficulty of its interaction with the methylenequinone intermediate.

The amino antioxidants retard the vulcanization, with efficiency related to chemical structure. The labile hydrogen of the amino, as well as the unshared electron pair on the nitrogen atom, are responsible for retarding the vulcanization, probably by interactions with the methylenequinone intermediate.

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Résumé—Des caoutchoucs styrène–butadiène ont été combinés avec divers antioxydants de type phénolique et amino et des composés modèles. Ils ont été ensuite vulcanisés par une résine *p*-octylphénol formaldéhyde. On a évalué les caractéristiques de vulcanisation par le rhéomètre à disque oscillant de Monsanto et par d'autres techniques. On a trouvé que les antioxydants de type phénolique n'ont pratiquement aucun effet sur la vulcanisation tandis que les composés de type amino la retardent. L'effet de retardement par ces derniers dépend de la densité électronique de l'atome d'azote et du nombre d'atomes d'hydrogène qui lui sont liés.

Sommario—Della gomma di stirene–butadiene è stata combinata con vari antiossidanti di tipo anmino e fenolico e con composti modello, e quindi vulcanizzata con una resina di *p*-octilfenolformaldeide. Le caratteristiche di vulcanizzazione sono state valutate a mezzo del reometro a disco oscillante di Monsanto e di altre tecniche. Si è trovato che gli antiossidanti di tipo fenolico non hanno effetto pratico sulla vulcanizzazione, mentre i composti di tipo amino la ritardano. L'effetto ritardante di quest'ultimi dipende dalla densità elettronica degli atomi di azoto e dal numero di atomi di idrogeno ad essi legati.

Zusammenfassung—Ein Styrol–Butadien-Kautschuk wurde mit verschiedenen phenolischen Antioxidatien und solchen vom Amino-Typ sowie einigen Modellverbindungen gemischt und dann durch ein *p*-Octylphenolformaldehyd-Harz vulkanisiert. Die Charakteristiken der Vulkanisation wurden durch das Monsanto Oscillations-Scheiben-Rheometer und andere Techniken bestimmt. Dabei wurde gefunden, daß Antioxidantien vom Phenol-Typ praktisch keinen Einfluß auf die Vulkanisation nehmen, wohingegen solche vom Amino-Typ die Vulkanisation verzögern. Der Effekt der Verzögerung hängt ab von der Elektronendichte am Stickstoffatom und von der Anzahl der Wasserstoffatome, die an es gebunden sind.