

## Rubber bound phenolic antioxidant and its application in thermoplastic elastomer

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**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 (MePPh<sub>3</sub>I) by Wittig reaction (0°C for 2 hrs, N<sub>2</sub> 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.

**Keywords:** natural rubber; phenolic antioxidant; 2, 6-di-*tert*-butyl-4-vinylphenol; compatibilizer; thermoplastic vulcanizate

### 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

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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 (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 2,6-di-*tert*-butyl-4-vinylphenol (DBVP) is a polymerizable antioxidant monomer. It behaves as a synthetic analogue of butylated hydroxyl toluene (BHT), primarily acting as a food additive that exploits its antioxidant property. The BHT is also documented as an antioxidant additive in such diverse product as rubber. The DBVP can be incorporated into polymer such as natural rubber by graft copolymerization resulted in natural rubber grafted DBVP. This product obtained can be used further as internal polymeric antioxidant in rubber product processing. Such graft copolymer have the advantage that the antioxidant can not be extracted and volatilized from the polymer molecule backbone.

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 proceeded at 0°C under N<sub>2</sub> 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 Characterization by FTIR spectroscopy

The FTIR spectrum of the NR, DBVP and NR-DBVP was performed using a FTIR spectrometer (Bruker, Switzerland Tensor 27 Model). The IR spectra of DBVP and NR-DBVP (NR) were recorded in solid state and solid film using a KBr pellet method at a spectral resolution of 4 cm<sup>-1</sup> at the rate of 32 scans/measurement.

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

Table 1 shows the thermoplastic vulcanizate prepared from blending of NR-DBVP/PP by varying NR-DBVP/PP ratio of 50/50, 60/40 and 70/30 (in phr) using phenolic vulcanization system and 5% phenolic resin modified polypropylene (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 (appropriate NR/PP ratio of 60/40). Samples were moulded in an electrically heated hydraulic pressed at 180°C, pressure at 1,500 lbs/in<sup>2</sup> for 10 mins and cool for 20 mins and then punched out for tensile testing.

Table 1 Preparation of thermoplastic vulcanizate with various ratios of PP and NR-DBVP in the presence of PhHRJ-PP as phenolic vulcanization system

Ingredients	Quantities (phr)		
	50/50	60/40	70/30
PP	50	40	30
PhHRJ-PP	5 (%wt. of PP)	5 (%wt. of PP)	5 (%wt. of PP)
NR-DBVP compound	50	60	70

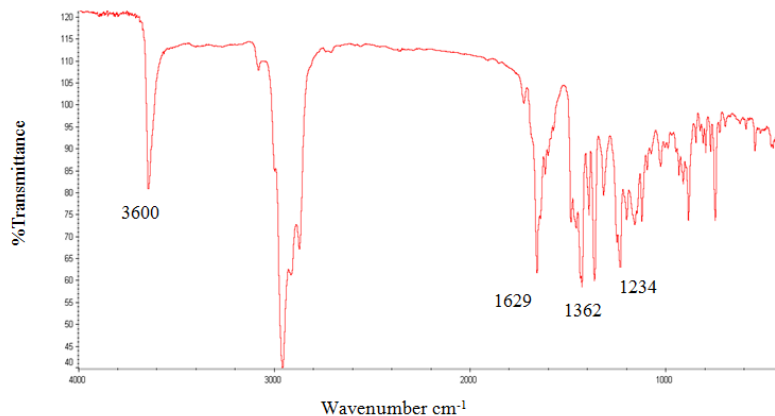


Fig. 1 FTIR spectrum of monomeric antioxidant 2,6-di-*tert*-butyl-4-vinylphenol (DBVP)

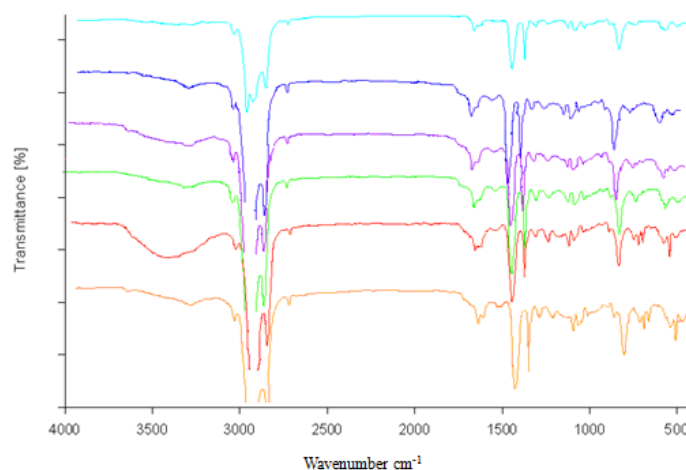


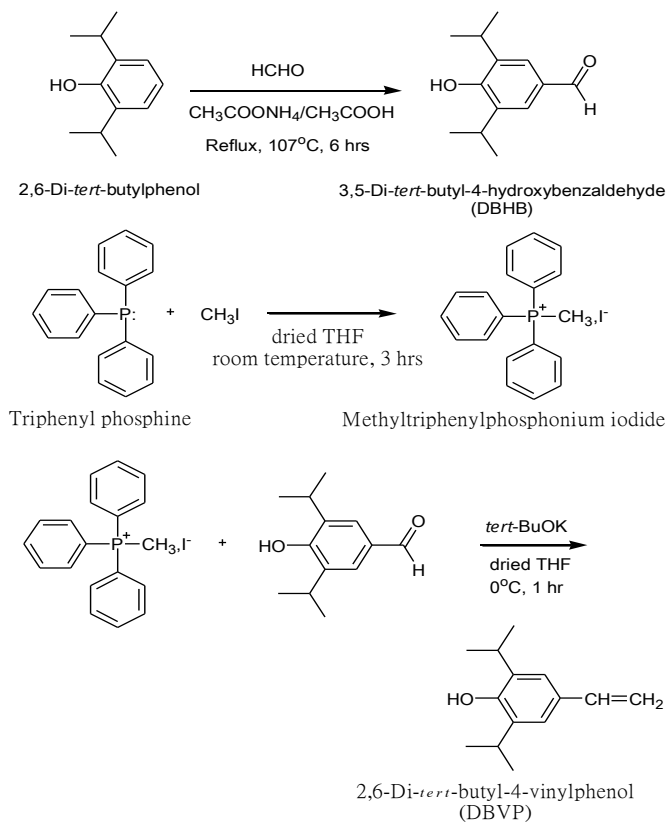
Fig. 2 FTIR spectra of NR-DBVP by varying 2-10 phr DBVP contents at 70°C for 2 hours compared with original NR

### 3. Results and discussion

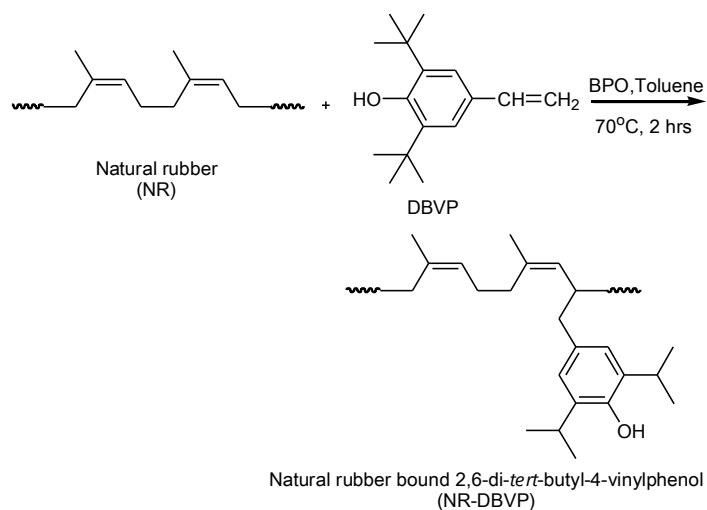
#### 3.1 Characterization of DBVP and NR-DBVP

The monomeric antioxidant DBVP obtained was confirmed by appearance of principal FTIR absorption peaks at 3600  $\text{cm}^{-1}$  and 1234  $\text{cm}^{-1}$  assigning to  $-\text{OH}$  and  $\text{C}-\text{O}$  stretching of phenol, at 1629  $\text{cm}^{-1}$  and 1362  $\text{cm}^{-1}$  assigning to  $-\text{CH}=\text{CH}_2$  and  $-\text{C}(\text{CH}_3)$  stretching, respectively (Fig. 1).

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  $\text{cm}^{-1}$  and 835  $\text{cm}^{-1}$  corresponding to  $\text{C}-\text{O}$  stretching and  $=\text{CH}$  out-plane bending



Scheme 1 Preparation of monomeric antioxidant 2,6-di-*tert*-butyl-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 hours

of DBVP and natural rubber, respectively. The grafting tendency of DBVP onto natural rubber molecule can be monitored using the absorption ratio of  $1234\text{ cm}^{-1}$  to  $835\text{ cm}^{-1}$ . It was shown that the grafting tendency increased with increase in DBVP amount from 2 phr and reached its maximum at 8 phr of DBVP. It can be concluded that the optimal amount for preparation of this copolymer for further study was 8 phr.

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

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

The NR-DBVP/PP 60/40 showed smallest difference in tensile strength after ageing as compared with NR-DBVP/PP 50/50 and 70/30. In case of elongation at break, NR-DBVP/PP 60/40 and 70/30 showed similar value in comparison with NR-DBVP/PP 50/50. We chose 60/40 blend ratio for further NR+BHT/PP blend. Fig. 3 and Fig. 4 show the tensile strength and

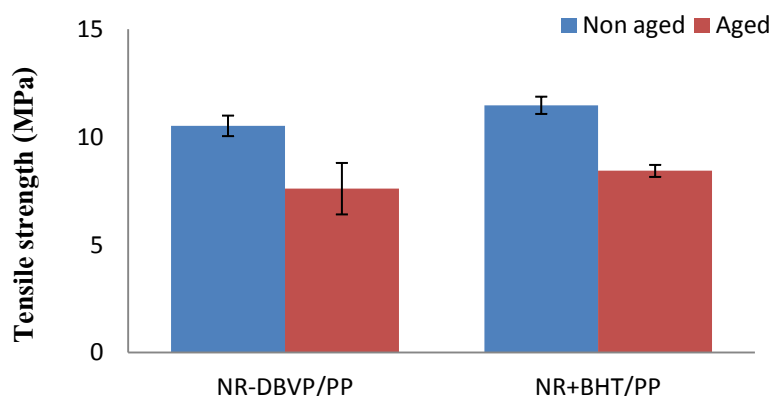


Fig. 3 Variation of tensile strength with NR-DBVP/PP (60/40) and NR+BHT/PP blends before and after ageing

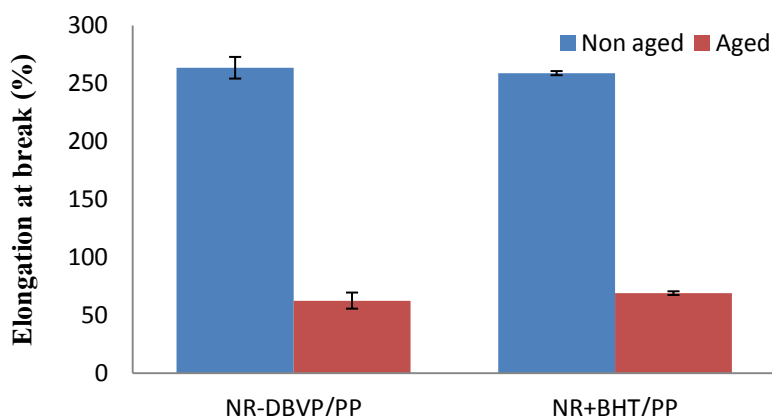


Fig. 4 Variation of elongation at break with NR-DBVP/PP (60/40) and NR+BHT/PP blends before and after ageing

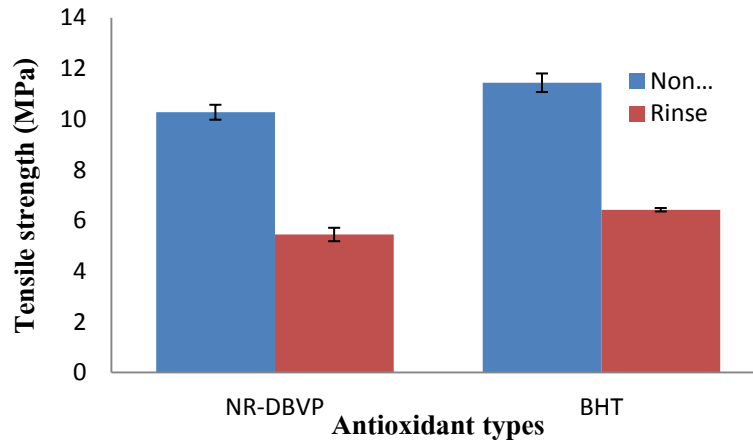


Fig. 5 Variation of tensile strength with NR-DBVP/PP (60/40) and NR+BHT/PP blends before and after ageing for water leaching 7 days

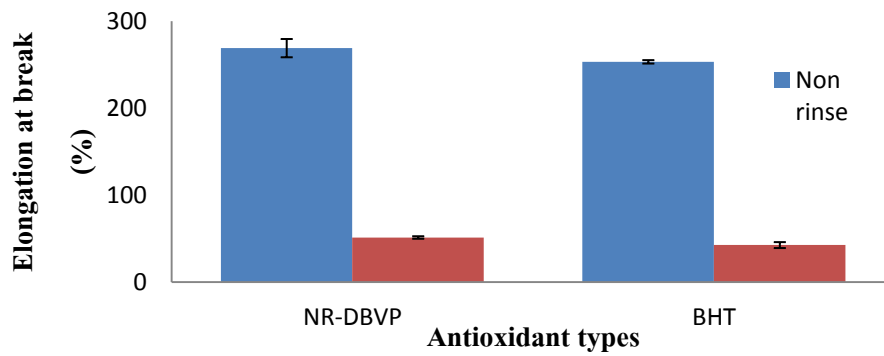
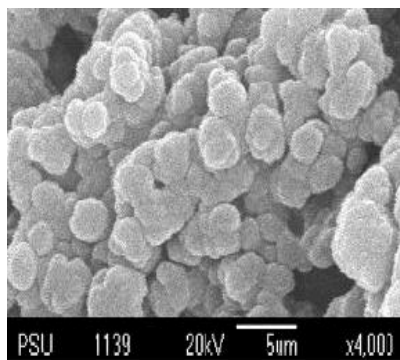
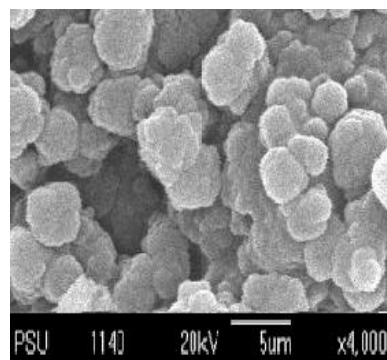


Fig. 6 Variation of elongation at break with NR-DBVP/PP (60/40) and NR+BHT/PP blends before and after ageing for water leaching 7 days



(a)



(b)

Fig. 7 Morphology of thermoplastic vulcanizate for NR-DBVP/PP (a) and NR+BHT/PP (b) blends (ratio of 60/40)

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. 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.

Moreover, The morphology of NR-DBVP/PP and NR+BHT/PP 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).

#### 4. Conclusions

The 2,6-di-*tert*-butyl-4-vinylphenol was successful 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.

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#### 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., 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. Lehocný, 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. and 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.