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# Preparation and Characterisation of Novel Polymer Bound Phenolic Antioxidants and Its Use in Natural Rubber

P. B. SULEKHA AND R. JOSEPH\*

*Department of Polymer Science and Rubber Technology  
Cochin University of Science and Technology  
Cochin - 682 022, India*

**ABSTRACT:** Phenol was chemically attached to low molecular weight chlorinated polyisobutylene and stearic acid respectively. These phenolic antioxidants were characterised by IR, <sup>1</sup>HNMR and TGA. The efficiency and permanence of these bound antioxidants were compared with conventional antioxidants in natural rubber vulcanisates. The vulcanisates showed comparable ageing resistance in comparison to vulcanisates containing conventional antioxidants. The presence of liquid polymer bound phenol reduce the amount of plasticiser required for compounding.

**KEY WORDS:** antioxidant, ageing, phenolic type, natural rubber.

## INTRODUCTION

**T**HE TREND TOWARDS the use of rubbers in aggressive atmosphere has led to a search for methods of producing non-extractable antioxidants. Phenol was one of the earlier materials used to retard the oxidation of rubber. Alkylated phenols were found to be more

\*Author to whom correspondence should be addressed. E-mail: rani@cusat.ac.in

effective, less toxic and less volatile. Efforts to obtain higher molecular weight non-staining antioxidants by alkylating phenols were done [1,2]. A wide variety of substituted phenols have been synthesised and evaluated as antioxidants during last 70 years. The patent literature represents one of the best sources of information on the current direction of research in the area of polymer stabilisation. Two books deal exclusively with the United States patent literature on antioxidants during the period of 1972–1979 [3,4]. For rubber applications, cost as well as low volatility and compatibility with the polymer are important and most of the research effort deals with the alkylation of phenols. Spacht [5] found that the reaction of *p*-cresol and dicyclopentadiene, when tertiary butylated in the ortho positions of the terminal phenol is an effective antioxidant. Goto [6] discovered that the three isomers of dicyclopentyl-*p*-cresol (2,6-, 2,5-, 3,5-) obtained by reacting cyclopentene with *p*-cresol, were as effective as BHT in retaining physical properties of NR vulcanisates when aged 3 days at 100°C. Scott and coworkers have demonstrated that simple hindered phenols which contain a methyl group in the ortho or para position, can react with natural rubber in the presence of oxidising free radicals to yield polymer bound antioxidants [7–9]. De Jonge and Hope [10] described the development of a novel type of antioxidant based on 2,6-diphenylphenol. These antioxidants display novel regenerative characteristics in the presence of thiodipropionate esters and lead maintenance of the antioxidant concentration during processing and to unusually low antioxidant requirements during further oxidation. Antioxidants like styrenated phenol bound to hydroxy-terminated liquid natural rubber by modified Friedel–Crafts reaction were also found to be effective in improving ageing resistance [11]. Synthesis and use of new polymeric antioxidants were reported in recent literature [12–17]. This paper describes the chemical binding of phenol to polyisobutylene and stearic acid respectively. These bound antioxidants were compared with conventional antioxidants in filled natural rubber.

## EXPERIMENTAL

### Materials

Natural rubber (NR) (ISNR-5, Mooney viscosity ML(1 + 4) 100°C-82) was supplied by the Rubber Research Institute of India, Kottayam. Polyisobutylene (PIB) with molecular weight 934 was supplied by Cochin Refineries, Balmer Lawrie Ltd Ambalamugal, Kerala.

Compounding ingredients zinc oxide, stearic acid, naphthenic oil and silica were of commercial grade. Benzthiazyl 2-sulphenmorpholide (MOR) and tetramethyl thiuramdisulphide (TMTD), styrenated phenol (SP) and 2,6 di-*t*-butyl *p*-cresol were rubber grade – supplied by Bayer India Ltd. Methanol, phenol, *o*-xylene, carbon tetrachloride, carbon disulphide, thionyl chloride and ether were analytical grade and used as such. Zinc dust and concentrated HCl were also used.

### Preparation of Polyisobutylene Bound Phenol

Polyisobutylene was dissolved in CCl<sub>4</sub> (50%) solution and pure dry chlorine gas passed through it for 5 h. The resulting solution was poured into water at 80°C and excess chlorine and CCl<sub>4</sub> were removed. The chlorinated polyisobutylene (PIB-Cl) was reprecipitated and dried in vacuum oven.

The phenol was alkylated using modified Friedel–Crafts alkylation reaction. 0.1 of PIB-Cl, 0.2 mol of phenol, 0.4 mol catalyst (anhydrous aluminium chloride and 60 mol of solvent(*o*-xylene)) were introduced into a two-necked flask fitted with a thermometer and soxhlet extraction unit which was packed with fused CaCl<sub>2</sub>. The reaction mixture was heated for 14 h. When the reaction was complete, the reaction mixture was neutralized with sodium carbonate and washed several times with water to remove the catalyst. The contents of the vessel were poured into excess methanol with stirring to precipitate the liquid phenol bound PIB. Phenol bound PIB (PIB-Ph) was separated, washed and dried in a vacuum oven. The PIB bound phenol was obtained in the form of a viscous liquid.

### Preparation of Alkylated Phenol Using Stearic Acid

0.1 mol of stearic acid (SA) was weighed and dissolved in CS<sub>2</sub> and to it 0.1 mol SOCl<sub>2</sub> was added drop wise by cooling the reaction mixture in an ice bath. The reaction mixture is then heated gently under reflux for 2 h. The acid chloride formed was separated and used for conducting Friedel–Craft's acylation. 0.1 mol of phenol was dissolved in CS<sub>2</sub> and mixed with 0.1 mol of anhydrous aluminium chloride catalyst. It is cooled using an ice bath and acid chloride dissolved in CS<sub>2</sub> was added drop wise, swirling the mixture during addition. After addition is complete remove ice bath and allow the mixture to stand at room temperature for additional 30 min. Swirl the reaction mixture frequently during this period. After addition the reaction mixture was heated on a hot plate with magnetic stirring for 5 h. When the reaction

effective, less toxic and less volatile. Efforts to obtain higher molecular weight non-staining antioxidants by alkylating phenols were done [1,2]. A wide variety of substituted phenols have been synthesised and evaluated as antioxidants during last 70 years. The patent literature represents one of the best sources of information on the current direction of research in the area of polymer stabilisation. Two books deal exclusively with the United States patent literature on antioxidants during the period of 1972–1979 [3,4]. For rubber applications, cost as well as low volatility and compatibility with the polymer are important and most of the research effort deals with the alkylation of phenols. Spacht [5] found that the reaction of *p*-cresol and dicyclopentadiene, when tertiary butylated in the ortho positions of the terminal phenol is an effective antioxidant. Goto [6] discovered that the three isomers of dicyclopentyl-*p*-cresol (2,6-, 2,5-, 3,5-) obtained by reacting cyclopentene with *p*-cresol, were as effective as BHT in retaining physical properties of NR vulcanisates when aged 3 days at 100°C. Scott and coworkers have demonstrated that simple hindered phenols which contain a methyl group in the ortho or para position, can react with natural rubber in the presence of oxidising free radicals to yield polymer bound antioxidants [7–9]. De Jonge and Hope [10] described the development of a novel type of antioxidant based on 2,6-diphenylphenol. These antioxidants display novel regenerative characteristics in the presence of thiodipropionate esters and lead maintenance of the antioxidant concentration during processing and to unusually low antioxidant requirements during further oxidation. Antioxidants like styrenated phenol bound to hydroxy-terminated liquid natural rubber by modified Friedel–Crafts reaction were also found to be effective in improving ageing resistance [11]. Synthesis and use of new polymeric antioxidants were reported in recent literature [12–17]. This paper describes the chemical binding of phenol to polyisobutylene and stearic acid respectively. These bound antioxidants were compared with conventional antioxidants in filled natural rubber.

## EXPERIMENTAL

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Rubber compounds were moulded in an electrically heated laboratory hydraulic press at 150°C up to their optimum cure time. Dumb-bell shaped tensile test pieces were punched out of these compression molded sheets along the mill grain direction. The tensile properties of the vulcanisates were evaluated on a Zwick Universal Testing machine using a cross head speed of 500 mm/min according to ASTM D-412-80. Tear resistance of the vulcanisates was evaluated as per ASTM D-624-81 using un-nicked 90° angled test specimens. Retention in tensile and tear properties were evaluated after ageing the samples at 100°C for 12, 24, 36 and 48 h. The compression set of the samples was determined as per ASTM D-395 method B (1982). The abrasion resistance of the samples was tested using DIN Abrader.

## RESULTS AND DISCUSSION

Figures 1-5 show the IR spectra of PIB, PIB-Cl, PIB-Ph, SA and SA-Ph respectively. The IR spectra of PIB (Figure 1) shows peaks at 2950  $\text{cm}^{-1}$  corresponding to aliphatic -CH stretching, at 1480  $\text{cm}^{-1}$  due to -CH bending, 1650  $\text{cm}^{-1}$  corresponds to C=C. The IR spectrum of PIB-Cl (Figure 2) shows a new peak at 780  $\text{cm}^{-1}$  due to the presence of C-Cl stretching and peak corresponding to C=C disappears. The IR spectra of PIB-Ph (Figure 3) shows additional peaks at 3500  $\text{cm}^{-1}$  due to the presence of -OH stretching, 3000  $\text{cm}^{-1}$  corresponding to aliphatic -CH stretching, 1600  $\text{cm}^{-1}$  corresponds to aromatic ring and -CO stretching frequency at 1210  $\text{cm}^{-1}$ . IR spectra of stearic

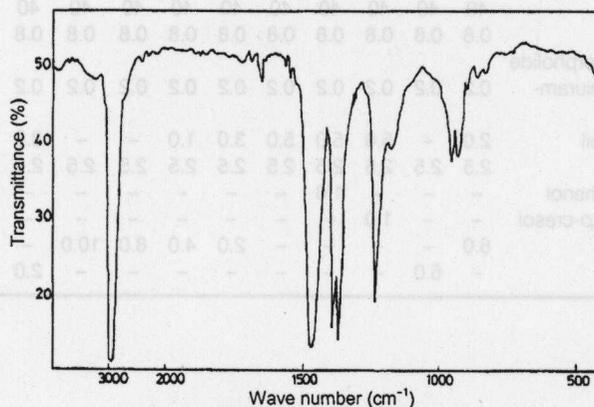


FIGURE 1. IR spectrum of PIB.

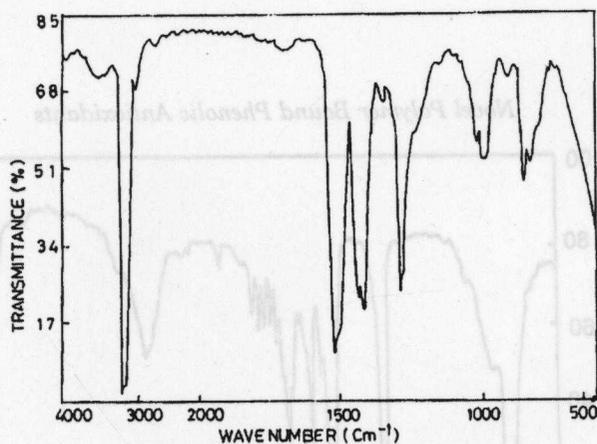


FIGURE 2. IR spectrum of PIB-Cl.

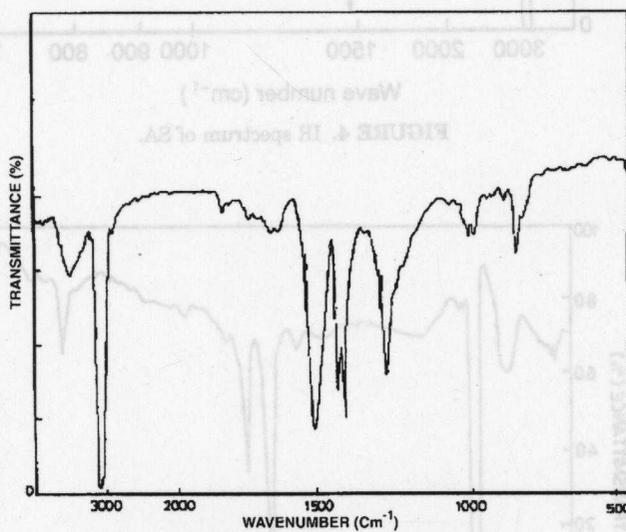


FIGURE 3. IR spectrum of PIB-Ph.

acid (Figure 4) shows distinct peak of  $\text{-C=O}$  at  $1709\text{ cm}^{-1}$ . IR spectra of SA-Ph (Figure 5) shows peak at  $3500\text{ cm}^{-1}$  due to  $\text{-OH}$  stretching and additional peak at  $1500\text{ cm}^{-1}$  due to the presence of aromatic ring. The disappearance of the peak at  $1709\text{ cm}^{-1}$  due to the absence of carbonyl group in the compound. All these confirms the binding of phenol to stearic acid.

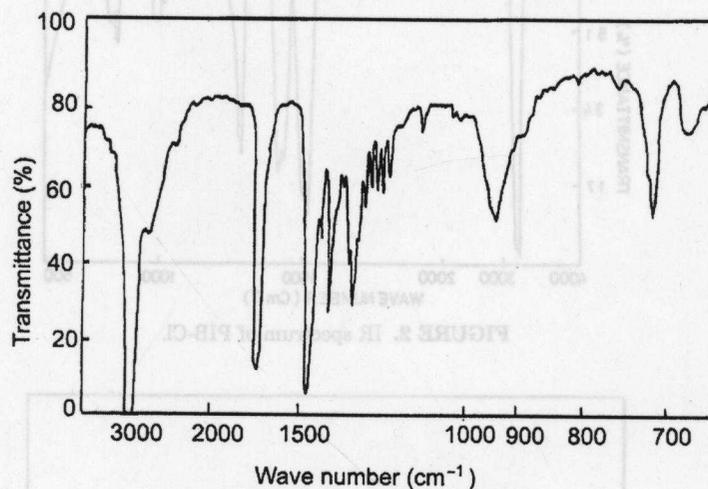


FIGURE 4. IR spectrum of SA.

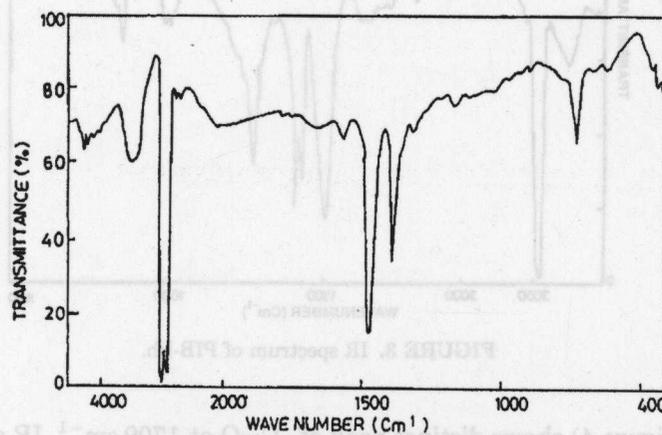


FIGURE 5. IR spectrum of SA-Ph.

Figure 6 shows the  $^1\text{H}$  NMR spectrum of PIB-Cl. It shows peaks at peaks  $\delta = 1.22$  ( $-\text{CH}_2$ ) and  $\delta = 1.6$  ppm ( $-\text{CH}_3$ ). Figure 7 shows additional peaks at  $\delta = 7.2$  ppm and  $\delta = 3.5$  ppm corresponding to aromatic ring and  $-\text{OH}$  proton present in PIB-Ph. This again confirms the chemical binding of phenol to PIB.

The chlorine content of the PIB-Cl is found to be 7.6%. This shows that addition reaction has taken place at the double bond.

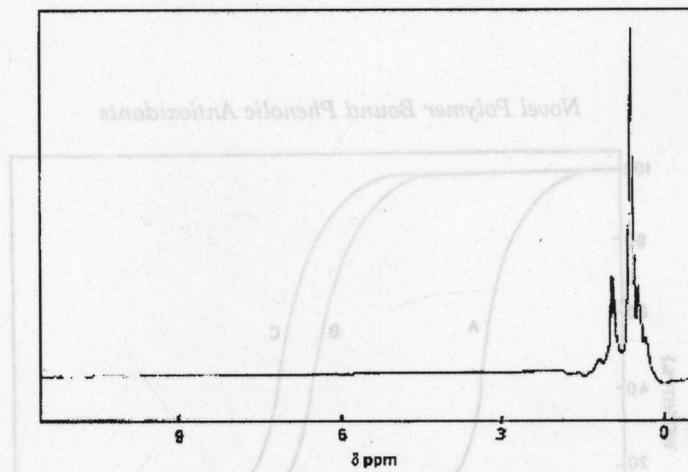


FIGURE 6.  $^1\text{H}$  NMR spectrum of PIB-Cl.

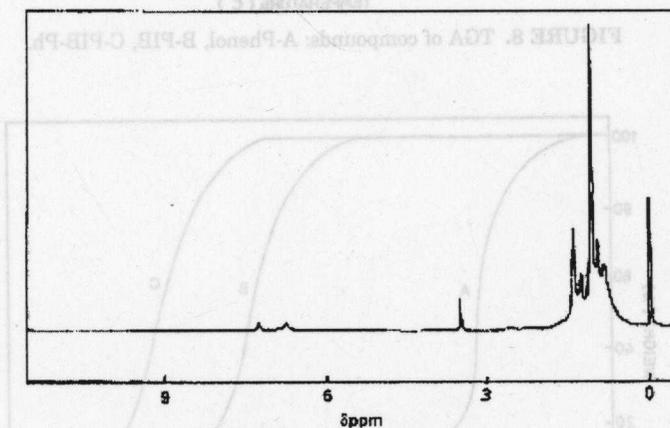


FIGURE 7.  $^1\text{H}$  NMR Spectrum of PIB-Ph.

Figure 8 shows the thermograms of Phenol, PIB and PIB-Ph. Figure 9 shows the thermograms of SA, phenol and SA-Ph. The low molecular weight phenol volatilises easily while rubber bound phenols are less volatile. This again confirms the chemical binding of phenol to PIB.

From the above data the binding of phenol and PIB may be represented as in Scheme 1.

Similarly the formation of SA-Ph can be represented as in Scheme 2.

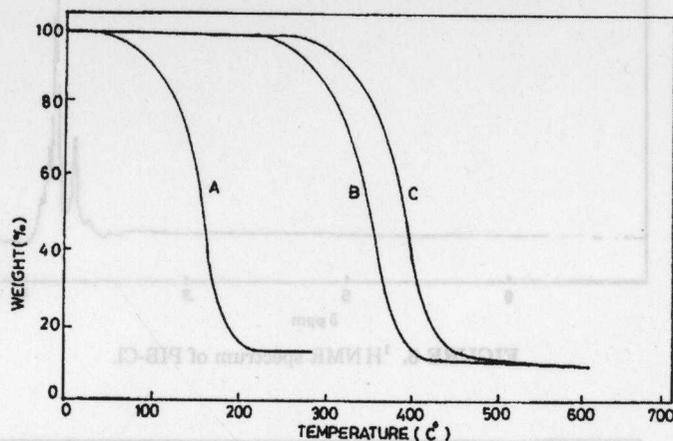


FIGURE 8. TGA of compounds: A-Phenol, B-PIB, C-PIB-Ph.

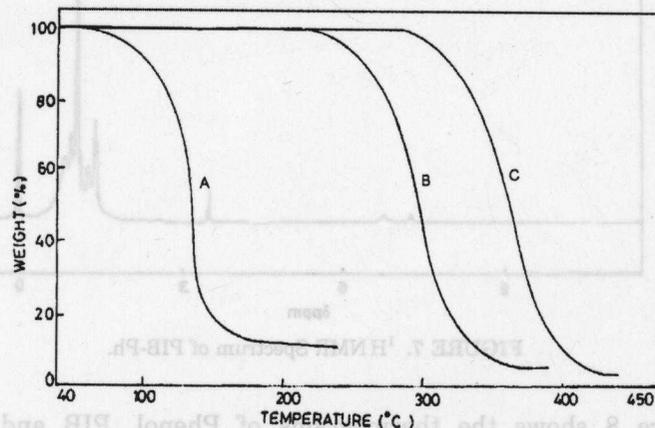
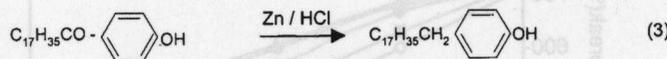
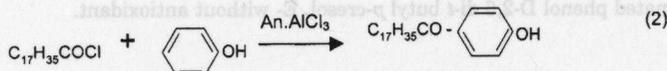
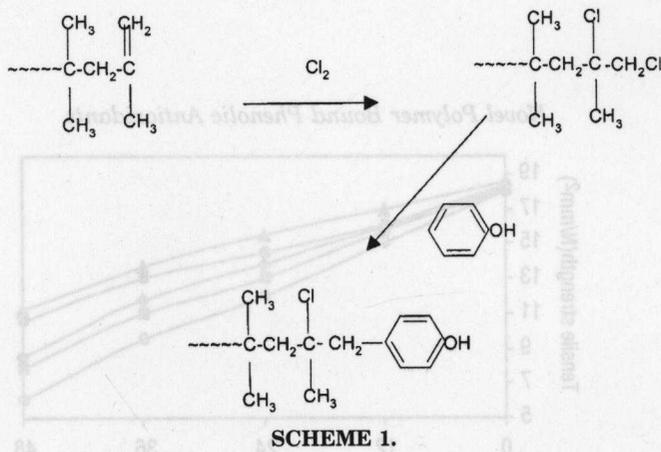


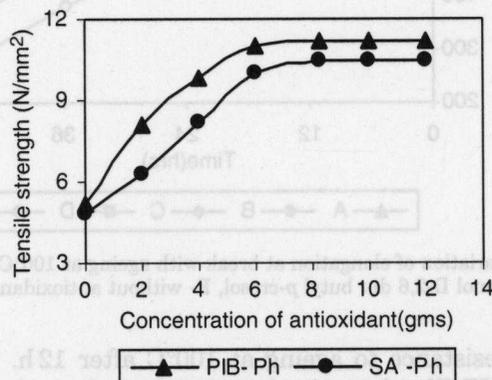
FIGURE 9. TGA of compounds: A-Phenol, B-SA, C-SA-Ph.

Figure 10 shows the variation in tensile strength after ageing at 100°C for 48 h after the addition of varying amounts of PIB-Ph and SA-Ph respectively to NR vulcanisates. The retention in properties is found to increase with the amount of the bound antioxidant, reach a maximum and levels off. The higher requirement of bound antioxidant in comparison to conventional antioxidant may be due to lower amount of effective antioxidant in the rubber bound product.

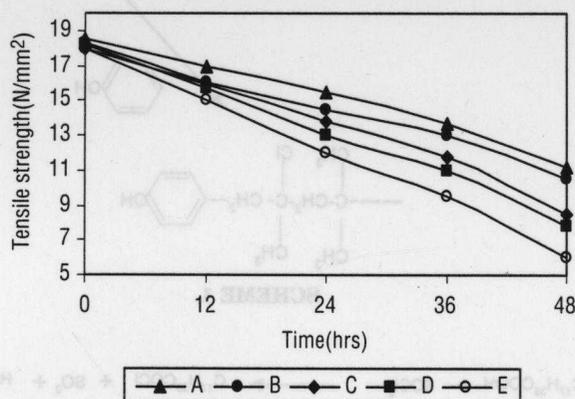
Figure 11 shows the tensile strength of the vulcanisates of compounds shown in Table 1 before and after ageing. All the vulcanisates show



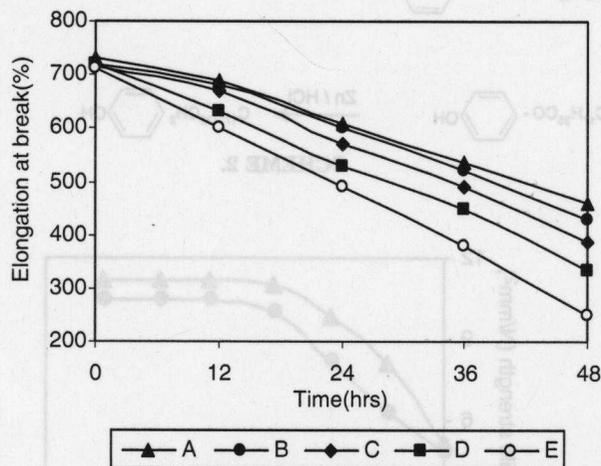
**SCHEME 2.**



**FIGURE 10.** Variation of tensile strength after ageing at 100°C for 48h with concentration of antioxidant.



**FIGURE 11.** Variation of tensile strength with ageing at 100°C, A-PIB-Ph, B-SA-Ph, C-styrenated phenol D-2,6 di-*t* butyl *p*-cresol, E- without antioxidant.



**FIGURE 12.** Variation of elongation at break with ageing at 100°C, A-PIB-Ph, B-SA-Ph, C-styrenated phenol D-2,6 di-*t* butyl *p*-cresol, E- without antioxidant.

fairly good resistance to ageing at 100°C after 12 h. The vulcanisates containing PIB-Ph show good resistance when the ageing time is increased to 48 h, which shows the superiority of bound antioxidant over conventional antioxidant. The vulcanisates containing SA-Ph show comparable ageing resistance in comparison to vulcanisates containing conventional type antioxidants.

Figure 12 shows the variation in elongation at break of the vulcanisates before and after ageing. The compound containing PIB-Ph shows

Table 2. Properties of vulcanisates.

Properties	A (PIB-Ph)	B (SA-Ph)	C (SP)
Abrasion resistance (volume loss, cc/h)	3.63	3.65	3.68
Compression set (%)	16.7	16.8	17.1

better retention in elongation at break after ageing while compound containing SA-Ph shows slightly less retention in elongation at break after ageing. This again shows that bound antioxidants can improve the ageing resistance of NR compound.

Table 2 shows the abrasion resistance and compression set of the vulcanisates containing PIB-Ph, SA-Ph and SP. The values are better than the vulcanisates containing conventional antioxidant.

## CONCLUSIONS

Phenol was chemically attached to low molecular weight chlorinated polyisobutylene and stearic acid respectively. These antioxidants have much superior resistance to evaporation compared to conventional antioxidants. These bound antioxidants can improve the ageing resistance of NR vulcanisates. The liquid polyisobutylene bound phenol can reduce the amount of plasticiser required for compounding.

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#### AUTHOR'S BIOGRAPHIES

Name: Sulekha P.B.  
 Designation: Research Scholar  
 Qualification: MSc, MPhil.  
 No. of papers published: Five, three communicated.

Name: Dr. Rani Joseph  
 Designation: Professor  
 Qualification: Ph.D  
 Teaching experience: Twenty Years  
 No. of papers published: Ninety