Effect of zinc oxide induced metal-ligand crosslink on the mechanical properties in the ethylene acrylic elastomer (AEM)

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ABSTRACT

The metal-ligand complex (sacrificial bonds) that exist in the mussels, bone and silk can dissipate energy and reinforce mechanical strength. Inspired by the high performance of metal-ligand complex, we introduced a kind of metal-ligand crosslink into the rubber network. In this work, ethylene acrylic elastomer (AEM) was filled with ZnO, and was cured by the amine cure system. The metal-ligand crosslink structure was verified by FTIR and XPS, and the tensile strength and dynamic properties were examined with a universal testing machine and rubber process analyzer (RPA). The results showed that coordination crosslink formed in the AEM matrix and exhibited outstanding tensile strength and unexpected dynamic properties due to the coordination bonds between Zn^{2+} and amine group.

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1. Introduction

The mussels, bone, and silk have miraculous modulus and strength due to the special structure caused metal-ligand complex [1–3]. The metal-ligand complex can sustain a force when undergoing a deformation, however, it will be cracked and the structure is survived, by which the mechanical energy is dissipated [4,5].

Inspired by the high performance of mussels, bone, and silk, metal-ligand complex has been successfully incorporated into polymer matrix to achieve biomimetic strength and toughness. Mozhdehi et al. [6] fabricated self-healing thermoplastic elastomers with a network of dynamic zinc-imidazole (metal-ligand) interactions. The mechanical and dynamic properties can be controlled by varying the number of molecular parameters and the ratio of zinc-imidazole. Zhang et al. [7] prepared metal-oxygen coordination crosslinks using ferric ion and epoxidized natural rubber (ENR), which involved abundant oxygen, reinforcing the strength and toughness. Tang et al. [8] reinforced elastomers via coordination bonds between pyridine groups in butadiene–styrene–vinylpyridine rubber (VPR) and metal ions (Zn^{2+}), and the tensile strength increased by 6.9 times.

Rubber materials used in the applications such as tire and shock absorbers need to mix with filler to further improve the modulus and strength [9]. In this work, the metal-ligand complex (sacrificial bonds) inspired us to explore a facile method, which reinforces the mechanical properties of rubber. Ethylene/acrylic elastomer (AEM) was introduced commercially in 1975 by the DuPont Company under the trademark VAMAC [10]. Because AEM is a type of saturated elastomer, hexamethylene diamine carbamate (amine) can be used as curing agent instead of sulfur. We introduced zinc oxide (ZnO) into AEM and reacted with the amine group via a facile way to achieve the metal-ligand complex. The mechanical properties and dynamic properties were characterized to prove that the metal-ligand complex allows energy to dissipate under external load and improve the mechanical properties of rubber.

2. Experimental

Zinc oxide (99.7%, Guangzhou Aichuan Chemical Co., Ltd., China), stearic acid, polyoxyethylene octadecyl ether phosphate (VANFRE VAM), accelerator DOTG, and hexamethylene diamine carbamate (Diak No. 1) were successively compounded with AEM (Type G, Dupont, USA) on a two-roll mill within 15 min. The formulation was as follows (unit: phr): AEM 100; stearic acid 1.5; VANFRE VAM 1.5; DOTG 4; Diak No. 1 1.5; and ZnO varied (0, 2, 4, 6, and 8). Finally, the rubber compounds were placed into

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hydraulic hot press at 175 °C for 30 min. All additives were commercial products.

Fourier Transform Infrared Spectroscopy (FTIR) was acquired on a Perkin-Elmer Spectrum GX FT-IR spectrometer at room temperature. XPS analysis was carried out on a Kratos Axis Ultra DLD equipped with an Al Ka radiation source (1486.6 eV). Tensile strength and elongation at break were measured using a universal testing machine, DUT-500CM (Daekyung Engineering, Korea). Crosslink density of vulcanizates was measured using the equilibrium swelling method [11]. The dynamic properties were examined with rubber process analyzer (RPA2000, Alpha Technologies, USA). The strain sweep test was carried out from 1° to 40° at 60 °C and a frequency of 1 Hz.

3. Results and discussion

Scheme 1 shows the metal-ligand complex structure of ZnO filled AEM using the amine cure system. The hexamethylene diamine carbamate (Diak No. 1, blue) linked with the molecules of AEM (red), while it coordinated with the Zn^{2+} ion due to the lone pairs of the N atom in the amine group.

Fig. 1 shows the FTIR results of hexamethylene diamine carbamate (Diak No. 1), AEM, and ZnO filled AEM. The Diak No. 1 and rubber samples were measured by KBr pellets and attenuated total reflectance (ATR), respectively. For Diak No. 1, the absorption peaks at 3338 cm^{-1}, 2925 cm^{-1}, 2854 cm^{-1}, 1636 cm^{-1}, and 1556 cm^{-1} correspond to the N—H stretching vibration, C—H symmetric and anti-symmetric stretching vibration, C=O stretching vibration, and C—N bending vibration, respectively. In the AEM matrix, the absorption peaks at 2925 cm^{-1}, 2854 cm^{-1}, 1727 cm^{-1}, 1432 cm^{-1}, and 1155 cm^{-1} correspond to C—H symmetric stretching vibration, C—H anti-symmetric stretching vibration, C=O stretching vibration, C—H$_3$ stretching vibration, and —O—CH$_3$ stretching vibration, respectively.

Compared to the pure AEM, the new absorption peak at 1609 cm^{-1} was observed in the sample of ZnO filled AEM, confirming the coordination between Zn^{2+} and amine group [8]. In addition, a new absorption peak was observed at 1539 cm^{-1}, indicating the presence of zinc stearate in the sample of ZnO filled AEM [12]. The characteristic absorption area at 400–550 cm^{-1} was caused by the Zn-O tetrahedral bond [13].

The X-ray photoelectron spectroscopy (XPS) results provided additional verification for Zn^{2+}-N coordination (Fig. 2). For pure AEM, the dominant peaks with binding energy of 399.05 eV was observed in the N 1s spectra, corresponding to free amine. When ZnO was added, an additional peak with a binding energy of 397.05 eV was observed, suggesting that the nitrogen atoms of amine groups coordinated with Zn^{2+} (N–Zn) [14,15].

Fig. 3-a shows the mechanical properties of AEM filled with different amounts of ZnO. The tensile strength and elongation at
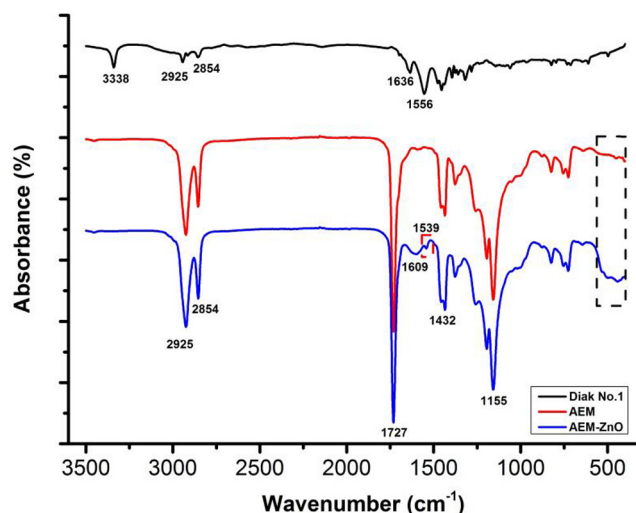

Fig. 1. FTIR spectra of pure AEM and AEM/ZnO matrix.

break of pure AEM was 1.92 MPa and 276%, respectively. The tensile strength and elongation at break increased to 9.29 MPa and 606%, respectively, when 4 phr of ZnO filled into AEM matrix. The tensile strength and elongation at break did not increase further with ZnO content greater than 4 phr. In addition, the crosslink density of AEM (Fig. 3-b) also increased with increasing amounts of ZnO until it reached ZnO load greater than 4 phr, at which point the crosslink density plateaued. According to the theory that the metal-ligand complex could counteracting the formation of cracks during bone fracture [3], we consider that coordinated bond could prevent the spread of microcracks in the AEM during tensile testing.

Fig. 4-a shows the relationship between storage modulus (G') and strain. Interesting results of cross points at critical strain were observed between the pure AEM and the samples of ZnO filled AEM during the strain sweep. Compared to pure AEM, the G' decreased with increasing ZnO content, even though the crosslink density increased with increasing the content of ZnO, when the strain was lower than the critical strain. However, an inverse order of G' corresponded to the content of ZnO in the matrix, when the strain was higher than the critical strain. Furthermore, the G' did not change further with ZnO content greater than 4 phr at before and after of critical strain. Fig. 4-b shows the variation of tan δ with strain for the different ZnO contents. The results of tan δ is contrary to the results of G', and cross points still exist in Fig. 4-b. The tan δ of AEM filled ZnO is higher than pure AEM when the strains lower than the critical strain, while it becomes lower than that of pure AEM, when the strain is higher than the critical strain.
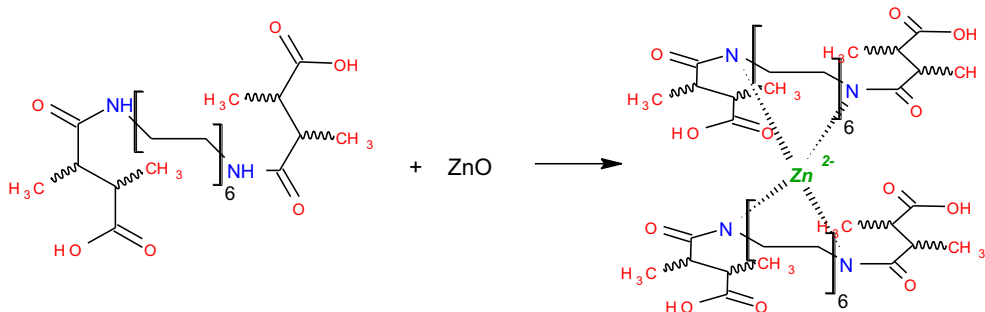
Scheme 1. Schematic Illustration for the coordination structure of Zn^{2+} with Diak No. 1 in the AEM matrix. (Red, AEM molecules; Blue, vulcanization agent of Diak No.1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)