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Silica-reinforced tire tread compounds compatibilized by using epoxidized natural rubber

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ABSTRACT

Silica-reinforced natural rubber (NR) tire tread compounds with epoxidized natural rubber (ENR) as a compatibilizer are investigated. The ENRs consisting of 10, 38 and 51 mole% epoxide are used in a range of 2.5–15.0 parts per hundred parts of rubber (phr). The addition of ENRs, especially ENR-38 and ENR-51, decreases the Mooney viscosity, Payne effect, flocculation rate constant and filler networking factor, which implies an improvement of silica dispersion in the compounds. Chemically bound rubber contents and interaction parameters of the compounds also increase with higher epoxide-contents of the ENRs, indicating more interactions and/or reaction between the epoxide-groups of the ENR and silanol groups on the silica surface. Tensile strength of the vulcanizates is improved with increasing mole% epoxide, and the optimum value is observed at 7.5 phr of ENR-51. The overall results show that silica-reinforced NR can be substantially improved by adding ENR as a compatibilizer, when compared to a compound without ENR, but somewhat less than with using a silane coupling agent.

1. Introduction

Silica and carbon black are reinforcing fillers that are widely used in rubber. Because of their different surface characteristics, both fillers can form agglomerates but the cause of such agglomeration is not the same, leading to a difference in dispersion ability. The filler–filler interaction of carbon black is mainly generated through relatively weak Van der Waal forces, which can be readily broken during mixing. In contrast, silica agglomeration is due to hydrogen bonding in addition to Van der Waal forces and other physical interactions, leading to a much stronger filler–filler interaction [1]. Silica has a high polarity and a hydrophilic surface due to silanol groups on its surface. Consequently, silica is incompatible with non-polar rubbers such as natural rubber (NR), styrene–butadiene rubber (SBR) and butadiene rubber (BR), but better compatible with polar rubbers such as polychloroprene rubber (CR) [2] and acrylonitrile butadiene rubber (NBR) [3]. Use of silica in non-polar rubbers without any compatibilizers results in poor dispersion and consequently inferior properties as a result of these strong filler–filler interactions [4]. In addition, polar functional groups on the silica surface may form hydrogen bonds with other polar components in rubber compounds such as accelerators. So, commonly basic accelerators are adsorbed on the acidic surface of silica which negatively affects cure properties [5]. Successful use of silica for rubber reinforcement therefore requires commonly silane coupling agents to enhance silica–rubber interaction and silica dispersion as well as to prevent accelerator adsorption on the silica surface.

Some polar rubbers bearing functional groups which can interact with the silica surface have been studied as

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alternatives to silane coupling agents to enhance the interaction in silica-filled compounds [6–9]. A non polar rubber such as polybutadiene was chemically modified to have epoxy groups on the main chain and the interaction of such epoxidized rubber with silica was consequently improved, as observed by a decrease of the Payne effect and a change of damping behavior in the glass transition region. The improvement of silica–rubber interaction was also demonstrated by a higher bound rubber content and better silica dispersion in the matrix [10]. Incorporation of silica into an epoxidized SBR showed a strong interaction between the silica and the epoxidized functional groups due to the highly polar character of the epoxidized rubber [11].

Epoxidized natural rubber (ENR) is also higher polar than virgin NR due to the epoxide groups in its structure. The chemical and physical properties of ENR change according to the epoxide contents, such as heat and swelling resistances [12]. By its polar functional groups, ENR interacts with hydroxyl groups on the silica surfaces [13]. It has been reported already that the mechanical properties of silica-filled ENR without coupling agent are higher than those of silica-filled virgin NR [14–15]. This was claimed to be due to improved interaction between ENR and the silica surface *via* hydrogen bonds. ENR as the rubber component in tire compounds has been reported to improve the silica dispersion leading to improved processability, better storage stability and tire performance [13,16–18]. ENR was used as a compatibilizer in silica-filled NR/NBR blends to enhance the mechanical properties [19]. In case of silica-filled NBR vulcanizates, the use of ENR as a compatibilizer improved tensile strength, tear strength and abrasion loss [20], as well as lowered the loss tangent [21], as the ENR acts as a coupling agent because it can self-crosslink with NBR and also link with silica at the vulcanization temperature [20–21]. Furthermore, ENR was used as a compatibilizer in organoclay-filled NR composites wherein cure characteristics, tensile and dynamic mechanical properties were improved [22–23]. Even though ENR has been used to compatibilize between silica and various rubber matrices, the use of ENR as compatbilizer for silica-filled virgin NR has not yet been extensively studied.

In the present study, ENRs with different mole% of epoxide groups are used as compatibilizers in a range of 2.5–15 phr for virgin NR/silica compounds. The effects of ENR contents and mole% of epoxide are investigated. The epoxide groups are supposed to interact with the silanol groups of the silica and so to improve silica–rubber compatibilization, while the unmodified parts of the ENR structure is compatible with the NR matrix.

2. Experimental

2.1. Materials

The rubbers used were Natural Rubber (Ribbed Smoked Sheet (RSS) #3), locally produced in Thailand, and Epoxidized Natural Rubbers with 10, 38 and 51 mole% of epoxide, denoted as ENR-10, ENR-38 and ENR-51, respectively, that were in-house prepared as detailed in 2.2. The compounding ingredients were highly dispersible silica (Zeosil 1165MP, Rhodia, France), bis-(3-triethoxysilyl-propyl)tetrasulfide (TESPT) (Evonik, Germany), treated distillate aromatic extract oil (TDAE oil) (Hansen & Rosenthal, Germany), N-cyclohexyl-2-benzothiazole sulfenamide (CBS), diphenyl guanidine (DPG) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) (all from Flexys, Belgium), ZnO, stearic acid and sulfur (all from Sigma-Aldrich Chemie, Germany).

2.2. Preparation of epoxidized natural rubber

High ammonia (HA) latex with 60 wt% of dry rubber content was used to prepare ENR via an *in situ* performic epoxidation reaction [13]. The reaction between C=C of the NR molecule and performic acid, arising from a reaction between formic acid and hydrogen peroxide, was carried out in a continuously stirred reactor at a temperature of 40 °C, where alkylphenol ethoxylate non-ionic surfactant (Teric N30, Huntsman Corp., Australia) was used as a stabilizer [24–25]. The ENRs with 10, 38, and 51 mole% of epoxide groups were obtained when the reaction times were varied at 2, 10 and 12 h, respectively. The ENR latex was subsequently coagulated with methanol. The ENR coagulum was sheeted, washed thoroughly with water and dried in an oven at 50 °C for approximately 4 days. The reaction time of epoxidation was set according to the required level of epoxide groups in the ENR product. The ^{1}H NMR spectroscopic technique was used to analyze the molecular structure of the ENR and the mole% of epoxide groups was calculated using Eq. (1):

$$mole\%\ of\ epoxide\ groups = \frac{b}{a+b} \times 100 \tag{1}$$

where a is the integrated peak area of the olefinic proton of NR at 5.1 ppm and b is the integrated peak area of H attached to the oxirane rings of ENR at 2.7 ppm. The NMR spectra of NR and ENR are shown in Fig. 1.

2.3. Compound preparation

Rubber compounds were prepared using the formulations as shown in Table 1. The ENR content was varied in a range of 2.5–15.0 phr. Amounts of TESPT and DPG were calculated relating to the silica CTAB specific surface area, as suggested by Guy et al. [26]. Mixing was carried out using an internal mixer (Brabender Plasticorder 350s) with an initial mixer temperature setting of 110 °C, rotor speed of 60 rpm, according to the mixing procedure as shown in Table 2. The silica-filled NR compounds with and without TESPT and without ENR were prepared and treated as reference.

2.4. Mooney viscosity, Payne effect and flocculation rate constant of unvulcanized compounds

Mooney viscosity (ML(1+4), 100 °C) was tested using a Mooney viscometer (MV 2000VS, Alpha Technologies) according to ASTM D1646. The Payne effect or filler–filler interaction of the uncured silica-filled compounds were studied by using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) at 100 °C, frequency 0.5 Hz and