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A novel whitening test method of a sulfur-cured EPDM composite filled with carbon black in calcium cation solution

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ABSTRACT

A simple and efficient whitening test method of a carbon black-filled sulfur-cured EPDM composite by formation of calcium stearate was established using Ca^{2+} solution and convenient analytical techniques. The sample was aged in 0.1 M $CaCl_2$ solution at 30–90 °C for 1 and 3 days. ATR-FTIR spectra of the aged sample surfaces displayed unique calcium stearate peaks. Level of the whitening of a rubber article can be determined by analysis of the cross section of the aged sample using an image analyzer and by analysis of calcium stearate on the aged sample surface using an ATR-FTIR.

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1. Introduction

A rubber article is composed of rubber(s), filler(s), curatives, antidegradants, and processing aids [1–4]. Sulfur-cured rubber composites such as natural rubber (NR), butadiene rubber (BR), and styrene-btadiene rubber (SBR) generally contain organic materials such as antidegradants of (*N*-phenyl-*N*′-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD) and 2,2,4-trimethyl-1,2-dihydroquinoline (TMDQ)), wax, fatty acid, cure activator and accelerator, sulfur, oil, and processing aids [5,6]. Organic materials in a rubber article can migrate to the surface. Some additives such as antidegradants and wax can accumulate on the sample surface. A carbon black-reinforced rubber article is black, but its surface changes to white when wax accumulates on the surface [7,8]. The phenomenon when a rubber article surface changes to white by aging is called “whitening”.

Recently, another reason for the whitening phenomenon has been found to be formation and accumulation of metal salts of stearic acids on an EPDM article’s surface [9–11]. Appearance of a black EPDM article changed to white by thermal aging under humid condition or in tap water. Some EPDM articles are exposed to humid condition [12–16]. When an EPDM article is used for long time under high humidity and high temperature, one can see the whitening. For example, black EPDM car components made by a sulfur cure system change to white by weathering. Calcium stearate can be formed by the reaction of stearic acid and calcium cation [9–11]. Stearic acid exists in a sulfur-cured rubber article since it is used as a cure activator for a sulfur cure system. And calcium cation comes from humid air or natural water. Content of stearic acid is determined by considering cure characteristics and physical properties of a rubber compound. Chukwu et al. [17] investigated physical properties of rubber vulcanizates according to the stearic acid content of 0.0–6.0 phr, and reported that the tensile strength and modulus increased with stearic acid level up to 4.0 phr.

A color change of a rubber article by aging impairs its appearance so the commercial valuation falls. In our previous work [10], an EPDM article used for a car component was aged in 80 °C humid air for 30 days and 80 °C tap water for 7 days, and the whitening was observed. An EPDM article cured by resole was also aged in 80 °C humid air and tap water, however the whitening was not happened. EPDM samples cured by zinc stearate instead of stearic acid/zinc oxide were aged in 90 °C tap water for 7 days, however the whitening was not observed [11]. For rubber vulcanizates cured by a sulfur cure system, the whitening by formation of calcium stearate is unavoidable phenomenon as far as it is exposed to humid condition. Thus, a way to avoid the whitening by formation of calcium stearate is use of zinc stearate instead of zinc oxide and stearic acid [11].

When a rubber article is aged outdoor under ambient temperature and low Ca^{2+} concentration, it is required too long time (even for several years) to observe whitening. Thus,

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development of accelerating aging system is needed. In general, accelerated aging tests are carried out to estimate the useful life of rubber articles by increasing temperature, light intensity, and so on [18–20]. One of common methods correlating accelerated test results with aging under service conditions is the Arrhenius methodology [19,20,5]. In the present work, a simple and efficient whitening test method for rubber articles was developed using $CaCl_2$ solution, and white material formed was characterized by image analysis and attenuated total reflectance-Fourier transform infrared spectrometer (ATR-FTIR). An image analyzer and an ATR-FTIR are convenient analytical methods as well as relatively inexpensive equipments. An ethylene-propylene-diene terpolymer (ethylene-propylene-diene rubber, EPDM) composite was employed as the model rubber article because an EPDM compound does not contain antidegradants including wax to cause whitening by accumulating on the sample surface. Since EPDM has saturated C–C backbones, it possesses excellent resistance to oxygen, ozone, heat, and UV light. The sulfur-cured EPDM composite was aged in $CaCl_2$ solution. Surface morphologies of the sample before and after thermal aging were observed using an image analyzer. The aged sample was cut and the thickness of the whitening materials accumulated on the surface was also measured using an image analyzer. Chemical strucures of the whitening materials were identified using an ATR-FTIR. And the level of the whitening was also estimated using an ATR-FTIR.

2. Experimental

The EPDM compound was made of EPDM [150.0 phr KEP 960 (ethylene and propylene contents are 70 and 24 wt%) of Kumho Polychem Co., Korea], carbon black (20.0 phr N550), cure activators (4.0 phr stearic acid and 2.0 phr ZnO), and curatives (1.8 phr *N-tert*-butyl-2-benzothiazole sulfenamide (TBBS) and 0.6 phr sulfur). Mixing was performed in a Kneader mixer and on a two-roll mill. The master batch (MB) compound was prepared by mixing EPDM, carbon black, stearic acid, and zinc oxide in a Kneader mixer for 12 min and milling for 5 min. The final mixing (FM) compound was prepared by mixing the curatives with the MB compound for 5 min using a two-roll mill. The EPDM vulcanizate was prepared by curing at 160 °C for 20 min in a compression mold (140 mm × 140 mm × 2 mm). Calcium cation solution was prepared by dissolving $CaCl_2$ in distilled water and its concentration was 0.1 M.

The EPDM sample (about 20 mm × 20 mm) was immersed in 200 mL 0.1 M $CaCl_2$ solution and sealed, and aged at 30–90 °C for 1 and 3 days in a convection oven. The sample surface was observed with an image analyzer (EG Tech video microscope IT Plus 4.0, Korea). The aged sample was cut to observe the cross section. The thickness of the materials accumulated on the aged sample surface was also measured using an image analyzer. Materials accumulated on the sample surface were analyzed with an ATR-FTIR (FTIR Spectrum 100 of PerkinElmer Inc.) equipped with zinc selenide (ZnSe) crystal.

3. Results and discussion

Fig. 1 shows photographs of the samples aged at 30–90 °C for 3 days. The sample aged at 30 °C did not change and retained the black color. However, the samples aged at 50, 70, and 90 °C changed to white. Degree of the whitening became more and more severe as the aging temperature increased. When the sample was aged in air or in distilled water at high temperatures of 50–90 °C for several days, the whitening did not occur. Although not whitening, Zhao et al. studied the appearance change of EPDM aged by fluorescent UV/condensation weathering and reported that the EPDM surface became redder, yellower and lighter by aging [21]. Sundararajan et al. analyzed chalking (whitening) materials of EPDM 345 kV transmission line suspension insulators used in a coastal line for five years using X-ray photoelectron spectroscopy (XPS) and reported that they were silicates [22]. In order to observe the aged sample surface in detail, the sample surface was magnified. Fig. 2 shows the magnified images (300×) of the aged sample surfaces. For the sample aged at 30 °C, the magnified image showed white materials on the sample surface although one

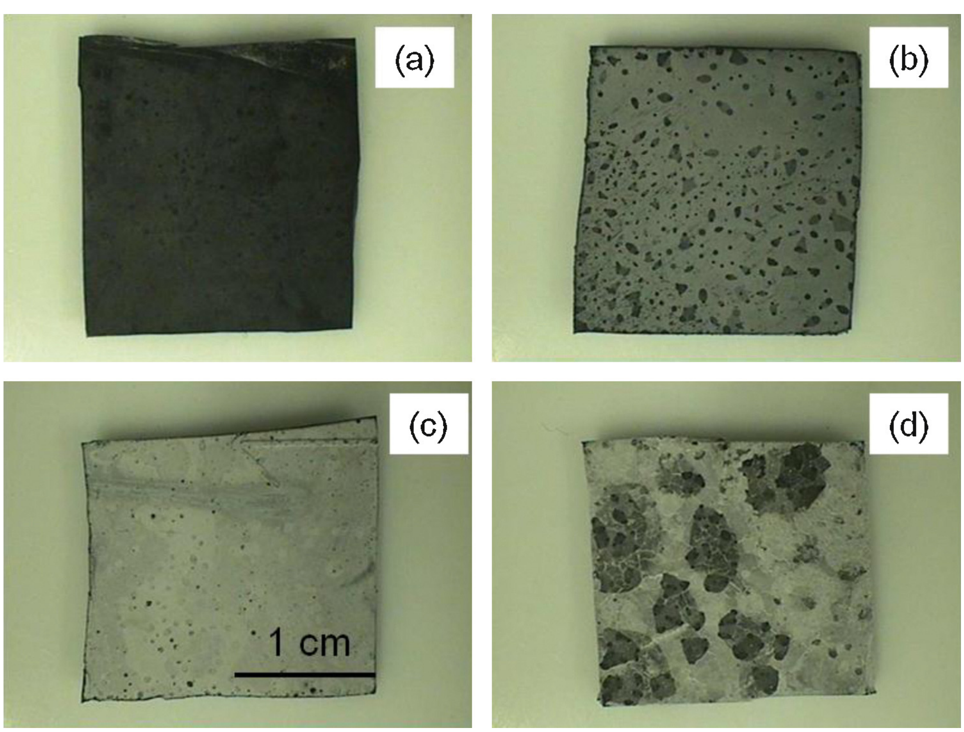

Fig. 1. Photographs of the EPDM samples aged at 30 (a), 50 (b), 70 (c), and 90 °C (d) for 3 days.

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