

Rubber bound phenolic antioxidant and its application in thermoplastic elastomer

*Pairote Klinpituksa¹⁾, Anyarat Kiarttisarekul^{2a)} and
Azizon Kaesaman^{2b)}

¹⁾Department of Science, ²⁾Department of Rubber Technology and Polymer Science,
Faculty of Science and Technology, Prince of Songkla University, Pattani, 94000
Thailand

¹⁾kpairote31@gmail.com

ABSTRACT

Natural rubber bound phenolic antioxidant, 2,6-di-*tert*-butyl-4-vinylphenol (2,6-DBVP), was prepared from natural rubber and 2,6-DBVP in both solution and melt state. The 2,6-DBVP had been synthesized from 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde and methyltriphenylphosphonium iodide (MePPh₃I) by Wittig reaction (0°C for 2 hrs, N₂ atmosphere). The conditions for preparation of natural rubber bound 2,6-DBVP (NR-DBVP) were optimized for both solution state (1 phr BPO and 8 phr 2,6-DBVP at 70°C for 2 hrs) and for melt state (1 phr BPO and 8 phr 2,6-DBVP at 70°C for 10 mins, with rotor speed of 60 rpm). A thermoplastic vulcanizate was obtained using a compatibilizer, polypropylene modified with phenolic resin (PhHRJ-PP), in a closed mixer (180°C for 3 mins, rotor speed 60 rpm). The antioxidant properties of vulcanized NR-DBVP, using phenolic as the vulcanization system, were similar to NR with the conventional antioxidant BHT. In addition, the antioxidant, water leaching property of the thermoplastic vulcanizate of NR-DBVP/PP were good in comparison to a NR blend with BHT; the morphologies of these thermoplastic vulcanizates were similar.

1. INTRODUCTION

Rubber products undergo degradation which is mainly caused by oxygen, ozone, heat and dynamics stress. Consequently, there is an effort to improve rubber stability during processing, when exposed to the vulcanization thermal conditions and during the lifetime when exposed to the external environment. The thermal oxidation of rubber is an autocatalytic, free-radical chain reaction where the oxidative products are carboxylic acid, aldehyde, ketone, epoxide, etc. The rate of the oxidation process can be reduced using antioxidant (Cibulková *et al.* 2005). The antioxidants are practically introduced in a rubber formulations for fabrication of rubber products. They usually loss during processing for example, through migration into surrounding environment, by leaching out into contact constituents, leads not only to premature failure of the rubber article but also to problems associated with health hazardous and toxicological effects

^{2a)} Graduate Student

^{2b)} Associate Professor

(Al-Malaika, 1977). These crucial problems may be overcome by attaching of these antioxidants moieties to the macromolecular natural rubber by covalent bond which so-called rubber-bound antioxidant. The important advantages of this approach relative to conventional antioxidants is resistant to extraction, non-volatile and not prone to migrate into other materials (Blackley, 1997). Several efforts have been devoted to investigating the associated problems of the performance and physical loss of antioxidants, for example the depolymerized natural rubber-bound diphenylamine antioxidant (Avirah and Joseph, 1994), natural rubber-bound *para*-phenylenediamine antioxidant (Avirah and Joseph, 1995), polyisobutylene-bound *para*-phenylene diamine (Sulekha *et al.* 1999), chlorinated polyisobutylene-bound alkylated phenolic antioxidant, (Sulekha and Joseph, 2003), natural rubber-graft-1,2-phenylenediamine (El-Wakil, 2007), natural rubber-*g*-N-(4-aminodiphenylether) acrylate (Al-Ghonamy and Barakat, 2010) natural rubber-bound 4-aminodiphenylamine antioxidant (Klinpituksa *et al.* 2011), and natural rubber-bound N-(4-hydroxyphenyl) maleimide antioxidant (Klinpituksa *et al.* 2012) as well as others elastomers such as the novel polymeric bound phenolic antioxidant using in natural rubber (Sulekha and Joseph, 2003), the oligomer-bound antioxidants in natural rubber/polybutadiene rubber and natural rubber/styrene-butadiene blends (Sulekha *et al.* 2004) and the polymeric antioxidant, hydroxyl terminated polybutadiene bound 2,2-thiobis-(4-methyl-6-*tert*-butylphenol) had less extraction than conventional sterically hindered phenol antioxidant 2,2-thiobis-(4-methyl-6-*tert*-butylphenol) and had remarkable effect on the thermo-oxidative ageing resistance for natural rubber vulcanizates of methanol extraction in the later step of ageing (Wang *et al.* 2012).

The aim of this work was to prepare rubber-bound antioxidant from the reaction of natural rubber with a phenolic antioxidant, 2,6-di-*tert*-butyl-4-vinylphenol (DBVP). The properties of thermoplastic vulcanizate NR-DBVP/PP blend using phenolic vulcanization system and polypropylene modified phenolic resin (PhHRJ-PP) as compatibilizer in comparison to NR blend with an identical conventional antioxidant 2,6-di-*tert*-butyl-4-methylphenol (BHT) was also investigated.

2. EXPERIMENTAL

2.1 Synthesis of 2,6-di-*tert*-butyl-4-vinylphenol (DBVP) antioxidant

A 250 mL round bottom flask fitted with a mechanical stirrer and water-cooled condenser immersing in oil bath was charged with 100 mL glacial acetic acid and 30.85 g ammonium acetate. 10.3 g (0.05 mole) 2,6-di-*tert*-butylphenol and 18.08 g (0.6 mole) formaldehyde were then introduced and refluxed at 107°C for 6 hours for obtaining an intermediate 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (DBHB). The 2,6-di-*tert*-butyl-4-vinylphenol (DBVP) was finally prepared from the reaction of 4.68 g (0.02 mole) DBHB obtained with 24.24 g (0.06 mole) methyltriphenylphosphonium iodide (obtaining by Wittig reaction of 13.1 g triphenylphosphine with 3.2 mL methyl iodide in 50 mL tetrahydrofuran) in the presence of 7.83 g (0.07 mole) potassium *tert*-butoxide in dried tetrahydrofuran. The reaction was proceed at 0°C under N₂ atmosphere for 1.30 hours. The DBVP with orange-yellow solid color was obtained by extracting with diethyl ether, separating and drying.

2.2 Preparation of natural rubber bound DBVP (NR-DBVP)

3 g of dried natural rubber was dissolved in 150 mL toluene in a 250 mL round bottom flask equipped with mechanical stirrer and nitrogen inlet immersing in water bath at 70°C. The 1 phr benzoyl peroxide, 2-10 phr DBVP were added into natural rubber solution and stirred in the period of 2 hrs. The NR-DBVP was obtained by precipitating the reaction mixture in acetone, washed several times with acetone and dried in oven at 50°C.

2.3 Effect of NR-DBVP/PP and NR+BHT/PP blends on thermoplastic vulcanizate properties

The thermoplastic vulcanizate was prepared from blending of NR-DBVP/PP and NR+BHT/PP by varying NR-DBVP/PP ratio of 50/50, 60/40 and 70/30 (in phr) using phenolic vulcanization system and 5% polypropylene modified phenolic resin (PhHRJ-PP) as compatibilizer (preparing as describe in previous work (Nakason *et al.* 2006) in a closed mixer (180°C for 3 mins, rotor speed 60 rpm). The butylated hydroxytoluene (BHT), an identical conventional antioxidant was also compared as an internal antioxidant for blending of natural rubber with polypropylene (NR/PP ratio of 60/40). Samples were moulded in an electrically heated hydraulic pressed at 180°C, pressure at 1,500 lbs/in² for 10 mins and cool for 20 mins and then punched out for tensile testing.

3. RESULTS AND DISCUSSION

3.1 Characterization of DBVP and NR-DBVP

The monomeric antioxidant DBVP obtained was confirmed by appearance of principal FTIR absorption peaks at 3600 cm⁻¹ and 1234 cm⁻¹ assigning to –OH and C–O stretching of phenol, at 1629 cm⁻¹ and 1362 cm⁻¹ assigning to –CH=CH₂ and –C(CH₃) stretching, respectively (Fig. 1).

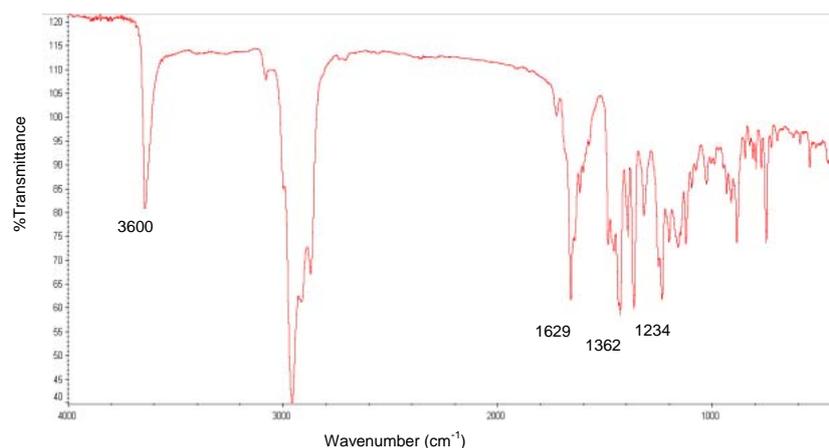


Fig. 1 FTIR spectrum of monomeric antioxidant 2,6-di-*tert*-butyl-4-vinylphenol (DBVP)

Moreover, The FTIR spectra of NR-DBVP at various DBVP contents compared with unbounded natural rubber (NR) was shown in Fig. 2. The appearance of principal absorption peaks was found at 1234 cm^{-1} and 835 cm^{-1} corresponding to C-O stretching and =CH out-plane bending of DBVP and natural rubber, respectively.

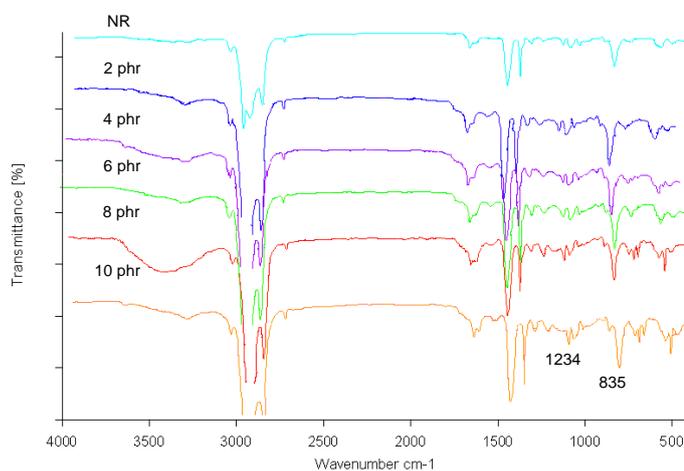
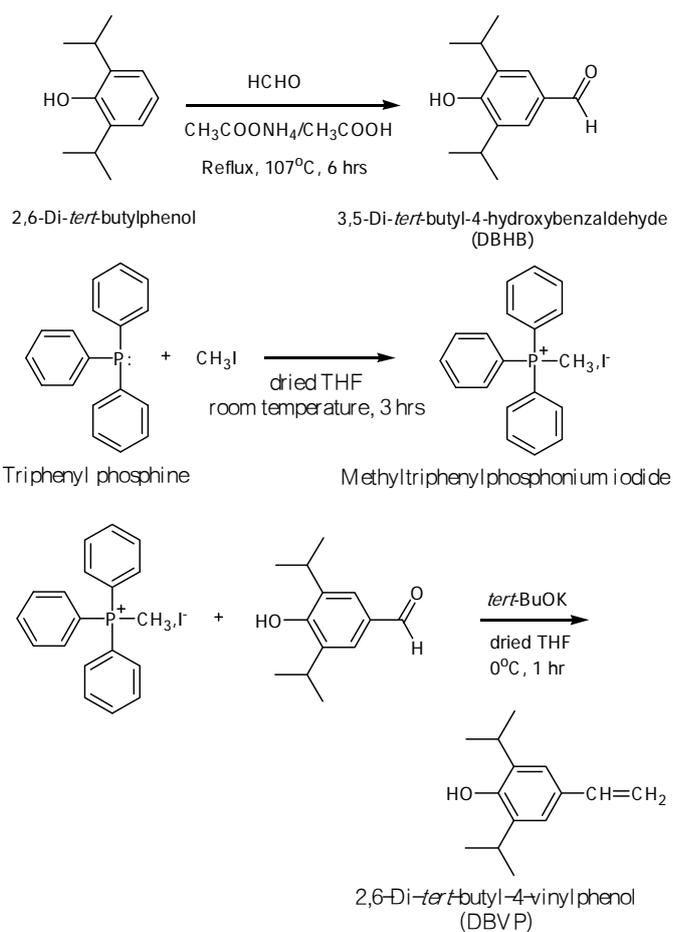
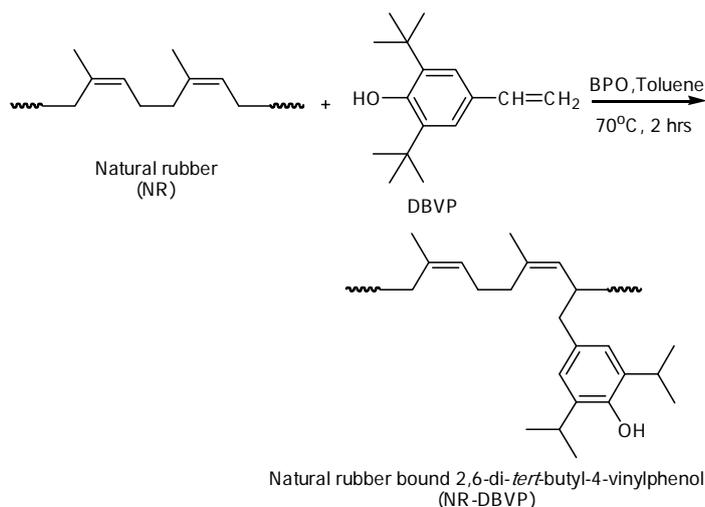


Fig. 2 FTIR spectra of NR-DBVP by varying 2-10 phr DBVP contents at 70°C for 2 hrs compared with original NR

The possible reaction for preparation of DBVP and NR-DBVP are illustrated in Scheme 1 and Scheme 2.



Scheme 1 Preparation of monomeric antioxidant 2,6-di-*tert*-4-vinylphenol (DBVP) from 2,6-di-*tert*-butylphenol *via* formylation and Wittig reactions



Scheme 2 A possible reaction for preparation of NR-DBVP in solution using 1 phr benzoyl peroxide (BPO) as initiator at 70°C for 2 hrs.

4.2 Properties of thermoplastic vulcanizate of NR-DBVP/PP and NR+BHT/PP blends

Fig. 3 and Fig. 4 show the tensile strength and elongation at break of thermoplastic vulcanizate before and after ageing for NR-DBVP/PP and NR+BHT/PP blends (60/40 ratio) using phenolic vulcanization system. Both thermoplastic vulcanizates show fairly good resistance to ageing. However, the tensile properties and ageing resistance of bound antioxidant was similar to that of NR blended with BHT.

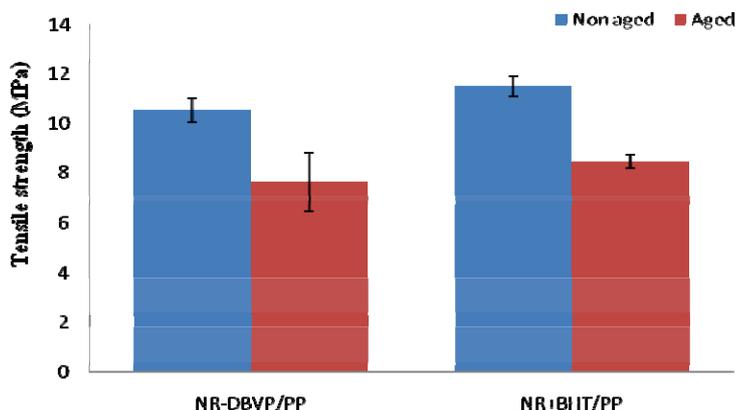


Fig. 3 Variation of tensile strength with NR-DBVP/PP (60/40) and NR+BHT/PP blends before and after ageing

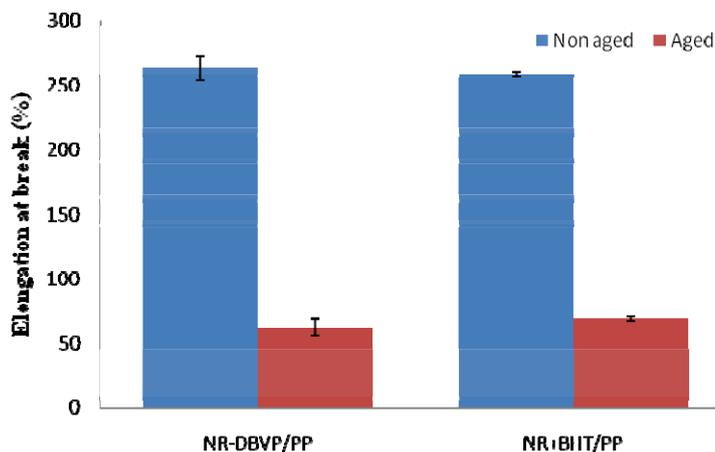


Fig. 4 Variation of elongation at break with NR-DBVP/PP (60/40) and NR+BHT/PP blends before and after ageing

Fig. 5 and Fig. 6 show the tensile strength and elongation at break of both thermoplastic vulcanizate blends for leaching testing by immersing the samples in distilled water for 7 days. The obtained samples were then aged (cell type ageing oven) at 100°C for 22 hours. The results showed that both tensile properties for the blends in term of water resistance was similar. This is may be due to the amount of DBVP bonded to NR was rather small compared to BHT used in NR blend.

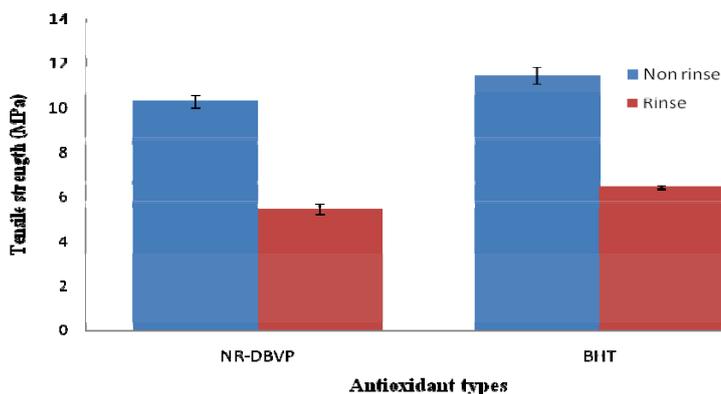


Fig. 5 Variation of tensile strength with NR-DBVP/PP (60/40) and NR+BHT/PP blends before and after leaching in water for 7 days

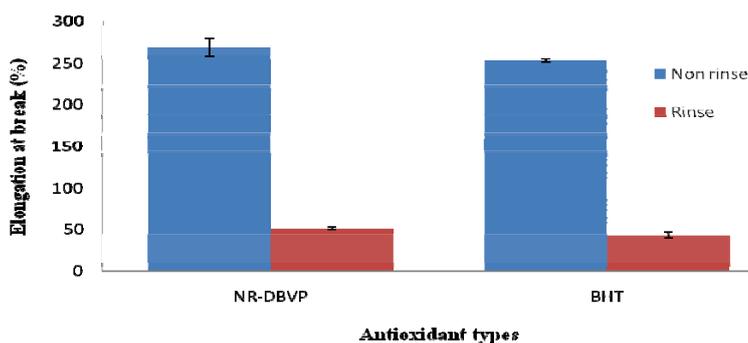


Fig. 6 Variation of elongation at break with NR-DBVP/PP (60/40) and NR+BHT/PP blends before and after leaching in water for 7 days

Moreover, The morphology of NR-DBVP/PP (Fig.7) and NR+BHT/PP (Fig. 8) blends was performed by using scanning electron microscope (SEM). It was showed that the dispersion of vulcanized rubber in polypropylene phase of both thermoplastic vulcanizate was similar fitting to similar tensile property mentioned above.

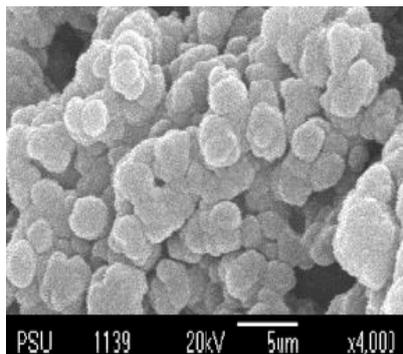


Fig. 7 Morphology of thermoplastic vulcanizate for NR-DBVP/PP blend (60/40)

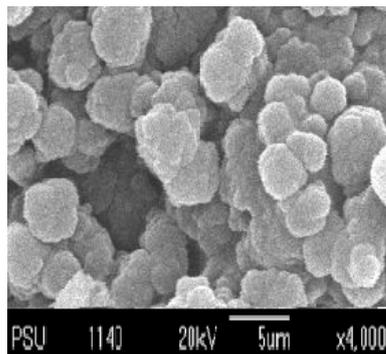


Fig. 8 Morphology of thermoplastic vulcanizate for NR+BHT/PP blend (60/40)

4. CONCLUSION

The 2,6-di-*tert*-butyl-4-vinylphenol was successfully synthesized in-house from 2,6-di-*tert*-butylphenol and bounded by chemical linkage to natural rubber molecule in solution and melt conditions. The natural rubber bound antioxidant 2,6-di-*tert*-butyl-4-vinylphenol (NR-DBVP) showed similar the ageing resistance, water leaching and morphology of NR-DBVP/PP thermoplastic vulcanizates compared to conventional antioxidant BHT.

ACKNOWLEDGEMENTS

Financial support by National Research Council of Thailand (NRCT) and Graduate School, Prince of Songkla University, Thailand is gratefully acknowledged.

REFERENCES

- Al-Ghonamy, A.I. and Barakat, M.A. (2010), "Study of the effect of grafted antioxidant on the acrylonitrile-butadiene copolymer properties", *Inter. J. Polym. Sci.*, 1-7.
- Al-Malaika, S. (1977), *Reactive Modification Modifiers for Polymer*, Chapman & Hall, U.S.A., pp. 266-267.
- Avirah, S.A. and Joseph, R. (1994), "Studies on natural rubber-bound diphenylamine antioxidant", *Polym. Degrad. Stab.*, **46**, 251-257.
- Avirah, S.A. and Joseph, R. (1995), "Studies on natural rubber bound para-phenylenediamine antioxidants in NBR", *J. Appl. Polym. Sci.*, **57**, 1511-1524.
- Blackley, D.C. (1997), *Polymer Latices: Science and Technology*, Springer England, p. 73
- Cibulková, Z. Šimon, P. Lehocký, P. and Balko, J. (2005), "Antioxidant activity of p-phenylenediamine studied by DSC", *Polym. Degrad. Stab.*, **87**, 479-486.
- El-Wakil, A.A. (2007), "Study on effect of natural rubber-graft-1,2-phenylenediamine as oxidation resistance for natural rubber", *Polym. Plast. Technol. Eng.*, **46**(6), 661-666.

- Klinpituksa, P. Hamad, A. Nakason, C. and Kaesaman, A. (2011), "Natural rubber bound 4-aminodiphenylamine antioxidant for rubber formulation improvement", *Sci. J. UBU.*, **2**, 66-71.
- Klinpituksa, P. Somkieowan, S. Waehamad, W. and Lopattananon, N. (2012), "Polymeric antioxidant based on natural rubber grafted with N-(4-hydroxyphenyl)maleimide", *Adv. Mat. Res.*, **488-489**, 211-215.
- Nakason, C. Saiwari, S. and Kaesaman, A. (2006), "Rheological properties of maleated natural rubber/polypropylene blends with phenolic modified polypropylene and polypropylene-*g*-maleic anhydride copetibilizers", *Polym. Test.*, **25**, 413-423.
- Sulekha, P.B. Joseph, R. and George, K.E. (1999), "Studies on polyisobutylene bound para-phenylenediamine antioxidant in natural rubber", *Polym. Degrad. Stab.*, **63**, 225-230.
- Sulekha, P.B., Joseph, R. (2003), "Preparation and characterization of novel polymeric bound antioxidants and its use in natural rubber", *J. Elast. Plast.*, **35**,85-97.
- Sulekha, P.B., Joseph, R.J. and Manjooran, K.B. (2004), "New oligomer-bound antioxidants in natural rubber/polybutadiene rubber and natural rubber/styrene-butadiene blends", *J. Appl. Polym. Sci.*, **93**, 437-443.
- Wang, Y.,Zeng, X., Li, H. And Guo, J. (2012), "Studies on extraction resistance of hydroxy terminated polybutadiene bound 2,2-thiobis-(4-methyl-6-*tert*-butylphenol) in NR vulcanizates", *Asian J. Chem.*, **24**(7), 3217-3222.