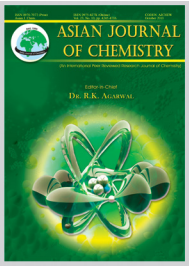
Asian Journal of Chemistry; Vol. 24, No. 7 (2012), 3217-3220

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Studies on Extraction Resistance of Hydroxyl Terminated Polybutadiene Bound 2,2-Thiobis(4-methyl-6-*tert*-butylphenol) in Natural Rubber Vulcanizates

YONGHONG WANG, XINGRONG ZENG*, HONGQIANG LI and JIANHUA GUO

College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, P.R. China

*Corresponding author: E-mail: wangyonghong666@163.com

(*Received*: 23 August 2011; *Accepted*: 24 February 2012) AJC-11105

A novel polymeric anioxidant, hydroxyl terminated polybutadiene bound 2,2-thiobis-(4-methyl-6-*tert*-butylphenol) (HTPB-IPDI-TPH) with excellent thermo-oxidative aging resistance, was synthesized from hydroxyl terminated polybutadiene (HTPB), 2,2-thiobis-(4-methyl-6-*tert*-butylphenol) (TPH) and isophorone diisocyanate (IPDI). The extraction resistance of HTPB-IPDI-TPH in natural rubber vulcanizates was studied by thermo-oxidative aging resistance of natural rubber vulcanizates after methanol and water extraction. The results showed that HTPB-IPDI-TPH 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 aging resistance for natural rubber vulcanizates of methanol extraction in the later stage of aging.

Key Words: Hydroxyl terminated polybutadiene, 2,2-Thiobis-(4-methyl-6-*tert*-butylphenol), Extraction resistance, Natural rubber.

INTRODUCTION

Polymers are subjected to heat, ozone, light and shearing stress, etc. during storage, processing and use. All of these factors cause oxidative aging of the polymer, which results in deterioration of physical and mechanical properties[1-3]. To avoid oxidative aging of polymer, antioxidants are added to polymers in a concentration not more than 1 % and capable of slowing down the rate of oxidation in the rubber chains[4,5]. There are several different types of antioxidants such as hindered phenols, hindered amines, organosulphurs and organophosphorous compounds, *etc*. and the hindered phenols and hindered amines are two most effective primary antioxidants among these anti-oxidants[6-9]. Although addition of antioxidant to polymer is effective way to protect polymer against oxidative aging, antioxidants are usually consumed by volatilization, extraction and evaporation from substrate due to lower molecular weight[10,11]. The loss of the antixidants is more serious in severe conditions such as the high temperature and high moisture. The best approach to minimize the physical loss would be to prepare polymer bound antioxidant[12,13]. Recently, some work has been carried out to study synthesis and application of polymer bound antioxidant[14-16]. However, little attention is given to a study on extraction resistance in polymer.

In this paper, hydroxyl terminated polybutadiene bound 2,2-thiobis-(4-methyl-6-*tert*-butylphenol) (HTPB-IPDI-TPH) with excellent thermo-oxidative aging resistance was synthesized and was employed as antioxidant in natural rubber vulcanizates. The effect of HTPB-IPDI-TPH on extraction resistance of natural rubber vulcanizates was evaluated by thermo-oxidative aging after methanol and water extraction.

EXPERIMENTAL

Hydroxyl terminated polybutadiene (HTPB) was supplied by Cray Valley Co., USA. Isophorone diisocyanate (IPDI) was obtained from BASF Co., Germany. 2,2-Thiobis-(4-methyl-6-*tert*-butylphenol) (TPH) was supplied by Zibo Debaiyi Industral and Trading Co. Ltd., China. Dibutyltin dilaurate (DBTDL) was purchased from GE Co., USA. Natural rubber, SCR5, was supplied by Hainan Natural Rubber Co. Ltd., China. ZnO, stearic acid, sulphur (S), *N*-cyclohexyl-2-benzothiazyl sulfenamide (CZ), dibenzothiazyl disulfide (DM) and nano-calcium carbonate were supplied by Guangzhou Longsun Technology Co. Ltd., China. Toluene, methanol and other chemicals (analytical pure reagents) were obtained from Guangzhou Chemical Co. Ltd., China. All chemicals were used without further purification.

Synthesis of hydroxyl terminated polybutadiene bound 2, 2-thiobis-(4-methyl-6-*tert*-butylphenol): HTPB-IPDI-TPH was synthesized *via* a two-step reaction in the presence of catalyst DBTDL. Firstly, HTPB (10 g) and toluene (4 g) were mixed in a four-neck boiling flask (100 mL) equipped with a mechanical stirrer, a reflux condenser, a thermometer and a N_2 inlet. Then a solution of IPDI (2.02 g) in toluene (5.00 g)

was added dropwise over 0.5 h. The mixture was stirred at 40 ºC for 270 min. Subsequently, a solution of TPH (9.79 g) in toluene (13.00 g) was added dropwise to the flask over 0.5 h and the reaction mixture was stirred at 75 ºC for 6 h. Finally, HTPB-IPDI-TPH was obtained after being dried at 45 ºC for 72 h under vacuum condition. HTPB-IPDI-TPH contains approximately 12.5 wt% of TPH structural units under this experimental conditions. The structure of HTPB-IPDI-TPH is presented in Fig. 1 and the detailed synthesis procedure was reported in literature[17].

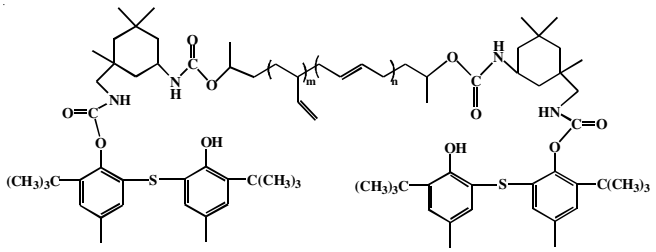


Fig. 1. Structure of HTPB-IPDI-TPH

Preparation of natural rubber vulcanizates sample: The formulation of natural rubber compound was as follows (phr): natural rubber 100; stearic acid 2; zinc oxide 5; nano-calcium carbonate 30; CZ 1.5; DM 0.5; sulfur 1.5; The contents of HTPB-IPDI-TPH and TPH were 8 and 1, respectively. All rubber compounds were prepared on an open two-roll mill (Shanghai First Rubber Machinery Factory, China) by a standard procedure. After mixing, the compounds were left overnight before vulcanization. The vulcanization of the natural rubber compounds was operated at 143 ºC for optimum curing time in a compression mold. The vulcanized rubber samples were kept at the temperature of 23 ± 2 ºC for 24 h before testing.

Extraction resistance of vulcanizates: Solvent extraction resistance of the samples was studied by keeping the vulcanizates in methanol for 48 h at room temperature. Water extraction resistance of the samples was studied by keeping the samples in water at 70 ºC for 24 h. Mechanical properties after methanol and water extraction were evaluated by aging the samples in a GT-7017-M aging oven (Gotech Testing Machine Inc. Taiwan) at 100 ºC for 24 h, 48 h, 72 h and 96 h. Tensile tests were measured using a Zwick/Roell Z010 (Ulm Germany) instrument according to the ASTM D 412 test method at a crosshead speed of 500 mm min^{-1}.

RESULTS AND DISCUSSION

Effect of HTPB-IPDI-TPH on solvent extraction resistance of natural rubber vulcanizates: Figs. 2 and 3 show the retained tensile strength and retained elongation at break of natural rubber vulcanizates at different time after extracting the samples in methanol at room temperature, respectively. As shown in Figs. 2 and 3, the decrease of the retained tensile strength and retained elongation at break follows a linear relationship over time. The decrease rate of the vulcanizates containing 8 phr HTPB-IPDI-TPH, which contains approximately 1phr of TPH structural unites is slower than that of without antioxidant and 1 phr TPH. HTPB-IPDI-TPH has remarkable effect on the thermo-oxidative aging resistance for natural rubber vulcanizates after aging 72 h, but TPH has no thermo-oxidative aging resistance for natural rubber vulcanizates. After aging 96 h, the retained tensile strength with HTPB-IPDI-TPH, TPH and without antioxidant reduce to 47.39, 39.83 and 36.72 %, respectively and the retained elongation at break reduce to 68.18, 66.17 and 66.17 %, respectively. This shows that the retention in mechanical properties by the vulcanizates containing HTPB-IPDI-TPH are superior to that of without antioxidant and TPH, which attributes to lower extractibility of the bound antioxidant by methanol.

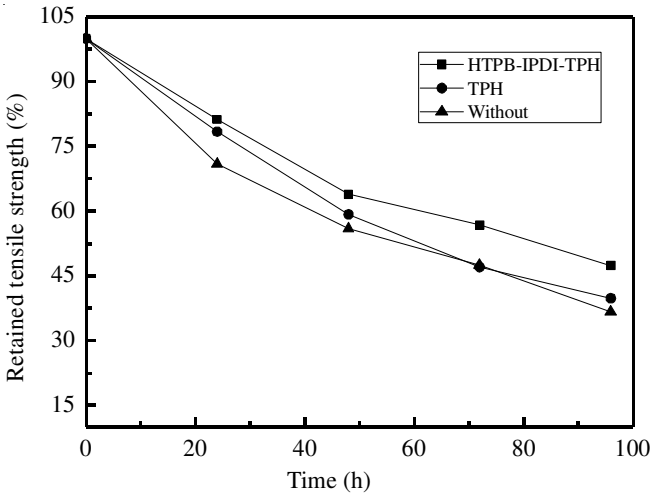


Fig. 2. Retained tensile strength of natural rubber vulcanizates at different time after methanol extraction

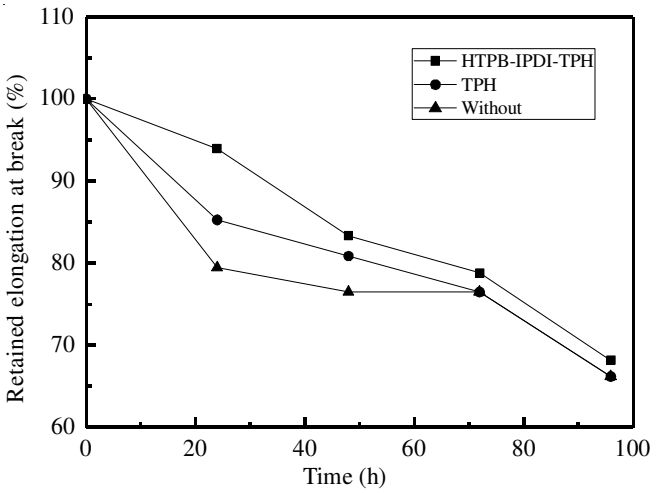


Fig. 3. Retained elongation at break of natural rubber vulcanizates at different time after methanol extraction

Fig. 4 shows the aging coefficient (K) of natural rubber vulcanizates at different time after extracting the sample in methanol at room temperature. The aging coefficient is calculated as follows:

$$K = \frac{f}{f_0} \quad (1)$$

$$f = \sigma_{break} \times \varepsilon_{break} \quad (2)$$

where, f_0 and f are the performance test values before and after aging, respectively. The eqns. (1) and (2) are empirical

equations in the aging coefficient calculation. As shown in Fig. 4, the aging coefficient increases with the increase of time up to 96 h. It consistents with the change of the retained value of tensile strength and elongation at break. This is because higher molecular weight of HTPB-IPDI-TPH leads to lower extraction in methanol, compared without antioxidant and with TPH.

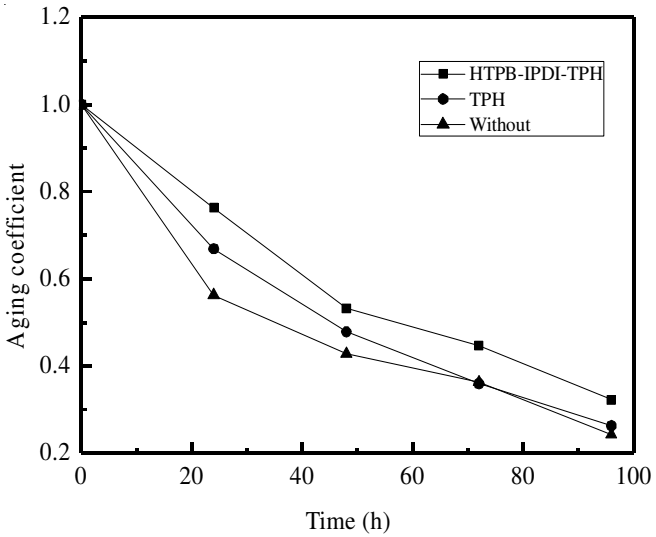


Fig. 4. Aging coefficient (K) of natural rubber vulcanizates at different time after methanol extraction

Effect of HTPB-IPDI-TPH on water extraction resistance of natural rubber vulcanizates: Figs. 5 and 6 show the retained tensile strength and retained elongation at break of natural rubber vulcanizates at different time after extracting the samples in water at 70 ºC. The retention in mechanical properties of natural rubber vulcanizates containing 8 phr HTPB-IPDI-TPH, which contains approximately 1 phr of TPH structural unites has the best thermo-oxidative aging resistance. Fig. 7 shows the aging coefficient (K) of natural rubber vulcanizates at different time after extracting the sample in water at 70 ºC. The aging coefficient increases with the increase of time up to 96 h. This is because many of conventional antioxidants are leached out during water extraction, whereas the antioxidants with higher molecular weight are not easy to migrate to surface.

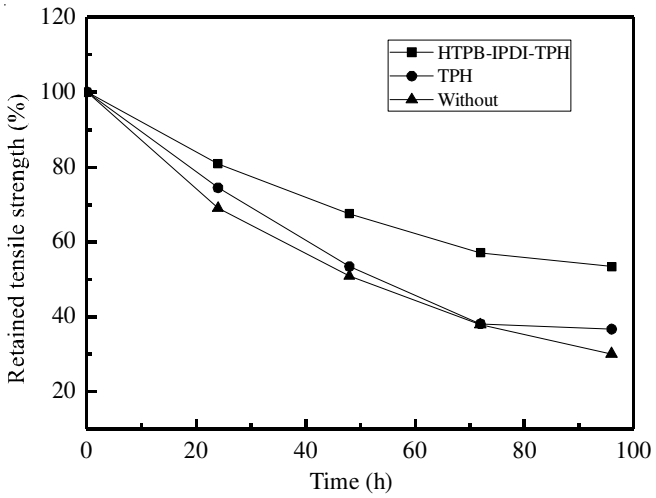


Fig. 5. Retained tensile strength of natural rubber vulcanizates at different time after water extraction

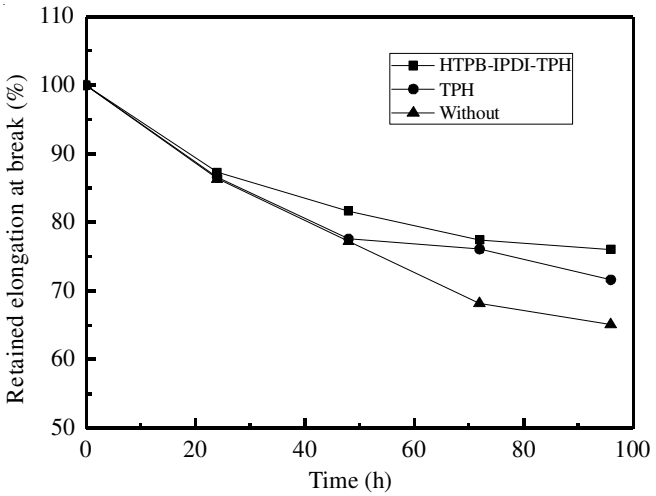


Fig. 6. Retained elongation at break of natural rubber vulcanizates at different time after water extraction

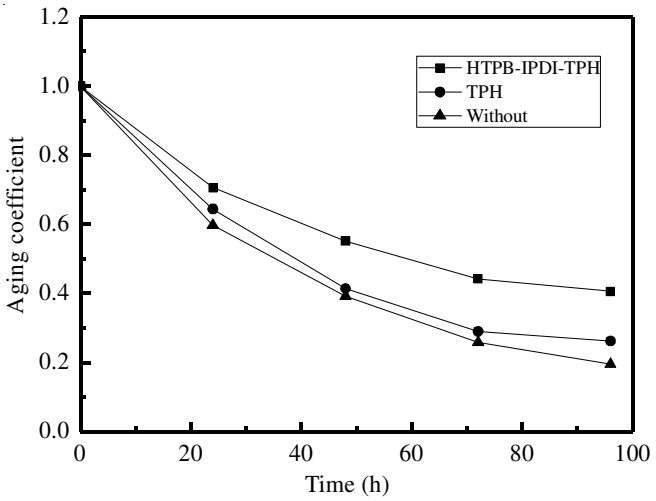


Fig. 7. Aging coeffient (K) of natural rubber vulcanizates at different time after water extraction

Conclusion

The results show that hydroxyl terminated polybutadiene bound 2,2-thiobis (4-methyl-6-*tert*-butylphenol) (HTPB-IPDI-TPH) has higher extraction resistance than conventional antioxidant TPH in water and methanol. It is worthwhile to note that HTPB-IPDI-TPH has remarkable effect on the thermo-oxidative aging resistance for natural rubber vulcanizates of methanol extraction after aging 72 h, whereas TPH lose the thermo-oxidative aging resistance which is extracted from natural rubber substrate by methanol.

REFERENCES

1. G.Y. Li and and J.L. Koening, *Rubber Chem. Technol.*, **78**, 355 (2005).
2. M. Narathichat, K. Sahakaro and C. Nakason, *J. Appl. Polym. Sci.*, **115**, 1720 (2010).
3. G.Y. Li and J.L. Koening, *Polym. Degrad. Stab.*, **81**, 377 (2003).
4. J.Q. Pan, P.W. Quek, N.C. Liu and W.W.Y. Lau, *J. Appl. Polym. Sci.*, **78**, 403 (2000).
5. F.M. Helaly, W.M. Darwich and M.A. Abd El-Ghaffar, *Polym. Degrad. Stab.*, **64**, 251 (1999).
6. K. Kurbanli and I. Mehmetoglu, *Asian J. Chem.*, **21**, 1910 (2009).
7. R. Aliyazicioglu, S. Kolayli, M. Kara, O. Yildiz, A.O. Sarikaya, S. Cengiz and F. Er, *Asian J. Chem.*, **21**, 2215 (2009).

8. D. Ahmed, M.A. Arshad, M.N. Asghar and M.I. Aujla, *Asian J. Chem.*, **22**, 4524 (2010).
9. H.N. Bhatti, W.U. Arifeen and A. Jabbar, *Asian J. Chem.*, **22**, 4629 (2010).
10. N. Haider and S. Karlsson, *J. Appl. Polym. Sci.*, **85**, 974 (2002).
11. M. Bertoldo and F. Ciardelli, *Polymer*, **45**, 8751 (2004).
12. J. Pospíšil, W.D. Habicher and S. Nešpurek, *Macromol. Symp.*, **164**, 389 (2001).
13. T. Nonaka, S. Maeda and T. Ogata, *J. Appl. Polym. Sci.*, **97**, 2097 (2005).
14. D.V. Arefjev, N.S. Domnina, E.A. Komarova and A.Y. Bilibin, *Eur. Polym. J.*, **35**, 279 (1999).
15. J.Q. Pan, N.C. Liu and W.W.Y. Lau, *Polym. Degrad. Stab.*, **62**, 165 (1998).
16. A. Ei-Wakil and M.A. Barakat, *J. Appl. Polym. Sci.*, **119**, 2461 (2011).
17. Y.H. Wang, X.R. Zeng, H.Q. Li and J.H. Guo, *J. Macromol. Sci. Phys.*, (2011) in press.