Preparation and Evaluation of Some Novel Organo-Phosphorus Compounds as Antioxidants and Antifatigue Agents in Rubber

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ABSTRACT: Six organo-phosphorus compounds were synthesized and incorporated in NR and SBR mixes. The rheometric characteristics of the green rubber mixes were determined using the oscillating disc rheometer. The prepared compounds were evaluated as antioxidants and antifatigue agents in NR and SBR vulcanizates. It was found that the prepared compounds are good antioxidant and antifatigue agents and their efficiency was better than that obtained by 4-methyl-2,6-di-*tert*-butyl phenol, which is used in the rubber industry. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2984–2992, 2002; DOI 10.1002/app.2327

Key words: organo-phosphorus compounds; antioxidant; antifatigue agent; vulcanizate

INTRODUCTION

In spite of the fact that some organic compounds, which can be used as accelerators, antioxidants, and antifatigue agents, are added in small amounts (1–2 phr), they play a very important role in determining the service characteristics of the obtained rubber vulcanizates.[1,2]

The addition of antioxidants to rubber mixes can prolong the service life of the rubber vulcanizates. Phenolics, amines, and organo-sulfur compounds are well known as antioxidants and antifatigue agents for natural and synthetic rubbers. The efficiency of the antioxidants greatly depends not only on different factors such as the rubber type, the type of aging, and the nature of the other rubber ingredients in the mixes but also on their chemical structure.[3–7]

The new trend in antioxidants is the derivatives of organo-phosphorus compounds. However, the synthesis of such compounds and their evaluation as antioxidants and antifatigue agents in rubber create an ongoing and increasing interest.[8–12]

The aim of the present work was to prepare some organo-phosphorus compounds, then evaluate their efficiency as antioxidants and antifatigue agents in NR and SBR.
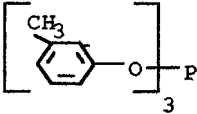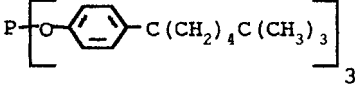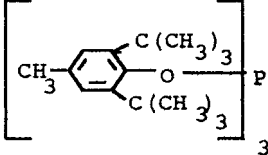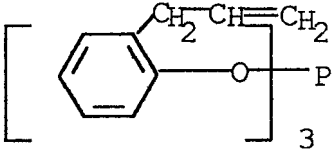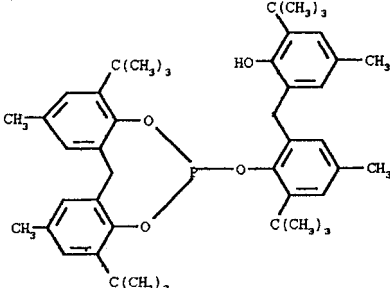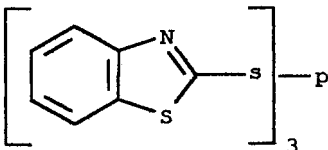
EXPERIMENTAL

Materials

Rubbers

The rubbers used in this investigation were natural rubber [SMR 20 (Polyisoprene): specific gravity, 0.913 ± 0.005; Row Mooney viscosity $M_L(1 + 4)$ at 100°C, 60–90; glass-transition temperature (T_g), −75°C] and styrene–butadiene rubber [SBR 1502: styrene content, $\cong 23.5$; specific gravity,

Table I The Prepared Compounds

No.	Name	Abbreviation	Formula
1	Tri(*m*-methyl phenyl) phosphite	*m*-TMPP	
2	Tri(*p*-*tert*-octyl phenyl) phosphite	*p*-TtOPP	
3	Tri(4-methyl-2,6-di-*tert*-butylphenyl) phosphite	TMdtBPP	
4	Tri(allyl phenyl) phosphite	TAPP	
5	2,2′-Methylene bis(4-Me-6-*tert*-butyl) phenyl, [2′-methylene (4-Me-6-*tert*-butyl) phenyl, 2-methylene (4-Me-6-*tert*-butyl) phenol] phosphite	MbMtBPP	
6	Tri(mercaptobenzothiazoyl) thiophosphite	TMBTTP	

0.945 $\pm$ 0.005; Row Mooney viscosity $M_L(1 + 4)$ at 100°C, 52 $\pm$ 3; T_g, −60°C].

Antioxidants

4-Methyl-2,6-di-*tert*-butyl phenol (MdtBP) and the prepared compounds, which are listed in Table I.

Solvents and Chemicals

All solvents and chemical reagents were of pure grade and were further purified, if necessary, by the usual techniques (e.g., distillation, recrystallization).

Preparation of Substituted Aryl Phosphite[13,14]

Three moles of substituted phenol or 3*M* of mercapto-benzothiazol and 3*M* of triethylamine, which act as a nitrogen base, were dissolved in dry benzene, after which 1*M* of phosphorus trichloride was dissolved in dry benzene then added dropwise over a period of 30 min. After complete addition the mixture was stirred for 3 h at room temperature, after which the reaction mixture was distilled to remove the excess PCl$_3$, benzene, triethylamine, and the unreacted alkyl phenol or mercapto-benzothiazol. The product was purified by means of distillation under vacuum; analysis

Table II   Analysis of the Prepared Compounds

No.	Compound	m.p. (°C)	Yield (%)	M^+ (m/z)	n_D^{20}	d_{20}
1	m-TMPP	—	79	310	1.577	1.127
2	p-TtOPP	—	71	646	1.529	1.093
3	TMdtBPP	104–105	55	688	—	—
4	TAPP	—	74	430	1.565	1.123
5	MbMtBPP	105–106	26	709	—	—
6	TMBTTP	72–73	60	529	—	—

was then carried out, the results of which are given in Table II.

Characterization of the Prepared Compounds

The prepared compounds were characterized using IR (Jasco FT/IR 300 E) and mass spectroscopy (EI + Q1MS LMR UP LR). The IR spectrum showed a characteristic P—O stretch strong band for P—O—Ph in the region 1180–1260 cm^{-1} and a strong absorption band in the region 850–950 cm^{-1}, attributed to bending of the P—O of P—O—Ph.[15] The IR absorption bands of the prepared compounds are listed in Table III.

Preparation of Rubber Mixes and Vulcanizates

All rubber mixes were prepared on a two-roll laboratory mill (diameter, 470 mm; working distance, 300 mm; speed of the slow roller, 24 rpm; gear ratio, 1 : 1.4). The roller temperature was kept at about 50°C during mixing. The compounded rubber was left overnight before vulcanization. The vulcanization press was operated at 142°C for natural rubber mixes and at 152°C for styrene–butadiene rubber mixes under a pressure of about 4 MPa.

Tests of Rubber Mixes and Vulcanizates

The following standard methods were used:

- ASTM D2084-95 (1994) for determination of optimum cure time (t_{C90}), scorch time (t_{S2}),

Table III   Absorption Band for P—O—Ph Linkage of the Prepared Compounds

Compound	Wave Number (cm^{-1})	Compound	Wave Number (cm^{-1})
m-TMPP	1174, 940	TAPP	1196, 851
p-TtOPP	1152, 865	MbMtBPP	1214, 954
TMdtBPP	1216, 868	TMBTTP	1241, 995

minimum torque (M_L), maximum torque (M_H), and cure rate index (CRI) using a Monsanto Rheometer 100 (Monsanto, St. Louis, MO).

- ASTM D412-98a (1998) for determination of the physicomechanical properties using a Zwick tensile testing machine (model 1425).
- ASTM D430-73 (1973) for determination of fatigue property using a Monsanto fatigue tester (model 445).
- ASTM D573-88 (1994) for thermal aging.
- ASTM D471-97 (1998) for swelling of rubber vulcanizates in toluene.

It is very useful to make use of the swelling data to calculate the molecular weight between two successive crosslinks (M_C) by the application of the well-known Flory–Rehner equation[16,17]:

$$Crosslinking\ density = \tfrac{1}{2}M_C$$

$$-\tfrac{1}{2}M_C = \tfrac{1}{2}\rho V_0[(1 - V_R) + V_R + \mu V_R^2/V_R^{1/3} - \tfrac{1}{2}V_R]$$

where ρ is the density of rubber; V_0 is the molar volume of the solvent (toluene V_0 = 106.3 cm^3/mol); V_R is the volume fraction of the rubber in the swollen material [calculated as V_R = 1/(1 + Q_m), where Q_m = $V/(W_d/\rho_1)$, V is the volume of the solvent absorbed by the rubber, and ρ_1 is the density of the solvent]; and the interaction parameter constants[18] (μ) for NR and SBR are 0.393 and 0.446, respectively.

RESULTS AND DISCUSSION

Effect of the Prepared Compounds on the Vulcanization of NR and SBR Mixes

The prepared compounds were incorporated into rubber mixes in equimolar quantities to 4-methyl-

Table IV   NR Formulations Containing Synthesized Compounds: Rheometric Characteristics and Physicomechanical Properties

	Formula Number							
	1	2	3	4	5	6	7	8
				Compound (phr)[a]				
Characteristic/Property	Without	MdtBP (1)	m-TMPP (1.61)	p-TtOPP (3.14)	TMdtBPP (2.96)	TAPP (2.94)	MbMtBPP (7.365)	TMBTTP (3.62)
Rheometric characteristics at 142°C								
Minimum torque (M_L), dN · m	2	1	2	1.5	1	1	1.5	2
Maximum torque (M_H), dN · m	75	50.5	66	68	63	53.5	55.5	74.5
Optimum cure time (t_{C90}), min	15.5	14.5	13.5	15	13.5	15	12.5	7.5
Scorch time (t_{S2}), min	5.5	6	3.75	5.25	3.5	4.5	3.25	2.5
Cure rate index (CRI), min^{-1}	10	11.76	10.26	10.26	10	9.25	10.81	19.05
Physicomechanical properties								
Tensile strength at break (T_b), MPa	19.3	18.2	18.88	19.97	18.82	18.76	20.48	21.04
Elongation at break (E_b), %	552	670	610	558	591	624	565	544
Modulus (M 200), MPa	6.17	6.32	4.62	5.54	4.71	3.36	5.36	6.91
Equilibrium swelling (Q), %	178	195	198	182	202	222	194	169
Mol. wt. between crosslinks (M_C)	1470	1730	1760	1516	1830	2174	1703	1353

[a] Parts per hundred rubber.

2,6-di-*tert*-butyl phenol (MdtBP). The basic formula is natural rubber (NR), 100; zinc oxide, 5; stearic acid, 0.8; high-abrasion furnace black (HAF), 40; processing oil, 3; sulfur, 2; *N*-cyclohexyl-2-benzothiazol sulfenamide (CBS), 1. Table IV lists the compounds' rheometric characteristics and physicomechanical properties.

From these data one can see that all NR mixes with and without antioxidants under investigation have almost the same level of minimum torque (M_L). NR mixes without antioxidant had the highest value of the maximum torque (M_H = 75 dN·m), whereas the mix with a phenolic-type antioxidant had the lowest value for M_H (~ 50 dN·m). On the other hand, NR mixes containing the prepared phosphorus compounds have an intermediate M_H value between 53 and 74 dN·m, depending on the substituent groups in the benzene ring of the prepared compounds. It is worthy to notice that the compound TMBTTP increases the rate of vulcanization and decreases both the optimum cure time and the scorch time, which can be explained by its accelerating effect. This may be attributed to the presence of the mercapto-benzothiazol moiety. On the other hand, the other compounds practically do not affect these parameters.

The NR mixes were vulcanized at the optimum cure time and the physicomechanical properties of the vulcanizates were determined and are also included in Table IV. These data show that the NR vulcanizates containing the prepared compounds have tensile strength and elongation at break almost at the same levels as those for vulcanizates without antioxidant. On the other hand, the vulcanizates containing the prepared compounds (except TMBTTP) have a modulus at 200% elongation in the range 3–5.5 MPa, which is less than that for vulcanizates without or containing phenolic antioxidant. This means that the vulcanizates with such organo-phosphorus have lower crosslinking density. These findings can be proved by the molecular weight between crosslinks (M_C) and swelling data, which is higher than that for blank vulcanizates. On the other hand, the NR vulcanizates containing the compound TMBTTP have a modulus at 200% elongation, which is somewhat higher than that of the blank vulcanizates. This can be explained on the basis that this compound can cooperate with CBS (the main accelerator) to create more crosslinks between NR chains.

The study was extended to evaluate the target compounds in SBR mixes. The recipes basically contain (in equimolar quantities) SBR, 100; stearic acid, 0.8; zinc oxide, 5; HAF, 40; processing oil, 5; sulfur, 2; CBS, 1. Table V presents the compounds' rheometric characteristics and physi-

Table V   SBR Formulations Containing Synthesized Compounds: Rheometric Characteristics and Physicomechanical Properties

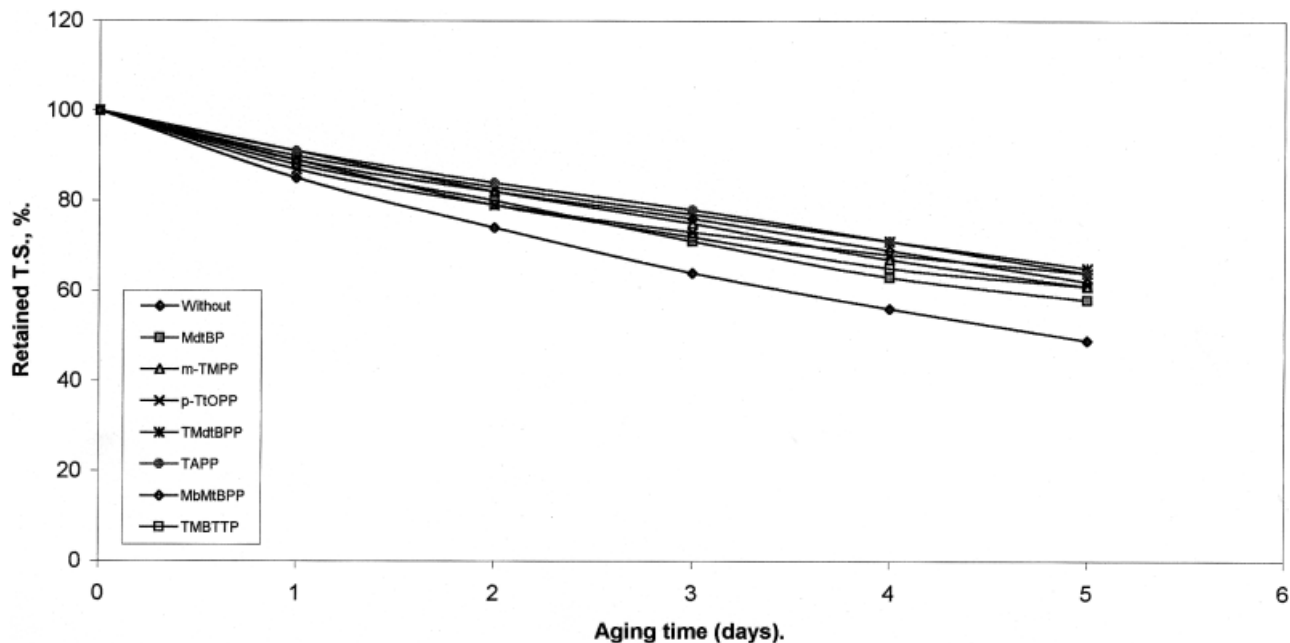|				Formula Number				
	1	2	3	4	5	6	7	8
				Compound (phr)[a]				
Characteristic/Property	Without	MdtBP (1)	m-TMPP (1.61)	p-TtOPP (3.14)	TMdtBPP (2.96)	TAPP (2.94)	MbMtBPP (7.365)	TMBTTP (3.62)
Rheometric characteristics at 152°C								
Minimum torque (M_L), dN · m	11.5	7.5	10.5	10.5	11	10	10	13
Maximum torque (M_H), dN · m	79	60	83	80.5	69	71.5	66	106
Optimum cure time (t_{C90}), min	26	23	22	19.5	21.5	25.25	25.25	11
Scorch time (t_{S2}), min	7.5	4.5	4.5	7.25	4	5	5.5	3.25
Cure rate index (CRI), min^{-1}	5.4	5.4	5.71	8.16	5.17	4.94	5.06	12.9
Physicomechanical properties								
Tensile strength at break (T_b), MPa	21	18.2	23.2	19.97	18.82	23	21.79	13.07
Elongation at break (E_b), %	613	580	552	558	519	619	668	363
Modulus (M 200), MPa	5.88	5.29	5.55	5.58	5.91	3.82	3.08	6.91
Equilibrium swelling (Q), %	215	256	192	182	202	234	236	168
Mol. wt. between crosslinks (M_C)	2670	3731	2149	2078	2817	3169	3196	1706

comechanical properties. The data in Table V show that SBR mixes with and without the prepared compounds are characterized by relatively high values for the rheometric parameters compared with values of NR mixes. This can be attributed to the nature of the SBR itself, which is a copolymer of butadiene and styrene. The SBR contains hard segments of styrene polymer, which is a plastic. The viscosity of the gum SBR greatly depends on the styrene content in the copolymer and it increases as the content of styrene in the copolymer increases. The gum SBR used in our case contains about 23% styrene, which explains the high values of M_L and M_H of SBR mixes. It is worthy to mention that SBR vulcanizes at a lower rate than that of NR mixes, which explains the high values of t_{C90} and the low values of CRI (taking into consideration that SBR mixes were cured at 152°C and NR mixes cured at 142°C). It is worth noting that the vulcanizates, which contain the compound p-TtOPP and have a substitution in the pare position in the benzene ring, have a CRI value that is relatively higher than that of the other compounds. The physicomechanical properties of SBR mixes cured at 152°C at the optimum cure time were determined and are given in Table V.

It is clearly seen from these data that the vulcanizates containing the compound m-TMPP,

TAPP, and MbMtBPP have the highest values of tensile strength and that the vulcanizate containing the compound TMBTTP has the lowest value of tensile strength. The other vulcanizates have intermediate values between the above-mentioned values. On the other hand, the ultimate elongation of SBR vulcanizates is in the same level, ranging between 500 and 600%; the vulcanizate containing the compound TMBTTP has the ultimate elongation, about 363%.

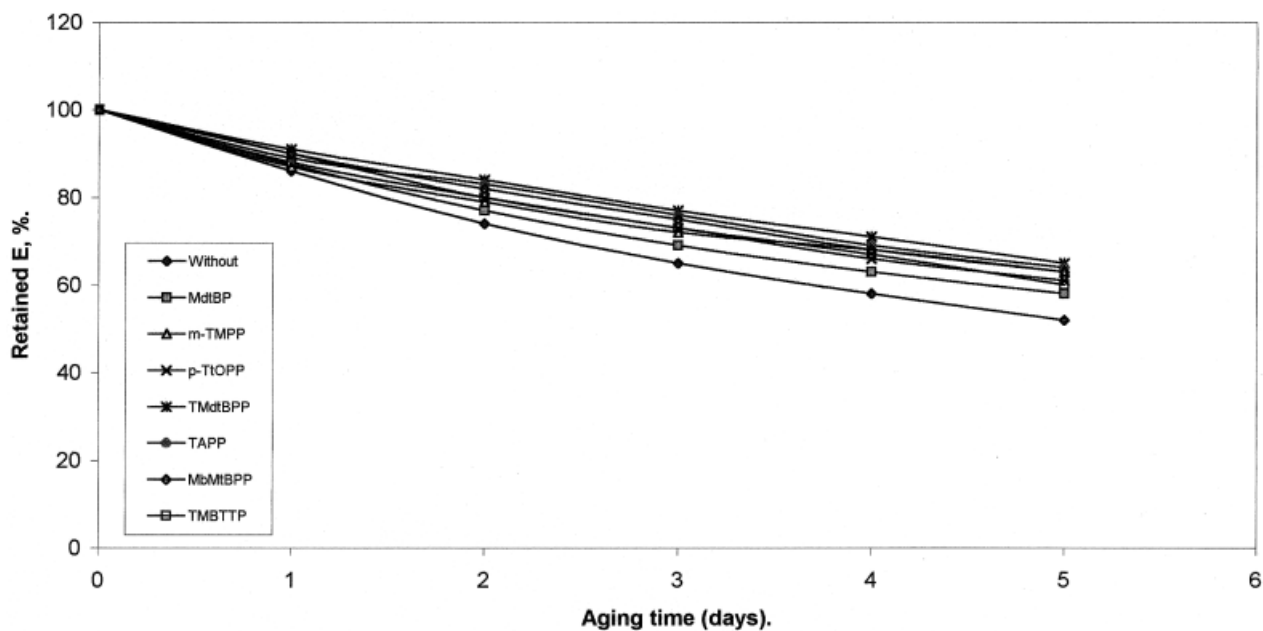## Effect of the Investigated Compounds as Antioxidants in NR and SBR Vulcanizates

The NR mixes containing the compounds shown in Table I were vulcanized at 142°C at the optimum cure time. The rubber samples were subjected to thermal oxidative aging in an oven at 90°C for different time periods. The physicomechanical properties of the aged samples were determined and the retained values of tensile strength and elongation at break were calculated and are 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 of the aging time. On the other hand, one can see that the prepared compounds are more efficient antioxidants than the reference compound, where the retained tensile

Figure 1 Retained tensile strength with respect to percentage of NR vulcanizates containing the prepared compounds.

strength and elongation at break after 5-day aging are higher than those of commercial compounds by about 12–16%. The efficiency of organo-phosphorus compounds greatly depends on the type of substitution groups in the benzene ring. As an example the NR vulcanizate containing compound TMBTTP has the lowest efficiency, in which the vulcanizate can retain only 61 and 60% of tensile strength and elongation at break, respectively, after aging 5 days. The substitution

Figure 2 Retained elongation at break with respect to percentage of NR vulcanizates containing the prepared compounds.
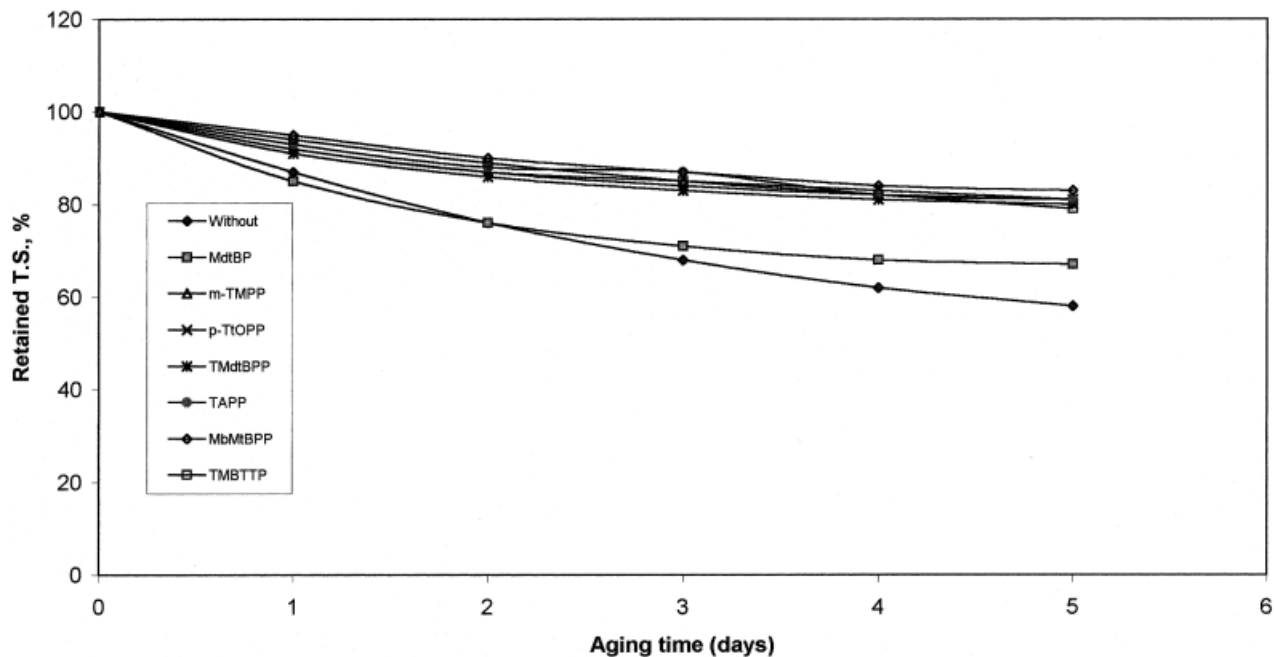
Table VI   Relative Change of Equilibrium Swelling with Respect to Percentage of NR Vulcanizates Aged at 90°C
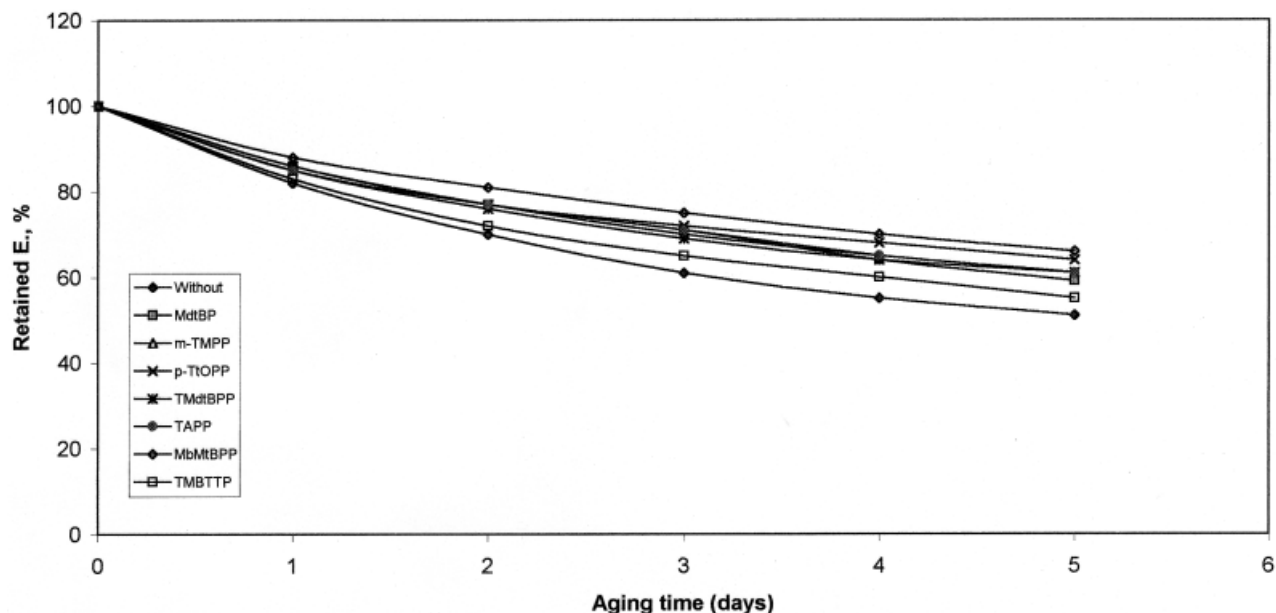
Compound	Time					
	0 Day	1 Day	2 Days	3 Days	4 Days	5 Days
Without	0	−11	−17	−20	−20	−21
MdtBP	0	−14	−18	−20	−21	−22
m-TMPP	0	−14	−21	−24	−25	−25
p-TtOPP	0	−15	−20	−21	−22	−23
TMdtBPP	0	−14	−22.5	−26	−27	−27
TAPP	0	−13	−19	−21.5	−23	−23
MbMtBPP	0	−14	−22	−24	−25	−25
TMBTTP	0	−17	−27	−32	−33	−34

in the benzene ring by either a methyl or a tertiary group improves the heat resistance of NR vulcanizates. On the other hand, the NR vulcanizates containing compound TMdtBPP have the highest efficiency of all organo-phosphorus compounds employed in NR mixes. Such vulcanizates can retain 65 and 65% of tensile strength and elongation at break, respectively, after aging 5 days. The efficiencies of all other prepared antioxidants are very close to each other and higher than that of the commercial antioxidant. The swelling data given in Table VI show the ten-

dency of NR vulcanizates to form more crosslinks as the aging time increases.

In the same way the SBR vulcanizates containing the target compounds (Table V) were subjected to thermal oxidative aging in an oven at 90°C for different time periods. The physicomechanical properties of the aged samples were determined and the retained values of tensile strength and elongation at break were calculated and are illustrated in Figures 3 and 4. One can see from these data that the efficiencies of the prepared compounds in SBR mixes are greater

Figure 3   Retained tensile strength with respect to percentage of SBR vulcanizates containing the prepared compounds.

Figure 4 Retained elongation at break with respect to percentage of SBR vulcanizates containing the prepared compounds.

than those in NR mixes. The SBR vulcanizates can retain at least 79 and 55% of the original values of tensile strength and elongation at break, respectively. Importantly, MbMtBPP and TMdtBPP are the most efficient antioxidants. The swelling data given in Table VII show the tendency of SBR vulcanizates to further crosslink during aging.

The differing effects of antioxidants in the case of SBR versus NR may be attributed to the fact that SBR contains the electron-donating phenyl group, which can create a sort of synergism with the electron-donating groups in the target compounds. The difference in the efficiencies of the prepared compounds can be attributed to the differences in their chemical structure.

Evaluation of Phosphorus Compounds as Antifatigue Agents in Rubber 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

Table VII   Relative Change of Equilibrium Swelling with Respect to Percentage of SBR Vulcanizates Aged at 90°C[a]

	Time					
Compound	0 Day	1 Day	2 Days	3 Days	4 Days	5 Days
Without	0	−12	−17.5	−20	−22	−23
MdtBP	0	−21	−27	−29	−31	−32
m-TMPP	0	−19	−24	−26.5	−28	−29
p-TtOPP	0	−20	−25	−26	−29	−30
TMdtBPP	0	−20	−26	−28	−30	−32
TAPP	0	−20	−25	−27	−30	−32
MbMtBPP	0	−21	−26	−27	−30	−32
TMBTTP	0	−18	−24	−31	−38	−39

[a] Generally, the heat resistance of SBR vulcanizates can be arranged in the following order, as evaluated by retained tensile strength: MbMtBPP > m-TMPP, p-TtOPP, and TAPP > TMdtBPP > TMBTTP > MdtBP > without.

Table VIII   Fatigue-to-Failure Tests for NR and SBR

Compound	Number of Cycles	
	NR	SBR
Without	24,500	48,900
MdtBP	76,000	92,000
m-TMPP	44,900	105,700
p-TtOPP	49,200	79,300
TMdtBPP	90,400	104,700
TAPP	49,000	175,500
MbMtBPP	82,000	175,800
TMBTTP	33,900	42,100

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 to rubber compounds, with the express aim of protecting them from fatigue failure under service conditions. The NR and SBR vulcanizates containing the synthesized compounds were tested according to standard methods 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 VIII. A careful study of the data given in Table VIII shows that the efficiency of the prepared compounds greatly depends on the type of rubber because of the difference in the chemical structure of NR and SBR. The difference in the efficiencies of the organo-phosphorus compounds can be attributed to the differences in their chemical structure. These compounds are generally more efficient in SBR than in NR vulcanizates.

CONCLUSIONS

On the basis of this work one can conclude that:

1. The investigated compounds can play the role of good antioxidant and antifatigue agents for both NR and SBR vulcanizates.
2. The prepared compounds are generally more efficient as antioxidant and antifatigue agents in SBR than in NR vulcanizates.
3. The efficiency of the prepared compounds as antioxidant and antifatigue agents greatly depends on their chemical structure.

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