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SOME SYNERGISTIC EFFECTS OF ANTIOXIDANTS IN NATURAL RUBBER

D. F. Parra and J. do Rosário Matos

Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo
CP 26077, 05599-970, São Paulo, SP, Brazil

Abstract

Some synergistic effects of antioxidants in natural rubber were investigated considering results obtained by differencial scanning calorimetry (DSC). Rubber formulations were obtained with mixtures of diaminic (DPPD, IPPD, HPPD) and monoaminic (ADPA, PBN) stabilizers and evaluated. The samples containing the mixture diamine/ADPA stabilizers showed synergistic effects while, for those containing diamine/PBN, no effect was observed. Additionally, the diffusion constants determined by use of vulcanized rubber disks confirmed the molar mass dependence of the stabilizer.

Keywords: amine stabilizers, natural rubber, oxidative induction time

Introduction

The effectiveness of stabilizers is an important feature in the protection of rubber formulations used in the tire industry and other industrial rubber products. That effectiveness improves rubber stability during the process when submitted to the vulcanization thermal conditions and during the lifetime when exposed to oxidative atmosphere of ozone and air, aging thermal conditions of internal heat releasing and external heating of hostile service environments. The characteristics of the formulation will improve the performance of the product with the benefit of the adequate stabilizer [1].

The combination of two stabilizers is a common procedure in the tyre industry but the literature does a poor job to justify the procedure [1, 2]. Different antioxidants have different reaction rates, for example, with free radicals generated during degradation of the rubber. Some react faster and are quickly consumed while others remain for a long time.

The synergistic effect was reported for distinct classes of stabilizers. Eickenemeier and Ovist [3, 4] registered the effectiveness of amines as synergistic antioxidants. The combination of amines and phenols stabilizers was reported regarding synergistic aspects by Meskia *et al.* [5]. Cho *et al.* evaluated the combination of aromatic monoamine with alkali metal compounds, hydroxybenzophenones or sulfur and phosphorus compounds [6]. They described that the addition of monoamine with a small concentration of one of the last compounds improves its effectiveness. Bauer *et al.* investigated antioxidant interactions of hindered amines light stabilizers combined with

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aromatic phosphites in polypropylene [7]. Synergistic effects were observed at different molar ratios. Scott [8] has described those antioxidants in the mixtures acting by different mechanism of oxidation inhibition. In case of aminic stabilizers of similar structure the mechanism of homo-synergism was attributed to the regeneration of the primary antioxidant. It was pointed out in the combination of two amines one can act as a peroxide decomposer while the other acts as a trap of free radicals [6].

Literature emphasized that a thin test piece ages faster than a thick one when heated in air. The thick piece is a reservoir for antioxidants, that can diffuse to the surface to inhibit the penetration of oxygen [9]. Discussion of the effect of the diffusion of commercial amine stabilizers in vulcanized rubber formulation was made in our previous paper [10]. One experimental system has been prepared composed of three disks in contact to examine the migration of the stabilizer. Two external disks without the antioxidant are pressed against a disk containing the antioxidant (the central disk). The diffusion constants of the stabilizers in rubber formulation were then calculated. The results strongly suggested that the molar mass is the driving force of the diffusion process.

The evaluation of thermal stability of rubber formulation can be conducted by thermal analysis [11, 12], a technique of significant use in rubber industry [13, 14]. The oxidation induction time (OIT) has been proved to be a useful diagnostic tool in assessing the extent of degradation in polymeric materials. OIT is measured using DSC in isothermal mode and is calculated as the time from heating in O_2 atmosphere until the onset of rapid oxidation reaction. Rapid oxidation occurs after the antioxidant of the sample has been exhausted. Thus, OIT is related to the amount and type of antioxidant in the sample, and is a measure of its consumption during aging.

The aim of this work was to evaluate the possible occurrence of synergistic effect of amine stabilizers combined in rubber formulation and to determine the diffusion rate of the stabilizers in a vulcanized system composed by one single disk.

Experimental

Materials

Natural rubber used was of SMR grade from Malaysian Federation origin. The additives were commercial amines: 5,5'-dimethyl-5,10-dihydroacridine (ADPA), from Uniroyal; N-phenyl-2-naphthylamine (PBN) from Bayer; N-N'-diphenyl-*p*-phenylenediamine (DPPD), from Bann; N-isopropyl, N'-phenyl-*p*-phenylenediamine (IPPD); and N-(1,3-dimethylbutil)-N'-phenyl-*p*-phenylenediamine (HPPD) from Monsanto.

Physical tests

The thermooxidative resistance of rubber stocks was measured by means of OIT according to ASTM E1858-97, using DSC cell – TA DuPont Model 1090. The sample tests prepared to OIT evaluations were composed by the stabilizer, 0.4 parts per hundred rubber (phr), added to crude natural rubber samples was mixed in roll-mill laboratory type at 20°C. The samples (4–5 mg) were weighed in aluminum pan uncovered and heated from ambient to 180°C, at 40°C min^{-1} rate under N_2 atmosphere. At that point temperature was allowed to equilibrate and then heating was continued isothermally at 180°C until exothermal event. After the temperature equilibration the purge gas was switched from N_2 to O_2. These conditions of sample mass and temperature revealed a clearly exothermic peak of thermal oxidation. The time interval between the O_2 insertion and oxidation onset point was measured and defined as OIT.

Formulations and processing of vulcanization for the diffusion experiments

The diffusion experiments were performed in a single vulcanized disk composed by formulations given in Table 1, where the material quantity is calculated as parts per hundred rubber (phr).

Table 1 Formulation of rubber used to the diffusion test system

Material	Mix 1/phr[a]	Mix 2/phr[a]
Natural rubber (SMR-L)	100	100
HAF carbon black	55.0	55.0
Sulfur	2.0	2.0
MOR[b]	1.2	1.2
Zinc oxide	4.0	4.0
Stearic acid	1.0	1.0
Antioxidant	3.0	–

[a] phr, parts per hundred (routinely used in the tire industry) [b] morpholine benzothiazol sulfenamide

The materials were mixed in two stages of standard laboratory routine. In the first stage, natural rubber, carbon black and zinc oxide were mixed at 140°C for 4 min. In the second stage, at 90°C for 1 min, sulfur, stearic acid, accelerator MBT and the antioxidant were added to obtain the crude mix. Crude mix 1 with antioxidant were distinguished from crude mix 2, absent of the antioxidant additive. A disk of crude mix 1 (3 mm thickness) was pressed between two disks of mix 2 (7 mm thickness). That piece was vulcanized at 151°C for 30 min in a laboratory hot press. The vulcanized disk of about 17 mm thickness and 7 mm diameter was cut in thin slices. In addition vulcanized disks left in storage were cut by the same procedure after periods of 7, 14, 21 and 28 days to provide the antioxidant quantification.

The diffusion system previously reported [10] was undertaken using 'sandwiches' composed of three vulcanized disks, one disk containing the antioxidant (source disk – mix 1) between two external disks of non-additivated rubber formulation (mix 2). These system sets were kept under slight pressure and disassembled after periods of 7, 14, 21 and 28 days. Including the disks recently vulcanized, the procedure of cutting in thin slices was carried out to quantify the stabilizers.

Quantification of the stabilizers

The slices of the disk were extracted with acetone in a Soxhlet amber apparatus for 16 h. Stabilizers were quantified by HPLC, HP5890 instrument with flame-ionization detector was maintained at 300°C and the injection port at 250°C; a stainless steel capillary column was used 5.5% phenylsilicon programmed from 190 to 290°C at 10°C min^{-1}, 20 min at 290°C; sample injections were of 0.1 μL.

Determination of diffusion rates

The stabilizer diffusion rates were determined by calculation following the Boltzmann–Matano model [10, 15, 16]. The experimental curves were obtained considering the center as the point of higher concentration of the stabilizer. The system used permitted an experimental curve without interface interference promoted by the insufficient contact among disks. The distance from the center point was considered *x* (cm), the concentration was *c* (%) and the diffusion rate (or diffusion coefficient) was determined as *D*(*c*) in ($\text{cm}^2\ \text{s}^{-1}$) according to the Eq. (1):

$$D(c)=\frac{1}{2t}\frac{\int_0^c x dc}{\frac{\mathrm{d}c}{\mathrm{d}t}} \tag{1}$$

Discussion

The effect of the composition of amine mixtures on the rubber stability is shown in OIT profiles in Figs 1 and 2. The mixtures of ADPA with the diaminic stabilizers showed a larger effect when associates in the proportion 1:1, Figs 1A, 1B, 1C. The presence of PBN in the mixture with the diamines had neither a synergistic nor an antagonistic effect. In these cases a decrease in OIT values occurred with concentration increasing of PBN.

The diffusion rate was determined from experimental curves following Matano modeling method described in a previous paper [10]. The results calculated confirm the evidence of molar mass (*MM*) dependence of the diffusion, but the diffusion constants are slightly superior in this system composed of a single vulcanized disk, as indicated in Table 2. In fact this system was submitted to heating during the vulcanization, and under heat, the stabilizer could migrate faster through the mix 1 to 2. Another difference is the internal contact surfaces in the ‘sandwich’ set, between a disk containing the stabilizer and other disk as indicated in the system mounted to the experiments previously studied. The surface between disks can present some difficulties to start the diffusion phenomenon.

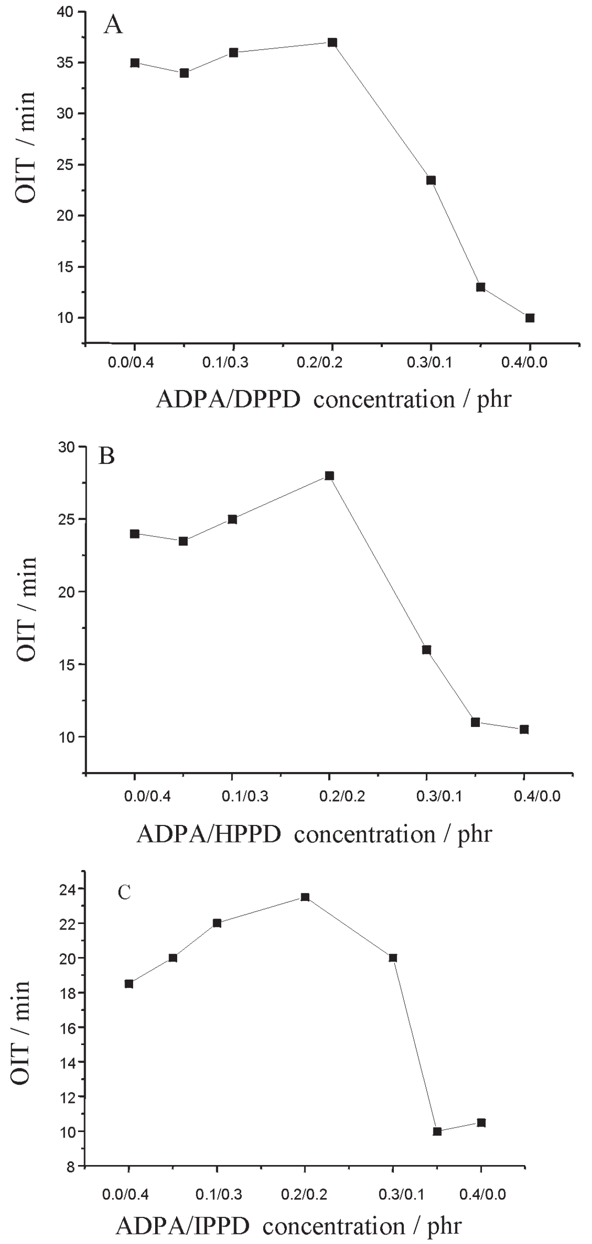

Fig. 1 OIT profiles of stabilizer/rubber stocks: A – Combination of DPPD/ADPA; B – HPPD/ADPA; C – IPPD/ADPA

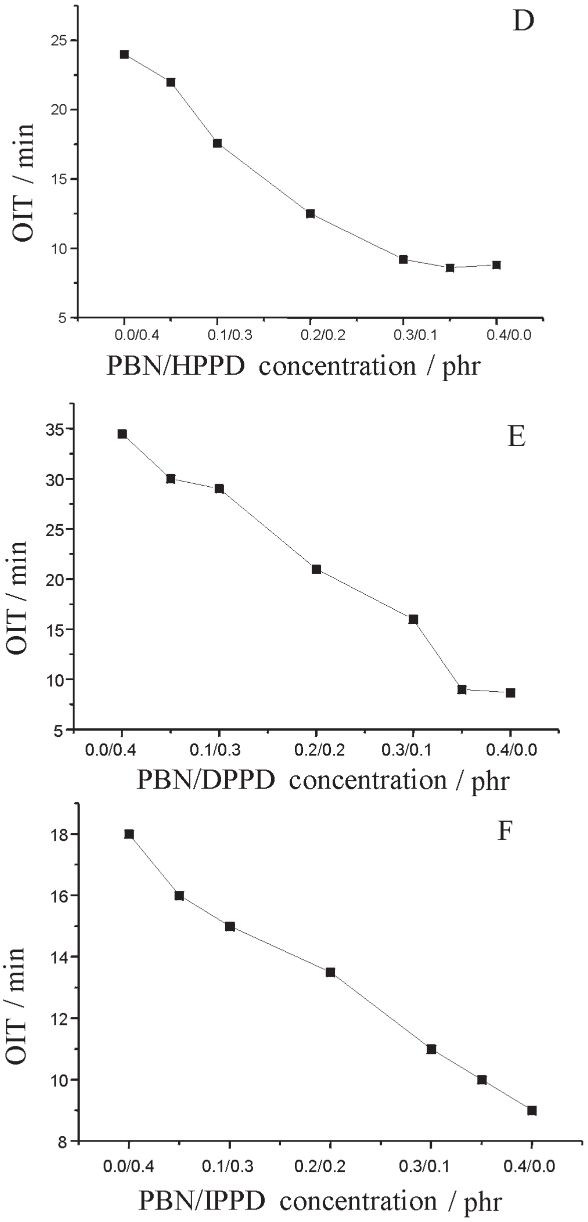

Fig. 2 OIT profiles of stabilizer/rubber stocks: D – combination of PBN/HPPD; E – PBN/DPPD; F – PBN/IPPD

Table 2 Comparation of diffusion constant D obtained in one disk system (I) and D of the previous work [10] (system of three disks with the stabilizer present only at central disk), (II)

Stabilizer	MM	$D/10^{-8}$ cm^2 s^{-1} (I)	$D/10^{-8}$ cm^2 s^{-1} (II)
ADPA	209	1.93±0.02	1.7±0.2
PBN	219	1.41±0.03	1.38±0.03
IPPD	226	1.36±0.03	1.3±0.3
HPPD	268	1.20±0.02	1.12±0.07

Mechanism of action [17–19]

The diaminic antioxidants are evidently more efficient than the aminic ones owing to the presence of two nitrogen atoms. The antioxidants in a synergistic mixture can operate by different mechanisms of oxidation inhibition. When associated, the combined effect becomes greater than the sum of individual effects. There are two major mechanisms of the antioxidant action of the stabilizers in the formulations submitted to termooxidative environment: 1. free radical trapping or radical scavenger stabilizer occurring when the nitroxyl radical (>NO·) reacts with macroradicals (R·, ROO·), 2. hydroperoxide (ROOH) decomposition, as demonstrated in Fig. 3, when the main activity is attributed to the formation and regeneration of a key transformation product, the corresponding nitroxyl radical [20, 21]. Consequently, they are considered as chain-terminator agents in a free-radical reaction caused by heat damage and oxidation. In addition, the diamines react with the end-group of disrupt chains promoting reticulation or regeneration of chemical bond between chains [19, 20], and in this case the diamine is consumed and inhibit the self-formation of nitroxyl radical. The synergism verified in Figs 1A, 1B, 1C suggests that ADPA competes with the diamines in the reaction with end-groups while PBN acts mainly as a peroxide decomposer.

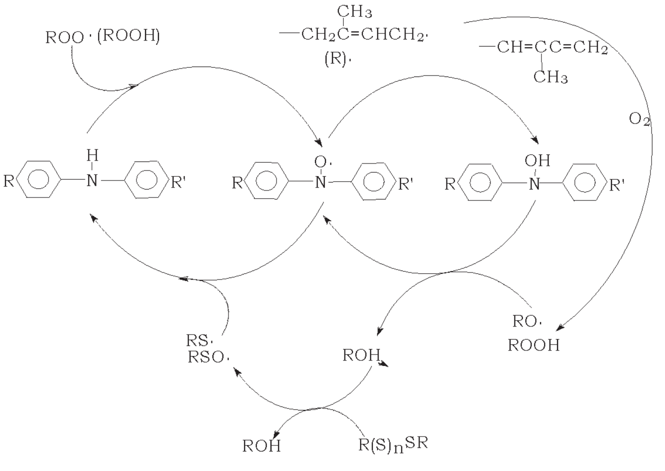

Fig. 3 Mechanism of action of aminic stabilizers as hydroperoxide decomposers and chain breaking radical scavanger [19]. R=alkyl

Conclusions

The diffusion constant of stabilizers was determined on a single vulcanized disk having the stabilizer in the center and confirms their molar mass dependence. Data obtained corroborate with *D* values previously determined [10] and the experiment proposed is more realistic in analogy with the diffusion that happens in the rubber compounds made with different formulations vulcanized together. The observed synergistic effects are related to the cooperation in the main activity that is attributed to the formation and regeneration of a key transformation product, the corresponding nitroxyl radical.

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