

Synthesis, Characterisation and Activity of Two New Phenol Antioxidants in Natural Rubber

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Two phenol derivatives which have sterically hindered groups in the ortho position, 2-(1-t-butyl-1,2,3,3-tetramethylbutyl)-4-methyl-6-t-butylphenol and 2-(1-t-butyl-1,2,3,3-tetramethylbutyl)-4,6-di-t-butylphenol were prepared and evaluated as non-staining antioxidants in natural rubber (NR). The efficiency of these antioxidants and 2,6-di-tertbutyl-4-methylphenol (BHT), 2,4,6-tri-tertbutylphenol (TTP) and styrenated phenol (SP) has been studied by comparing physico-mechanical properties of the non-black NR vulcanisates. The work described in this paper shows that the phenol derivatives are powerful compared to BHT, SP, TTP, and their activities depend on the substituted groups in the ortho and para positions of the phenol structure. The sterically hindered groups in the ortho position increase activity of the phenol derivative.

Phenols, amines, organo sulphur and organo phosphorus compounds are well known as antioxidants for natural and synthetic rubber^{1,2}. In most rubber systems, amines are more effective in preventing long-term oxidative degradation. However, amine antioxidants usually discolour with ageing and may not be suitable for light or brightly coloured rubber articles where colour retention is important. Phenolic antioxidants in contrast to amine antioxidants, do not discolour on ageing^{3,4}. Phenolic antioxidants can be sub-divided into several categories by common chemical types⁴:

- Hindered phenols
- Hindered bisphenols
- Hindered thiobisphenols
- Poly hydroxy phenols.

Applications have been developed for synthesis of two novel rubber antioxidants which are both non-volatile and non-staining and are more effective than conventional hindered phenol antioxidants which are used in non-black rubber, especially for medical and paramedical applications⁵. These antioxidants are synthesised from very cheap materials such as P-cresol, 4-tertbutylphenol,

acetone and isobutylene to yield 2-(1-t-butyl-1,2,3,3-tetramethylbutyl)-4-methyl-6-t-butylphenol (I) and 2-(1-t-butyl-1,2,3,3-tetramethylbutyl)-4,6-di-t-butylphenol (II).

EXPERIMENTAL

Materials

P-cresol, isobutylene, 4-tertbutylphenol and 2,6-di-tertbutyl-P-cresol and 2,4,6-tri-tert butylphenol, acetone were purchased from Merck Chemical Company, and 2,2,3,4,5,5-hexamethyl-3-hexene was prepared according to published procedures^{7,8,9}. With the exception of isobutylene, they were purified according to known procedures^{6,7}. Six masterbatches containing pale crepe, 1 p.h.r. stearic acid, 5 p.h.r. zinc oxide, 25 p.h.r. calcium carbonate and 5 p.h.r. titanium oxide, were used in the physical experiments. Except pale crepe, these materials and styrenated phenol were obtained from Bayer Company.

Synthetic Procedures

2,2,3,4,5,5 Hexa methyl-3-hexene was synthesised from tertbutylmethyl ketone^{8,9} and tertbutylmethyl ketone was synthesised

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from acetone⁷ Synthetic methods for the other substances are given below

2-(1-*t*-butyl-1,2,3,3-tetramethylbutyl)-4-methylphenol According to the recent method, 108 g (1 mole) of *p*-cresol in a 1 litre three-necked flask fitted with a condenser, in nitrogen atmosphere, was condensed by the drop-wise addition of 168 g (1 mole) of 2,2,3,4,5,5 hexamethyl-3-hexene at 140°C at the rate of 3.7 g/min. The condensation reaction was catalysed by the addition of 3.25 g of sulphuric acid (96%). On cooling, the reaction mixture containing yellow oil was removed by dissolving in 500 ml of benzene. The benzene solution was washed with three 200 ml portions of 2% sodium hydroxide solution and then with water until the washings were neutral. The washed benzene solution was dried over anhydrous sodium sulphate and freed of solvent by distillation at approximately 30 mm pressure. There was a 60% yield of 2-(1-*t*-butyl-1,2,3,3-tetramethylbutyl)-4-methylphenol (1) with a boiling point of 191°C at 10 mm pressure.

2-(1-*t*-butyl-1,2,3,3-tetramethylbutyl)-4-methyl-6-*t*-butylphenol 136 g (0.5 mole) of (1) were butylated by adding 56 g (1 mole) of isobutylene at 100°C for 4.5 h. This reaction was catalysed through the addition of 1.5 g of sulphuric acid (96%). On cooling, the reaction

mixture solidified and was removed by dissolving in 200 ml of benzene. The benzene solution was washed with three 100 ml portions of 2% sodium hydroxide solution and then with water until the washings were neutral. The washed benzene solution was dried over anhydrous sodium sulphate and freed of solvent by distillation at approximately 30 mm pressure. The benzene free residue was distilled at 10 mm pressure in a flask equipped with a Vigreux column. The fraction boiled at 212°C. It was cooled to give a white solid material (I) which weighed 70 g.

2-(1-*t*-butyl-1,2,3,3-tetramethylbutyl)-4-*t*-butylphenol 150 g (1 mole) of 4-*tert*-butylphenol were condensed by the drop-wise addition of 168 g (1 mole) of 2,2,3,4,5,5 hexamethyl-3-hexene at 150°C at the rate of 6 g/min. The condensation reaction was catalysed by the addition of 3.5 g of sulphuric acid (96%). There was a 50% yield of 2-(1-*t*-butyl-1,2,3,3-tetramethylbutyl)-4-*t*-butylphenol (2). This composition has a boiling point of 205°C at 10 mm pressure.

2-(1-*t*-butyl-1,2,3,3-tetramethylbutyl)-4,6-di-*t*-butylphenol 153 g (0.5 mole) of (2) were butylated by adding 56 g (1 mole) of isobutylene at 120°C for 4.5 h. This reaction was catalysed through the addition of 1.5 g of sulphuric acid

TABLE 1 FORMULATION FOR NATURAL RUBBER

Material (phr)	Formulation					
	1	2	3	4	5	6
Pale crepe	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5
Calcium carbonate	25	25	25	25	25	25
Titanium oxide	5	5	5	5	5	5
Sulphur	2.25	2.25	2.25	2.25	2.25	2.25
TMTD ^a	0.25	0.25	0.25	0.25	0.25	0.25
MBT ^b	0.5	0.5	0.5	0.5	0.5	0.5
SP	—	1	—	—	—	—
BHT	—	—	1.5	—	—	—
TTP	—	—	—	1.2	—	—
(I)	—	—	—	—	1	—
(II)	—	—	—	—	—	1

^a Tetramethylthiuram disulphide

^b 2-Mercapto benzothiazole

96%). The fraction boiled at 221°C at 10 mm pressure. It cooled to give a yellow solid material (II) which weighed 140 g.

Formulations

The rubbers were compounded according to the formulations given in *Table 1* using a laboratory 45 cm two-roll mill (Schwabenthan Polymix 200 L) according to *ASTM D3182*. The amounts of antioxidants were optimised by use of resistance of heat ageing.

Measurement

Identification of synthetic antioxidants was carried out by nuclear magnetic resonance (^1H -NMR varian 90 MHZ instrument). A solution of 0.1 g of antioxidant in 0.5 ml CDCl_3 was used. Physical tests were conducted for all moulded compounds after moulding and exposure of press cured samples in a circulating air oven at 80°C for up to 24 h. Tensile strength, modulus and elongation were determined according to *ASTM D412* using Instron 6025 tensile tester with 10 KN load cell and a crosshead speed of 50 cm/min.

Shore A hardness tests were performed on moulded samples using a hand-held Shore A durometer.

Cure characteristics which include scorch time, optimum cure time (t_{90}) and torque values, were automatically measured over a 20 min period at 141°C for NR using a Zwick torsional thrust vulcameter.

Resilience was measured according to *ISO/DIS 4662* using Frank resilience elasticity tester 23567.

RESULTS AND DISCUSSION

Figure 1 shows the NMR spectra of 2-(1-*t*-butyl-1,2,3,3-tetramethylbutyl)-4-methyl-6-*t*-butylphenol (I). 2 H (δ : 6.7 p.p.m.) are in the aromatic range, suggesting a di-substituted benzene $-\text{C}_6\text{H}_2-$. The 3 H (δ : 3.3 p.p.m.) have a shift expected for benzylic proton, giving CH_3 , $-\text{C}_6\text{H}_2-$. 1 H (δ : 4.3 p.p.m.) is phenolic proton, 34 H (δ : 1.3 p.p.m. and 2 p.p.m.) are *tert*butyl and branched *tert*butyl protons in the ortho position.

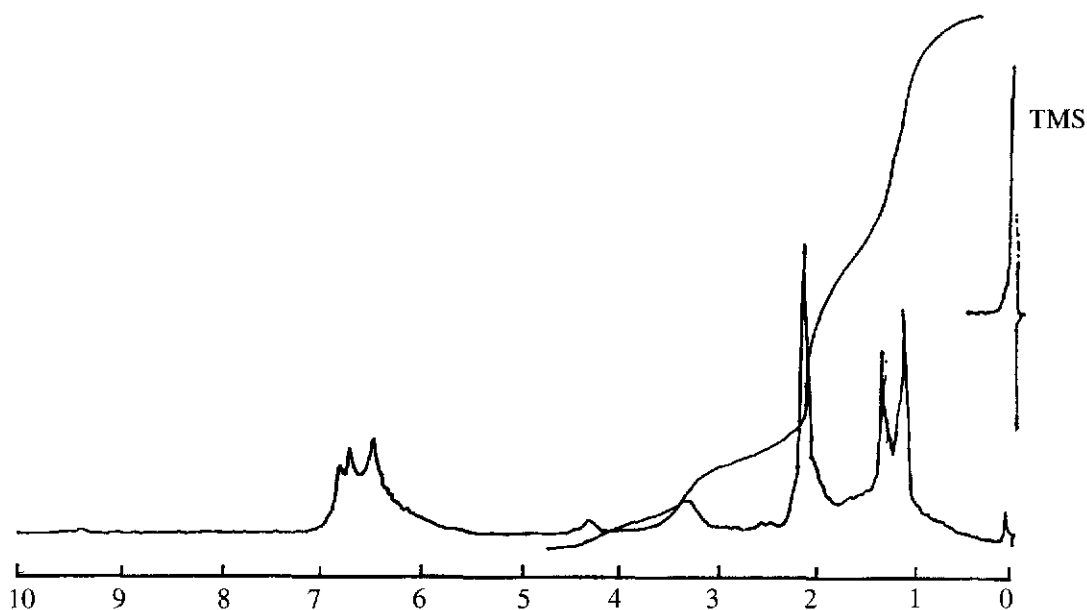


Figure 1. NMR spectra for 2-(1-*t*-butyl-1,2,3,3-tetramethylbutyl)-4-methyl-6-*t* butylphenol.

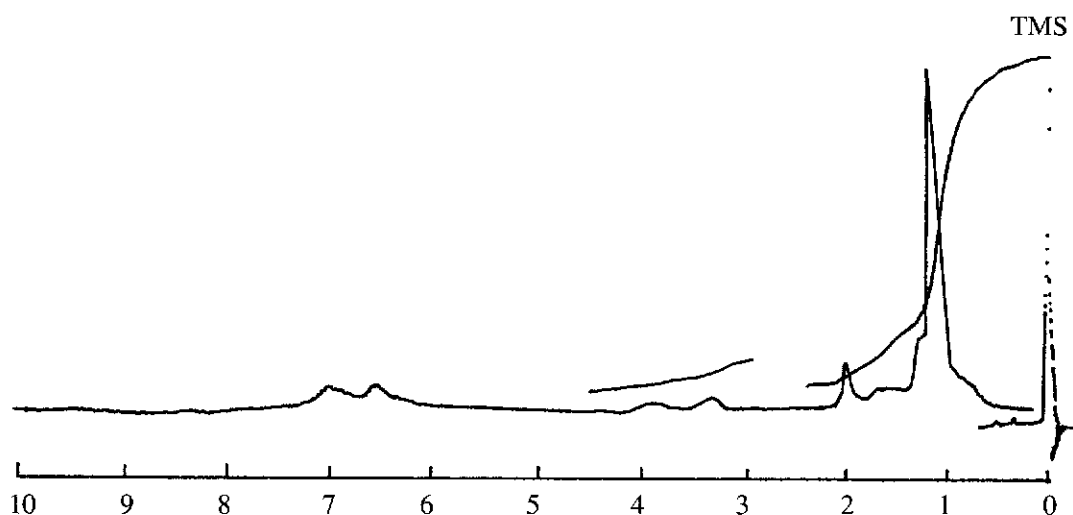


Figure 2. NMR spectra for 2-(1-t-butyl-1,2,3,3-tetramethylbutyl)-4,6-di-t-butylphenol.

Figure 2 shows the NMR spectra of 2-(1-t-butyl-1,2,3,3-tetramethylbutyl)-4,6-di-t-butylphenol (II). 2 H (δ : 7 p.p.m.) are in the aromatic range $-C_6H_2-$. H (δ : 4.5 p.p.m.) is phenolic proton. 43 H (δ : 1.2 p.p.m.) are tert-butyl on para and ortho positions and branched tertbutyl in the ortho position.

The physical properties for the NR compounds are given in Table 2 which show

no significant difference between compounds during mixing and vulcanisation. Figures 3 and 4 show the dependence of the relative change in elongation at break and tensile strength with ageing time. It can be seen that these antioxidants protect NR vulcanisates against oxidative ageing.

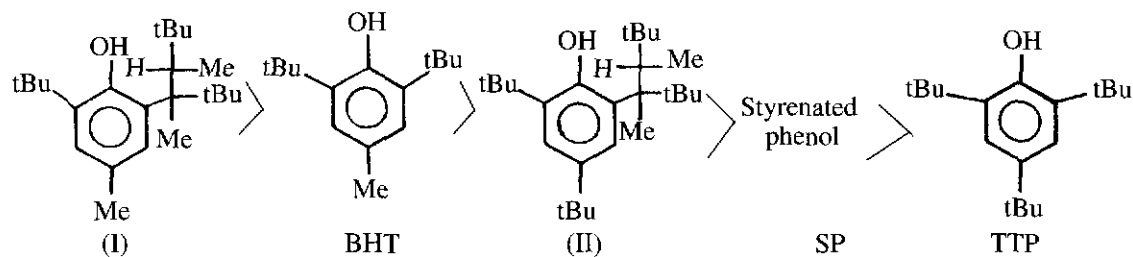
Based on the ability of the antioxidants to aid in the retention of tensile strength

TABLE 2. PHYSICAL PROPERTIES OF NR RUBBER COMPOUNDS FROM TABLE 1

Property	NR compound					
	1	2	3	4	5	6
90% Optimum cure at 141°C, min	4.66	4.67	4.87	4.87	4.77	4.85
Scorch (min)	2.22	2.35	2.06	2.12	2.10	2.17
Minimum torque (N.m)	0.35	0.40	0.33	0.36	0.35	0.34
Maximum torque (N.m)	3.43	3.35	3.34	3.37	3.35	3.36
Modulus 300% (MPa)	3.47	3.53	3.65	3.51	3.80	3.62
Tensile strength at break (MPa)	20.56	21.76	22.25	21.10	22.27	21.92
Elongation at break	605.4	632.6	642.0	622.3	661.0	635.0
Hardness (Shore A)	51	51.5	50.7	51.5	51	51
Resilience (%)	85	82	82	83	84	84

and retention of percent elongation at break, the relative efficiencies of the five antioxidants

tested in NR follow the order as shown in *Scheme 1*.



Scheme 1

There are alkyl groups in the ortho and para positions of the antioxidants. Therefore these antioxidants are more active than phenol¹⁰. 2-(1-t-butyl-1,2,3,3-tetramethylbutyl)-4-methyl-6-t-butylphenol antioxidant is the most active, because there are branched alkyl groups in the ortho positions and a non-branched alkyl group (methyl) in the para position. The

molecular weight of (II) is high. BHT has tert butyl groups (branched alkyl group) in the ortho position and a non-branched alkyl group in the para position. The molecular weight of BHT is lower than those of the other antioxidants, but its activity is high in spite of the molecular weight, therefore the chemical structure is overcome. Another antioxidant

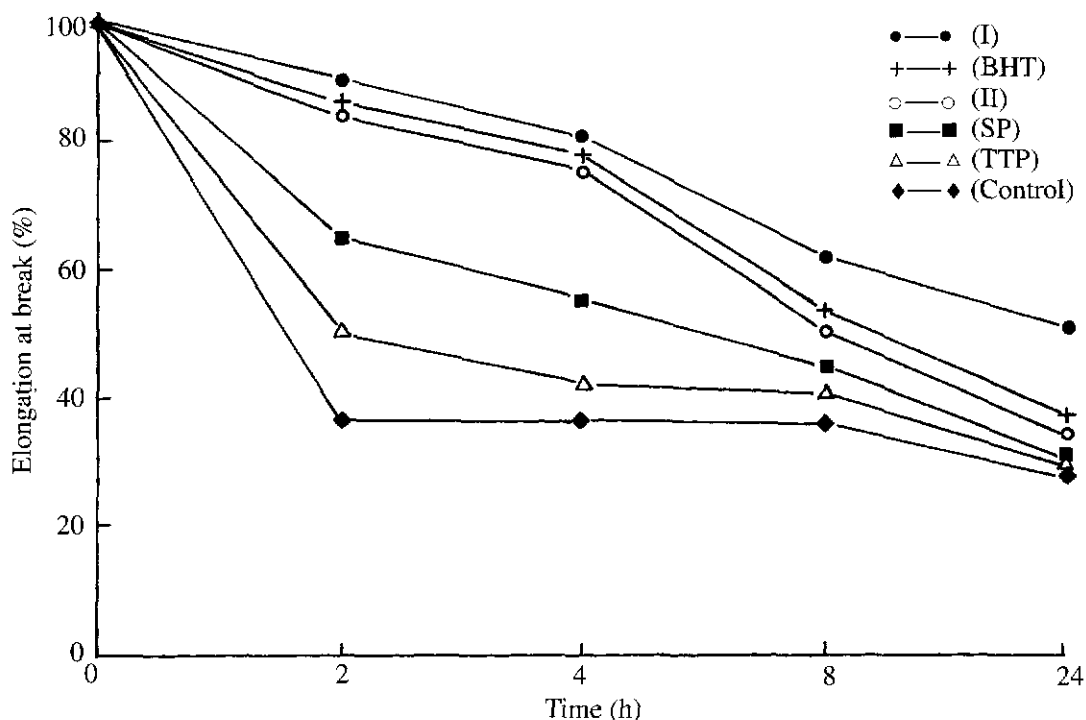


Figure 3. Elongation at break versus heat ageing time at 80°C.

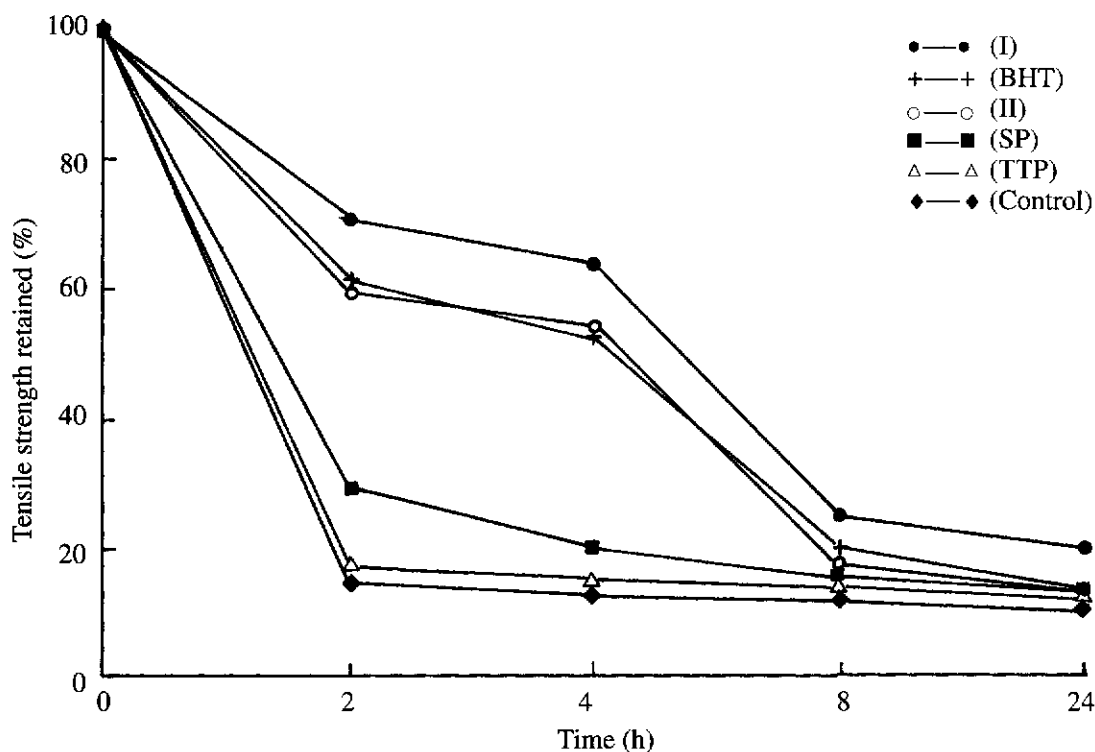


Figure 4. Tensile strength retained versus heat ageing time at 80°C.

is (II) whose molecular weight is the highest of all the antioxidants described here. According to Badran *et al.*¹ and Scott¹⁰, antioxidants with high molecular weight do not bloom to surface thus increasing their activity. Because of the branched alkyl group in the para position of (II), the activity is lower compared to BHT and (I). TTP is the poorest antioxidant because its molecular weight is low and there is a branched alkyl group in the para position (tert butyl). SP antioxidant is a mixture of styrenated phenol which is used widely in non-black compounds and its antioxidant activity is compared with the other compounds.

CONCLUSION

Our results show the high activity of (I) and (II) antioxidants which are synthesised from cheap materials using simple procedures. It

is evident that there is a lot of information on the relationship between the activity of antioxidants and their structures. Electron releasing groups such as methyl, tert butyl, *etc.* in the ortho and para positions increase antioxidant activity. Sterically hindered groups in the ortho position increase considerably the antioxidant activity, whereas branched para alkyl groups decrease it. High molecular weight antioxidants often do not lead to surface blooming and volatilisation from the compound, hence increasing antioxidant activity in rubber. Both molecular weight and chemical structure are important in the determination of antioxidant activity of phenol but the later is the more important factor.

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