



Preparation of boric acid supported natural rubber as a reactive flame retardant and its properties



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ABSTRACT

Boric acid supported natural rubber (BSNR) was prepared from the reaction between hydroxyl group in diol functionalized natural rubber and boric acid. The optimum condition was assessed by the influences of different boric acid concentrations used in a term of [boric acid]/[diol unit] molar ratio and reaction time. The increase of them led to increasing the participation of boric acid into the rubber molecules, which was structural as boronic acid unit in BSNR. The determination of boron element quantity of BSNRs was found to increase with increasing mole% of boron containing rubber. Furthermore, the increase of mole% of boron content caused the increase of Mooney viscosity, glass transition temperature (T_g), thermal stability and improving flammability behaviors by the reduction of HRR_{max} , THR, EHC, MRL, CO_2 and burning rate as well as the increase of LOI values over original epoxidized natural rubber (ENR).

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1. Introduction

Natural rubber (NR) is one of most polymeric materials, which are organic chemicals containing mainly carbon and hydrogen atoms [1]. This nature allows NR to ignite easily and burn rapidly leading to a serious using for many applications (e.g., bedding, floor paneling and interior elements in building and transportation). Consequently, to approach the flame resistance of NR, three strategies to resist its combustion are applied: a chemical modification into the rubber molecule (i.e., reactive flame retardants), mixing flame retardant additives or fillers to the rubber (i.e., additive flame retardants) and polymer blending technology. From aforementioned techniques, the reactive flame retardants have some superiors over the other to improve efficiency of NR for inhibiting or suppressing the combustible process. The remarkable distinctions are the retaining effective of their flame retardant properties because these reactive components, which are structured into the molecule, are capable to keep the flame retardant in rubber

products for longer lifetime and resist to volatilization, leaching process and extraction with solvents [2–4]. As a result, it can maintain flame retardant performance and lesser potential for loss of chemical in the product to the atmosphere and environment. To achieve the reactive flame retardants, there are basically two chemical modification techniques performing via the reaction of functional groups and free radicals depending on the molecule characteristics of polymer and reagent holding flame retardant groups.

In recent years, an increase in attention of chemicals used as flame retardant has been paid to the regard of halogen-free flame retardant (HFFR) type since halogen-containing flame retardant (i.e., bromine and chlorine-based flame retardants) is considered as a source of generating toxicity, corrosion, and smoke [5,6]. Boron compounds are classified as a halogen-free flame retardant group similar to phosphorus and nitrogen flame retardants. The outstanding natures of boron compounds are low mammalian toxicity, ease of handling and treatment, low cost and minimal environmental impact [7]. Therefore, these properties lead to be interesting one and used widely to enhance flame resistance property for several materials such as wood, fiber and cellulose [8]. The fire-proof mechanism of boric acid is mainly a physical mechanism achieved by dehydrating and coating action or

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protective layer on the material surface at high temperature [3]. In most usages of the flame retardant based boron compounds, they have been applied as additives [9–11] or surface coating method [12] to improve flame retardant property of materials. Whereas, there are a few study in the reactive flame retardant in either polymeric rubbers or plastics with boron compounds, for instance, polystyrene [13], polyetherketones [14], soybean-oil-based copolymers [15], phenolic resin [16,17], phenol aldehyde resin [18] and novolax [19]. From these works, they showed that boron modified polymers have enhanced the flame retardant properties by increasing LOI values and giving greater yields of char residues in comparison to those of the unmodified one.

This paper described the achievement of the reactive flame retardant, which is a derivative of NR. It was carried out according to the simple chain reaction by introducing boric acid onto NR containing a precursor of reactive hydroxyl groups, which obtained from ring opening of oxirane ring in epoxidized natural rubber in order to provide boron supported NR (BSNR). The characterization of BSNR and evaluation of its properties such as thermal and flame retardant behaviors were investigated and compared to unmodified rubber.

2. Experimental

2.1. Materials

Epoxidized natural rubber containing 50 mol% of epoxide groups (ENR-50) was manufactured by Muang Mai Guthrie Co., Ltd. (Phuket, Thailand). Boric acid (Analytical reagent, AR) purchased from Ajax Finechem Pty Ltd., Australia. Tetrabutylammonium bromide (TBAB) (Analytical reagent, AR) was purchased from Acros organics, Germany. Formic acid (Analytical reagent, AR) and tetrahydrofuran (THF) (Analytical reagent, AR) were manufactured by Fisher Scientific, UK.

2.2. Preparation of diol functionalized natural rubber (DNR)

10 g of ENR-50 was cut into small pieces and put into a 500 mL three neck round bottom flask containing 300 mL THF. The rubber was dissolved completely by agitation with a magnetic stirrer overnight. Thereafter, the reaction flask was placed into a water bath set at 60 °C with vigorously agitation. A mixture of 5 mL formic acid and 15 mL distilled water was introduced gradually into the rubber solution. The hydrolysis reaction time of ENR-50 was prolonged for 48 h, and then it was precipitated into methanol and washed with water in several times until the pH value of washing water showed neutralization. Finally, the rubber was dried in a vacuum oven at 40 °C overnight, and kept it in a desiccator. The obtained products were analyzed by ¹H NMR and FT-IR.

DNR: ¹H NMR (CDCl₃, δ ppm): 5.14 (s, 1H), 2.70 (t, 1H), 3.85 (t, 1H), 3.76 (t, 1H), 3.36 (s, 2H), 2.2–2.4 (m, 2H). FT-IR: ν(OH) = 3470 cm⁻¹, ν(C=O) = 1732 cm⁻¹, ν(C=C) = 835 cm⁻¹ and ν(C–O–C) = 870 cm⁻¹.

The amount of diol functionalized units from ring opening of epoxide groups was determined in term of diol unit content (%), which was defined as the mole percent of diol functional groups in ENR-50 by using the following relationship in Eq. (1). The results showed that the partial conversion of epoxide ringopening can be converted into hydroxyl group of the diol structure of 44.8 mol% and also paltry furan rings [20].

$$\% \text{ Diol units} = \frac{\frac{I(3.36)}{2}}{\frac{I(3.36)}{2} + I(2.73) + I(3.85) + I(5.17)} \times 100 \quad (1)$$

$I(3.36)$, $I(3.85)$, $I(2.73)$ and $I(5.17)$ being the intergrations of the signals characteristic of protons of the hydroxyl groups in diol units (OH–C–CH–OH), furan rings (>CH–O–), oxirane rings in epoxidized units (–CH₂–CH–O–) and carbon-carbon double bonds in 1,4-polyisoprene units (–CH=C<), respectively.

2.3. Preparation of boric acid supported natural rubber (BSNR)

A solution of 5 g DNR in 150 mL THF and 0.29 g of TBAB as a catalyst were placed in 500 mL three neck round bottom flask equipped with a mechanical stirrer and a condenser. Boric acid solutions at different concentrations of 0.8, 1.6 and 2.4% w/v corresponding to molar ratios of [boric acid]/[diol unit] = 0.5, 1.0 and 1.5, respectively, in 20:80 deionized water/THF were introduced into the reactor with vigorous stirring, and then heated at 65 °C for appropriated time. After reaction, the modified rubber was coagulated in methanol, and reprecipitated into THF two times. The product was then dried at 40 °C under vacuum until constant weight obtained.

2.3.1. Determination of the addition level of boric acid onto natural rubber

The addition level of boric acid onto rubber (T_b) was determined by using the following relationship in Eq. (2):

$$T_b(\%) = \frac{\frac{I(3.49)}{2}}{\frac{I(3.49)}{2} + I(3.36) + I(3.85) + I(2.73) + I(5.17)} \times 100 \quad (2)$$

$I(3.49)$, $I(3.36)$, $I(3.85)$, $I(2.73)$ and $I(5.17)$ being the intergrations of the signals characteristic of protons of hydroxyl group in boric acid supported rubber chain (–B–(OH)₂), hydroxyl group in diol units (OH–C–CH–OH), furan rings (>CH–O–), oxirane rings in epoxidized units (–CH₂–CH–O–) and carbon-carbon double bonds in 1,4-polyisoprene units (–CH=C<), respectively.

2.4. Characterization of BSNR and instrumentation

¹H NMR spectra were recorded using a Varian unity inova 500 NMR spectrometer (Varian, Inc., USA) at 400 MHz. Samples were analyzed by dissolving it in deuterated chloroform-D (CDCl₃), and the spectra were plotted in the chemical shift range of 0–12 ppm.

FTIR spectra of BSNRs and ENR-50 were recorded on Bruker equinox 55 (Bruker, Germany). The sample was prepared in a liquid form, which was coated on NaCl plate, and analyzed at a resolution of 4 cm⁻¹ in the spectral range of 4000–400 cm⁻¹.

Elemental analysis was used to quantify boron element in BSNRs. It was performed on Perkin Elmer optima 4300 DV ICP optical emission spectrometer (Perkin-Elmer Inc., USA).

Mooney viscosities of ENR-50 and BSNRs with different boron contents were determined using Mooney viscometer, model Visc tech (Tech Pro Inc., USA). The typical viscosity was reported as ML (1 + 4, 100 °C). A large size serrated disk rotating in the rubber was fixed rotor speed of 2 rpm. Test temperature was preheated at 100 °C for 1 min and testing for 4 min according to ASTM D1646-04.

Differential scanning calorimeter (DSC), model DSC Q100 (TA Instruments, New Castle, USA) equipped with a sample chamber and a cryogenic unit. The temperature range used in this work was –90 °C to 100 °C with the sample weight of approximately 10 mg. The analysis was performed in nitrogen atmosphere. This

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