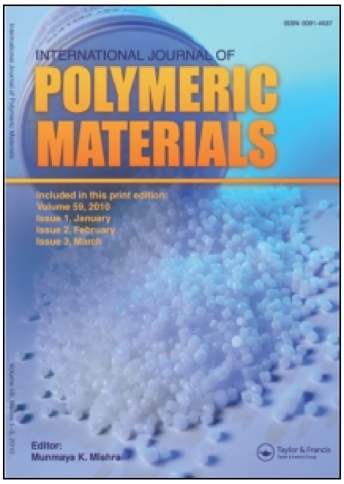

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Evaluation of Some Diphenylamine Derivatives as Thermal Stabilizers and Antifatigue Agents in Natural Rubber Vulcanizates

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Evaluation of some Diphenylamine Derivatives as Thermal Stabilizers and Antifatigue Agents in Natural Rubber Vulcanizates

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Four compounds of diphenylamine derivatives were prepared and evaluated as thermal stabilizers and antifatigue agents in natural rubber (NR) mixes. The efficiencies of these compounds were compared with phenyl-B-naphthylamine, which is widely used in rubber industry. The rheological characteristics were determined using an oscillating disc rheometer. The physico-mechanical properties of the rubber vulcanizates were measured before and after exposure to accelerated thermooxidative ageing. The results revealed that the prepared compounds were good antioxidants and antifatigue agents for rubber vulcanizates. In addition, it was found that the chemical structure of the compounds has a great effect on their efficiency as stabilizers, that is, the presence of electron donating group increases their efficiency, whereas the presence of electron withdrawing group decreases it.

Keywords: diphenylamine derivatives, thermal stability, natural rubber, rheological characteristics, physico-mechanical properties, accelerated ageing, antifatigue agents

INTRODUCTION

All elastomeric materials undergo some sort of deterioration depending on their structure and the environmental conditions. The most common environmental factors are oxygen, ozone, heat, light, mechanical stress, oxidizing chemicals, and metal contamination.

Oxidative ageing of rubber is one of the most important problems in rubber technology. During the ageing process small amounts of oxygen are absorbed by natural or synthetic rubbers or by their vulcanizates. This causes considerable changes in their physico-mechenical properties. Consequently, it is necessary to add ingredients to rubber mixes

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to protect the rubber articles from oxidative degradation. These rubber ingredients are generally called antioxidants. The addition of antioxidants to rubber mixes can prolong the service life on the rubber vulcanizates. However, the efficiency of the antioxidants depends on different factors such as the type of rubber, the type of ageing, and the nature of the other ingredients in the mixes. The efficiency of the antioxidants also greatly depends on their chemical structure [1, 2].

Antioxidants generally belong to serveral chemical classes known as amino, phenolic, and organo phosphorus compounds [3]. The development of heat resistant rubber is considered to be a very important task [4–23].

In the present work the effect of chemical structure of some p-substituted diphenylamines on their efficiencies as antioxidants and antifatigue agents in natural rubber mixes has been investigated.

MATERIALS AND EXPERIMENTAL TECHNIQUES

Materials

Rubber: Natural rubber, NR type SMR-20.
Accelerator: N-cyclohexyl–2-benzothiazol sulphenamide (CBS).
Activators: (i) stearic acid. (ii) Zinc oxide.
Curing agent: Sulfur.
Filler: High abrasion Furnace carbon black (HAF).
Plasticizer: Naphthenic processing oil.
Antioxidants: Phenyl-B-naphthylamine (PBN) and the prepared compounds listed in Table 1.
Solvents and chemicals: All solvents and chemical reagents were of pure grade. They are products of International Companies.

Experimental Techniques

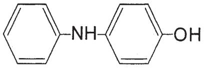
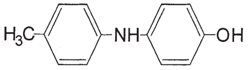
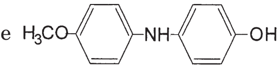
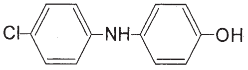
Preparation of Compounds under Investigation [24]

They were prepared by refluxing a mixture of hydroquinone (1 mole) with 1.5 moles of (aniline, p-toluidine, p-anisidine hydrochloride, and p-chloro aniline) in 50 ml of ethanol. The mixture was refluxed for 10 h then cooled and the reaction product was filtered, washed with petroleum ether 60–80. The products were crystallized from ethanol.

Preparation of Rubber Mixes and Vulcanizates

All rubber mixes were prepared on a two roll laboratory mill diameter 470 mm and width 300 mm, with speed of slow roller at 24 r.p.m. and gear ratio 1:1.4. The roller temperature was kept at about 50°C during

TABLE 1 The Prepared Compounds

No.	Name	Formula	Abbr.	m.p.c.
1	4-hydroxy diphenylamine		HDP	118–120
2	4-hydroxy-4′-methyl diphenylamine		HMDP	120
3	4-hydroxy-4′-methoxyl diphenylamine		HXDP	145–153
4	4-hydroxy-4′-chloride diphenylamine		HCDP	65–70

mixing. The vulcanization press was operated at 142°C under a pressure of about 4 Mpa.

The rheometric characteristics of NR mixes were studied using a Monsanto oscillating disc rheometer R-100 according to ASTM designation [25]. Initiation time (t_i) and the rate constant (K) were calculated from rheometric data. The vulcanized sheets prepared for mechanical and ageing tests were cut into five individual dumb-bell shaped specimens by a steel die of constant width (0.4 cm). The thickness of the test specimen was determined by a gauge calibrated in hundredth of mm. A working part of 15 mm was chosen for each test specimen.

The mechanical properties were determined according to standard methods [26] using an Instron tensile testing machine (model 5568). The equilibrium swelling (Q) was carried out in toluene [27]. Ageing of the rubber vulcanizates was carried out in an air oven at 90°C for different time periods [28]. The fatigue property was determined using a Monsanto fatigue tester (model 445) [29].

RESULTS AND DISCUSSION

Effect of the Prepared Compounds on the Vulcanization of NR Mixes

The prepared compounds were incorporated in natural rubber mixes in equimolar quantities to 1 phr phenyl-B-naphthylamine (PBN). Diphenyl amine (DPA) was also used as a control to compare the efficiencies of the prepared compounds as antioxidants and antifatigue agents. The basic formula in part per hundred parts of rubber (phr)

TABLE 2 Rubber Formulations, Rheometric Characteristis, and Physico-Mechanical Properties of NR Vulcanizates

	Formula No.						
	F1	F2	F3	F4	F5	F6	F7
Ingredients							
PBN	—	1	—	—	—	—	—
DPA	—	—	0.77	—	—	—	—
HDP	—	—	—	0.85	—	—	—
HMDP	—	—	—	—	0.91	—	—
HXDP	—	—	—	—	—	0.98	—
HCDP	—	—	—	—	—	—	1
Rheometric characteristics at 142°C							
ML, dN·m	1.0	1.0	0.5	0.0	1.0	1.0	1.0
MH, dN·m	72.5	66.5	59	66	73	67	72.5
t_{c90}, min	12	12.5	14.5	8.5	8	11.5	8.5
t_{s2}, min	6.5	7	7.5	4.5	3.5	4	4
CRI, min^{-1}	18.2	18.2	14.3	25	22.2	13.3	22.2
K, min^{-1}	0.559	0.53	0.369	0.78	0.889	0.427	0.671
t_1, min	7.26	7.7	7.62	4.6	4.22	4.37	4.47
Physico-mechanical properties							
M 200% Mpa	2.8	2.8	2.8	3.6	2.9	3.3	3
T.S. Mpa	22	23.2	22.37	23.3	21.2	21.2	24.42
E %	528	541	524	500	471	466	508
Q %	253	243	296	225	232	243	219

ML: minimum torque; MH: maximum torque; tc_{90}: optimum cure time; t_{s2}: scorch time; CRI: cure rate index; K: rate constant; ti: initiation time; M 200%: modulus at 200% elongation; T.S.: tensile strength; E: elongation at break; Q: equilibrium swelling.

was: natural rubber (NR)-100, Zinc oxide-5, stearic acid-0.5, high abrasion furnace carbon black (HAF)-40, processing oil-3, sulfur-2, N-cyclohexyl-2-benzothiazol sulfenamide (CBS)-1. Table 2 contains the rubber formulations, rheometric characteristics, and the physico-mechanical properties. From these data it is clear that the compounds (HDP), (HMDP), and (HCDP) had an accelerating effect as seen from the decrease in the optimum cure time and the initiation time, and also the increase of both cure rate index and rate constant. It is clear that the prepared compounds practically had no effect on the physico–mechanical properties.

Effect of the Investigated Compounds as Antioxidants in NR Vulcanizates

The NR mixes containing the evaluated compounds were vulcanized at 142°C at the optimum cure time. The rubber samples were subjected to thermal oxidative ageing in an oven at 90°C for different time periods. The physico-mechanical properties of the aged samples were determined and the retained values of tensile strength and elongation at break were calculated and illustrated in Figures 1 and 2. From these figures it is clearly seen that the retained values of tensile strength and elongation at break decrease with increase ageing time. On the other hand, one can see that the prepared compounds are more efficient antioxidants than the reference compound. It is also clear that compounds containing methyl or methoxy group attached to the benzene ring measurably improve the heat resistance of NR vulcanizates by about 4–11%. This can be attributed to the electron donating behavior of these groups. The prinicipal requirement of the majority of antioxidants is the presence of labile hydrogen in their chemical structure. It is quite evident the p–Cl substitution had the lowest antioxidant efficiency due to the electron-withdrawing behavior of Cl atom.

Figure 3 depicts the dependence of the swelling values in toluene on the ageing time. The decrease of swelling values prove the tendency of NR vulcanizates to form more crosslinks as the ageing time increases.

From these data, it can be concluded that the electron donating groups (CH_3, OCH_3) decrease the rate of change of the physico-mechanical properties, whereas the electron withdrawing group (Cl) increases the rate of change of properties with ageing time.

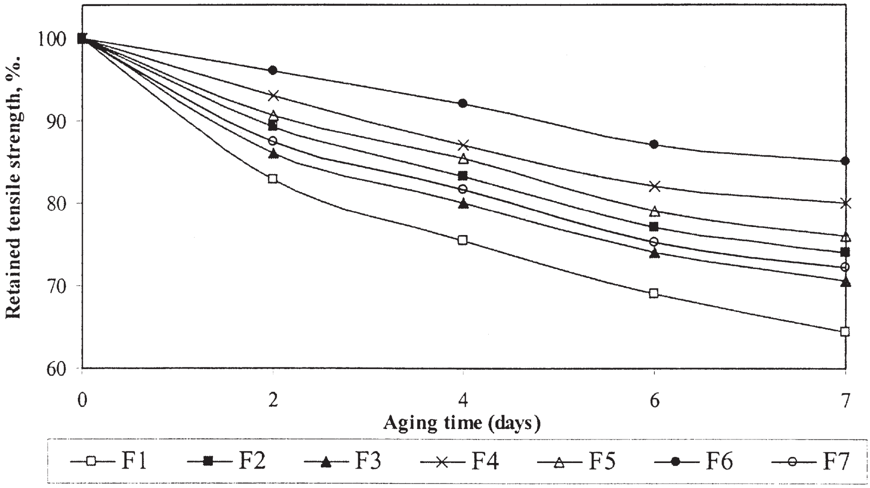


FIGURE 1 Retained tensile strength vs. ageing time for NR vulcanizates.

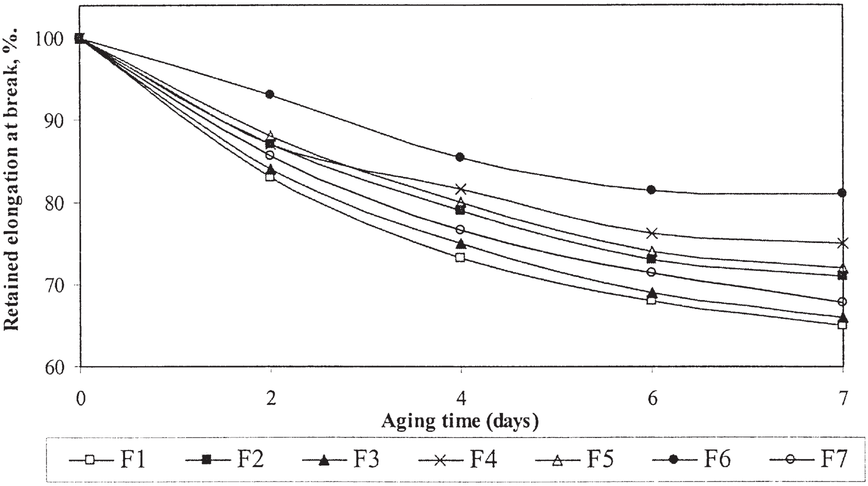


FIGURE 2 Retained elongation at break vs. ageing for NR vulcanizates.

Generally, the heat resistance of NR vulcanizates can be arranged in the following order: HXDP > HDP > HMDP > PBN > HCDP > DPA > without antioxidant.

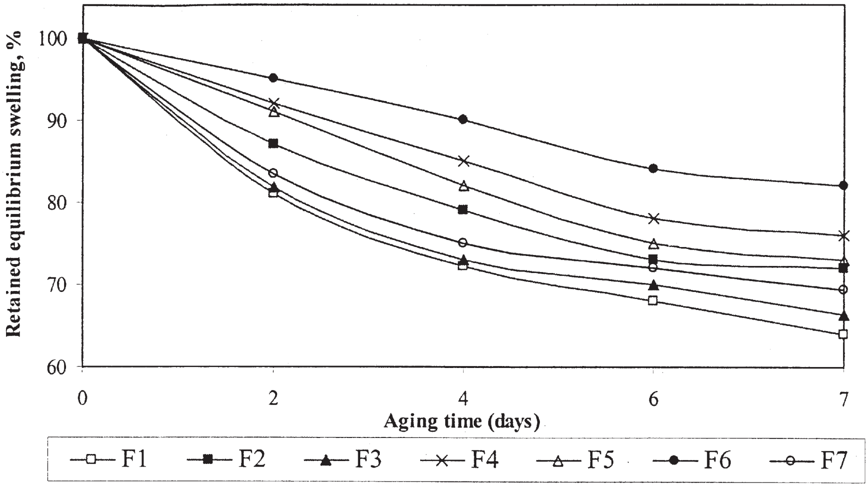


FIGURE 3 Retained equilibrium swelling vs. ageing time for NR vulcanizates.

Effect of Different Concentrations of HXDP Compound in NR Vulcanizates

In the previous study, (HXDP) had shown the highest efficiency as antioxidant for NR mixes. It was selected to extensively study the relationship between the concentration of that compound and its efficiency as antioxidant. For this purpose, NR formulations containing different concentrations of (HXDP) up to 2 phr were prepared. The rheometric characteristics of the mixes and the physico-mechanical properties of the vulcanizates were determined and listed in Table 3.

From these data it is apparent that the increase of (HXDP) concentration above 1 phr leads to the increase of optimum cure time, whereas both cure rate index and rate constant were decreased. On the other hand, the modulus 200% increased whereas the equilibrium swelling decreased as the concentration of (HXDP) had been increased.

The prepared vulcanizates were subjected to thermal ageing at 90°C for different time periods. Figures 4–6 represent the dependence of tensile strength, elongation at break and the equilibrium swelling on ageing time. It is clear that the efficiency of (HXDP) as antioxidant increased with the increase of its concentration up to 1.5 phr and then remained approximately constant. Consequently, the optimum concentration of the compound can be taken as 1.5 phr.

TABLE 3 Rheometric Characteristics and Physico-Mechanical Properties of NR Vulcanizates Contains Different Concentrations of HXDP

Property conc. phr	Without	0.5	1	1.5	2
Rheometric characteristics at 142°C					
Minimum torque (ML), dN.m	1	2	1	1	1
Maximum torque (MH), N.m	72.5	67	67	66	62
Optimum cure time (tc_{90}), min.	12	11.5	11.5	12.5	13.5
Scorch time (ts_2), min	6.5	5.5	4	4.5	4
Cure rate index (CRI),$^{-1}$	18.2	16.7	13.3	12.5	10.5
Rate constant (K), min^{-1}	0.559	0.462	0.424	0.308	0.284
Initiation time (t_i), min	7.26	6	4.37	4.75	4.06
Physico-mechanical properties					
Modulus (M 200%), Mpa	2.8	2.4	3.3	3.4	4.52
Tensile strength (T.S.), Mpa	22.7	19.39	21.2	22.6	21.73
Elongation at break (E), %	528	536	466	490	500
Equilibrium swelling (Q), %	253	283	243	236	225

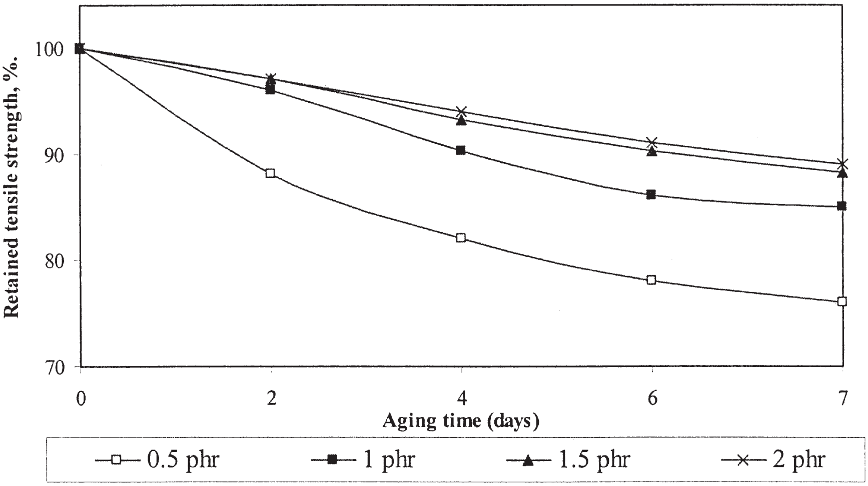


FIGURE 4 Retained tensile strength vs. ageing time for NR vulcanizates containing different concentrations of (HXDP).

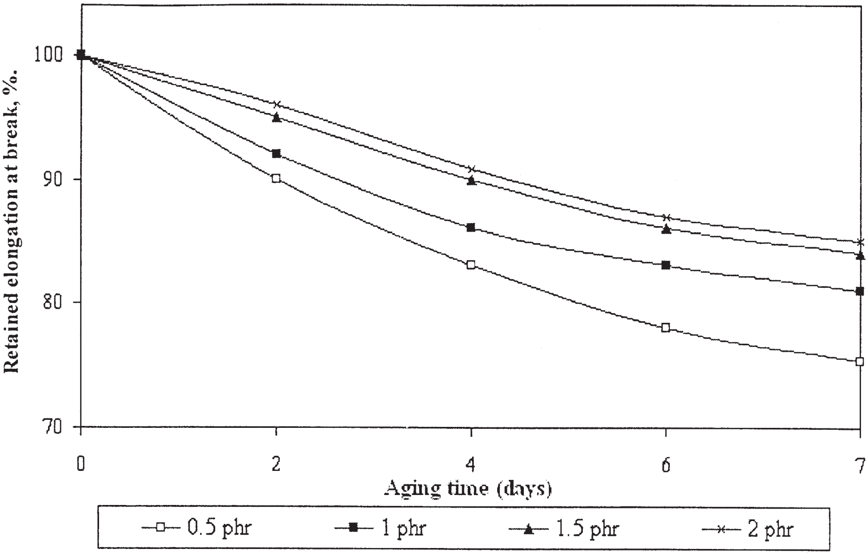


FIGURE 5 Retained elongation at break vs. ageing time for NR vulcanizates containing different concentrations of (HXDP).

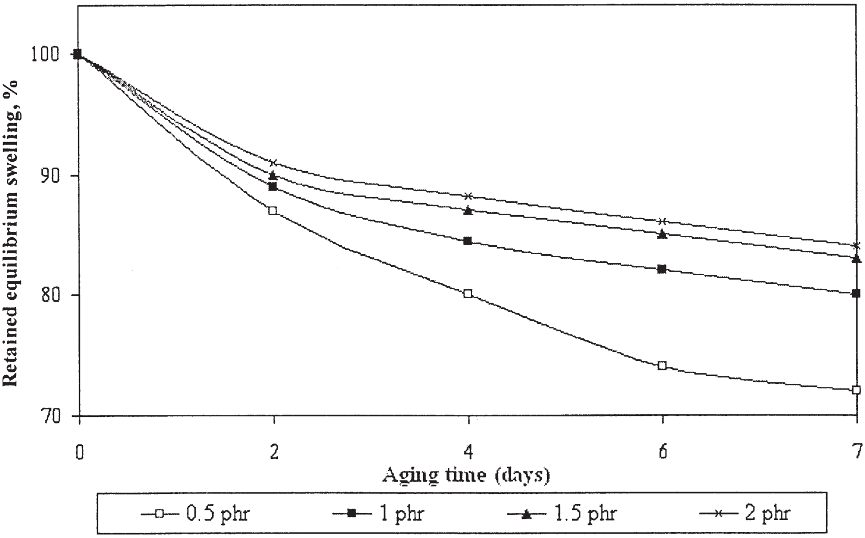


FIGURE 6 Retained equilibrium swelling vs. ageing time for NR vulcanizates containing different concentrations of (HXDP).

Evaluation of the Investigated Compounds as Antifatigue Agents in NR Vulcanizates

The major source of failure in rubber products under dynamic service conditions is the development of cracks, first at the surface, then propagating within the bulk of the rubber article. On repeated deformation these cracks can grow and lead to catastrophic failure of the rubber article. Fatigue crack resistance of rubber articles is one of the important properties in tire service as well as for other rubber products. Therefore, it is an absolute necessity to add antifatigue agents

TABLE 4 Fatigue to Failure Tests for NR Vulcanizates

Formula no.	Compounds	Number of cycles
F1	Without	24600
F2	PBN	56500
F3	DPA	55700
F4	HDP	58100
F5	HMDP	61000
F6	HXDP	65500
F7	HCDP	54200

to rubber compounds, with the express aim of protecting them from fatigue failure in service conditions. The NR vulcanizates containing the synthesized compounds were tested according to standard methods [29] for determination of fatigue property, using a Monsanto fatigue-to-failure testing machine. The number of cycles was taken as a measure of the service life of the rubber. The data obtained are given in Table 4. Careful study of the data given in Table 4 shows that the efficiency of the prepared compounds greatly depends on their chemical structure.

CONCLUSIONS

On the basis of this work it can be concluded that:

1. The investigated compounds are good thermal stabilizers and antifatigue agents for NR vulcanizates.
2. The compound (HXDP) is the most efficient antioxidant and the optimum concentration is 1.5 phr.
3. The efficiency of the investigated compounds as antioxidants and antifatigue agents depends on their chemical structure, especially compounds containing an electron donating group in the p-position.

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