Analysis of Whitening Phenomenon of EPDM Article by Humid Aging

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ABSTRACT: An ethylene–propylene–diene terpolymer (EPDM) article used for a car component was aged in 80°C humid air (60% relative humidity) for 30 days and in 80°C tap water for 7 days. The aged sample surfaces were changed to white. The aged sample surfaces were analyzed using GC/MS, image analyzer, SEM, EDX, and ATR-FTIR. Calcium stearate was found on the aged sample surface. To confirm the whitening phenomenon, three sulfur-cured EPDM composites with different reinforcing systems (talc/carbon black, calcium carbonate/carbon black, and clay/carbon black) and one resole-cured EPDM composite were prepared and aged in 90°C tap water for 7 days. The sulfur-cured EPDM composites contained stearic acid, whereas the resole-cured EPDM composite did not contain stearic acid. Whitening occurred in the sulfur-cured EPDM samples irrespective of the filler systems but the aged resole-cured EPDM composite surface was not changed. The whitening was due to the formation of calcium stearate as a result of reaction between calcium cation and stearic acid. The calcium cation came from humid air and tap water, while the stearic acid came from the sulfur-cured EPDM samples. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 2451–2457, 2012

Key words: whitening; EPDM; calcium cation; fatty acid; calcium stearate

INTRODUCTION

Ethylene–propylene–diene terpolymer (EPDM) consisting of ethylene, propylene, and unsaturated diene is one of the popular synthetic rubbers. In general, 5-ethylidene-2-norbornene (ENB), dicyclopentadiene (DCPD), and 1,4-hexadiene (HD) are used as the diene. Since EPDM has saturated backbone, it possesses excellent resistance to oxygen, ozone, heat, and UV light, whereas the nonpolar structure endows EPDM with excellent electrical resistivity and resistance to polar solvents. Hence, it has broad application to electrical insulation, building, construction, and automotive sectors. Due to its importance, lots of studies about EPDM in various fields have been performed.[1–10]

Aging properties of elastomeric materials to determine their service lifetime are very important. Principal parameters that cause aging are heat, oxygen, ozone (and radicals), and UV light.[9–18] Changes of physical properties, crosslink densities, and appearance of rubber articles by thermal aging have been examined.[9–18] Change of the appearance by aging impairs feeling of the articles so the commercial evaluation falls. Sundararajan et al.[12] reported that EPDM insulators showed severe chalking and discoloration on the side facing the sun. Zhao et al.[14] reported that an EPDM surface exposed to artificial weathering environment became redder, yellower, and lighter.

In general, appearance contamination of a rubber article is occurred by the blooming of some organic materials remaining in the sample. Here, the terminology "blooming" refers to a phenomenon when organic additives ooze out from the inside to the surface of rubber articles. Sulfur-cured rubber composites such as natural rubber (NR), butadiene rubber (BR), and styrene-butadiene 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 accelerator, sulfur, oil, and processing aids.[19–22] The organic materials can migrate to the sample surface and be accumulated on the surface. A carbon black-reinforced rubber article is black, but its surface is changed to white when wax migrates and is accumulated on the surface.[23,24] Since common rubbers of NR, BR, and SBR have unsaturated C = C backbone, antidegradants, and wax should be used for the manufacturing of rubber articles to prevent oxidation of the backbone. Excess antidegradants and wax cause blooming and bad appearance. However, since EPDM has saturated backbone and excellent weathering property, lots of antidegradants

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TABLE I
Formulation of Model EPDM Compounds (phr)

Compound No.	1 (Talc)	2 ($CaCO_3$)	3 (Clay)	4 (Resole)
EPDM	150.0	150.0	150.0	150.0
N550	20.0	20.0	20.0	10.0
Talc	10.0	0.0	0.0	0.0
$CaCO_3$	0.0	10.0	0.0	0.0
Clay	0.0	0.0	40.0	30.0
ZnO	2.0	2.0	2.0	2.0
Stearic acid	4.0	4.0	4.0	0.0
TBBS	1.8	1.8	1.8	0.0
Sulfur	0.6	0.6	0.6	0.0
Resole	0.0	0.0	0.0	10.0

and wax are not needed. Hence, the blooming of antidegradants and wax hardly occur in EPDM articles. Nevertheless, whitening or blooming occurs in EPDM articles. Here, "whitening" means a phenomenon when a rubber article surface is changed to white by aging.

Sugiura et al.[25] reported blooming of stearic acid and zinc stearate. By artificial weathering, chalking and discoloration appeared on the EPDM article surface.[12,14] To prevent blooming of organic additives in EPDM articles, their usage has been remarkably reduced recently. However, after use of an EPDM article for long time under high humidity and high temperature, one can see whitening of the surface. EPDM articles are also used in water.[26–30] In this work, the causes of whitening of an EPDM article aged under high humidity and high temperature were examined. An EPDM automobile component was used as the EPDM specimen since one of the most popular application areas of EPDM is automobile sectors. The EPDM sample was aged in tap water and in humid air. The sample surface was observed using an image analyzer and scanning electron microscope (SEM). The bloomed materials were analyzed with gas chromatography/mass spectrometry (GC/MS) and energy dispersive X-ray microanalysis (EDX). To clarify the cause of whitening phenomenon, model EPDM composites with sulfur or resole cure systems were prepared, aged, and analyzed.

EXPERIMENTAL

An EPDM article used for a car component was used as the EPDM specimen. The sample was aged in 80°C humid air (60% relative humidity) for 30 days and in 80°C tap water for 7 days. Four model EPDM compounds were prepared. Of them, three compounds had sulfur cure system and one had resole one. The model EPDM compounds with sulfur cure system were made of EPDM (KEP 960 of Kumho Polychem Co., Korea), carbon black (N550), inorganic filler (talc, calcium carbonate, or clay), cure activators (stearic acid and ZnO), and curatives (TBBS and sulfur). The model EPDM compound with resole cure system was made of EPDM (KEP 960 of Kumho Polychem Co., Korea), carbon black (N550), clay, ZnO, and resole (Hitanol 2500 of Hitachi Chemical Co., Japan). The formulations are shown in Table I. Mixing was performed in a Kneader mixer and a two-roll mill. The vulcanizates with sulfur cure system were prepared by curing at 160°C for 20 min in a compression mold (140 mm × 140 mm × 2 mm), while the vulcanizates with resole cure system was prepared by curing at 190°C for 15 min. The model EPDM samples were aged in 90°C tap water for 7 days.

The sample surfaces were observed with an image analyzer (EG Tech video microscope IT Plus 4.0, Korea) and field emission scanning electron microscope (FE-SEM, Hitachi *S*-4700, Japan). Bloomed materials on the aged sample surface were collected with THF-soaked absorbent cotton and were filtered to analyze with GC/MS. Organic materials remaining in the aged samples were also extracted with THF and analyzed with GC/MS. GC/MS chromatograms and mass spectra of the collected and extracted materials were acquired with 6890*N*/5987 GC/MS of Agilent Co. DB-5MS capillary column (length 30 m) was used. Injector temperature of the GC was 250°C. The GC oven temperature program was as follows: (1) the initial temperature was 70°C and kept for 3 min, (2) the temperature was increased from 70 to 300°C at a rate of 10°C/min. The sample surfaces were also analyzed with attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) (PerkinElmer spcetrum100). Zinc selenide (ZnSe) crystal was used. Elemental analysis on the sample surface was performed with EDX.

RESULTS AND DISCUSSION

Analysis of the EPDM article used for a car component

The EPDM article was black since it was reinforced with carbon black. It was burned to collect the ash which was analyzed with EDX. The ash content was about 17 wt %. Major components of the ash were oxygen (O), sulfur (S), calcium (Ca), and zinc (Zn). The atomic percents of sulfur, calcium, and zinc were 3.5%, 16.5%, and 3.5%, respectively. The observed calcium indicates that the EPDM article was reinforced with calcium carbonate ($CaCO_3$) as well as carbon black. Figure 1 shows the SEM image of the ash of the EPDM article. The morphology of the ash is similar to $CaCO_3$ powder. The observation of sulfur and zinc means that the EPDM article had a sulfur cure system. Sulfur came from the curatives such as cure accelerators and sulfur, while zinc

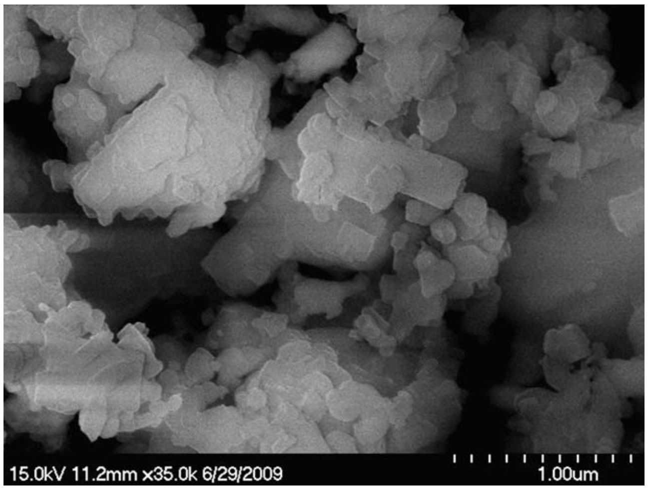

Figure 1 SEM image of the ash extracted from the EPDM article.

came from zinc oxide. Zinc oxide was used as a cure activator along with fatty acids such as stearic acid in sulfur-cured rubber composites.

Analysis of the aged EPDM article used for a car component

The sample surfaces aged in humid air and tap water changed from black to white. To observe the aged sample surfaces in detail, the surfaces were analyzed with an image analyzer. Figure 2 shows the magnified images of the sample surfaces before and after aging. The unaged sample was black, whereas the aged sample surfaces had lots of white spots and stains. Whitening appeared via thermal aging in humid air or in tap water. When the sample was thermally aged in dry air, its surface did not change to white. The bloomed materials were collected by scrubbing the surface with THF-soaked absorbent cotton to analyze with GC/MS. Organic materials remaining in the EPDM article were also extracted with THF and analyzed with GC/MS to compare with the accumulated materials. The two GC/MS TIC chromatograms showed broad oil peaks, but a specific difference between the two chromatograms was not observed. Most of the materials collected from the bloomed sample surface were not dissolved in organic solvents such as THF, acetone, *n*-hexane, acetonitrile, methanol, isopropanol, dichloromethane, toluene, and so on. Elemental analysis of the aged sample surfaces and the inner part was performed with EDX. Along with carbon (C), several elements such as oxygen (O), sulfur (S), calcium (Ca), and zinc (Zn) were observed in both the aged sample surface and the inner part. There was no specific difference in the EDX results of the aged sample surface and the inner part.

To examine the reason for the whitening phenomenon, the aged sample surface was analyzed using ATR-FTIR. Figure 3 displays the ATR-FTIR spectra of the unaged and aged samples. The ATR-FTIR spectra of the samples aged in humid air and in tap water were nearly the same, while those of the unaged and aged samples were very different. Several new peaks at 1392, 1539, 1574, and 3450 cm^{-1} appeared after the aging. If the whitening phenomenon is caused by general blooming of the organic

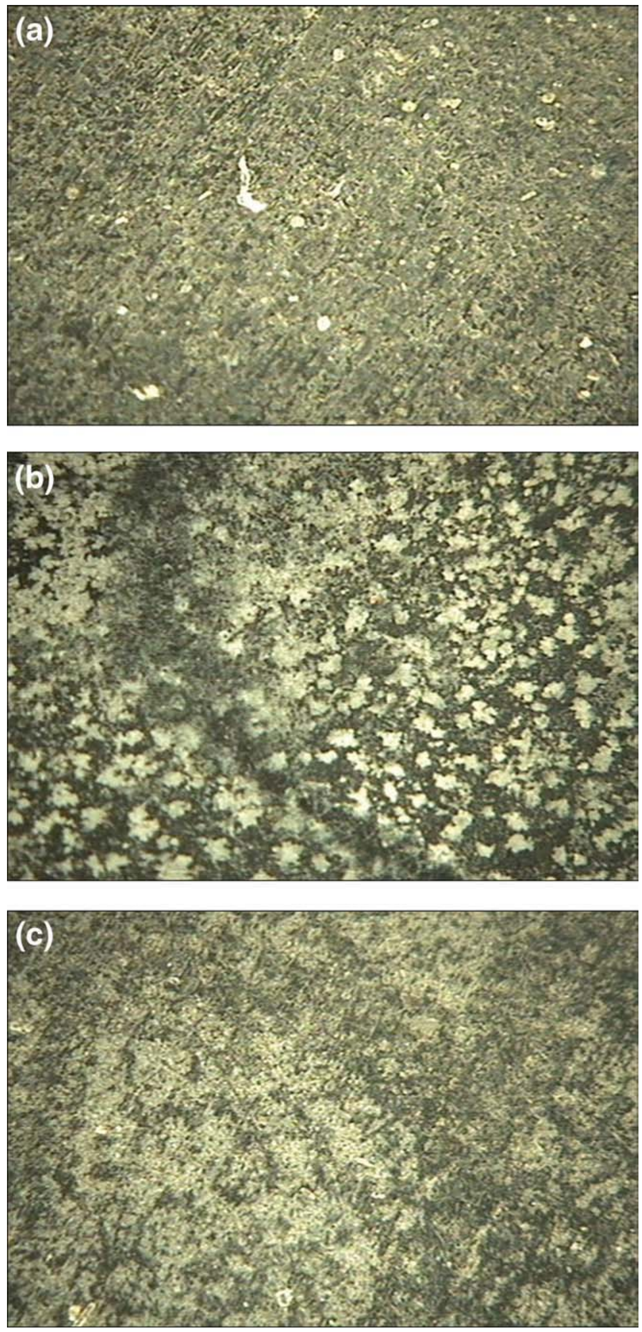

Figure 2 Magnified images (×300) of the unaged sample surface (a) and the aged sample surfaces in humid air (b) and tap water (c).

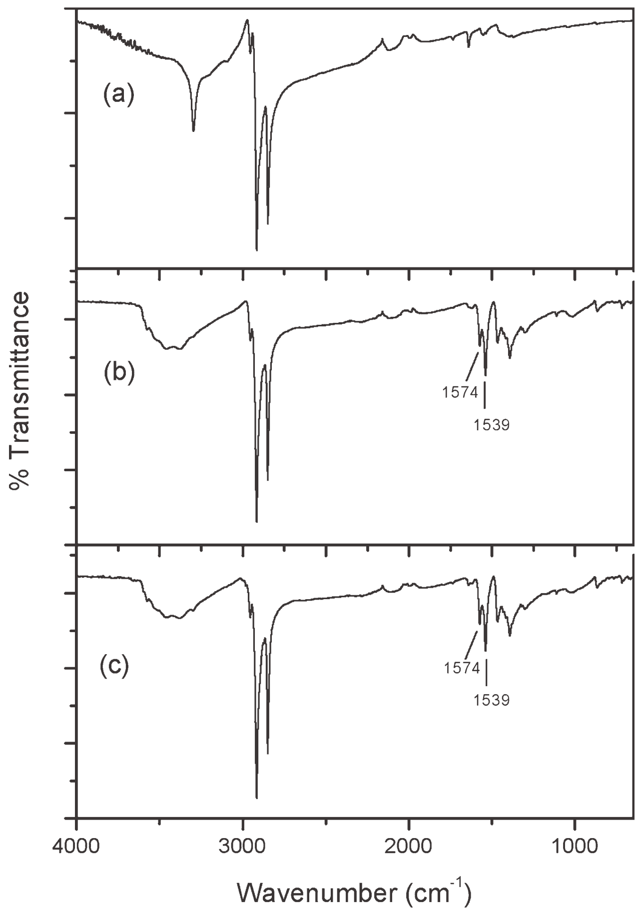

Figure 3 ATR-FTIR spectra of the unaged sample surface (a) and the aged sample surfaces in air (b) and tap water (c).

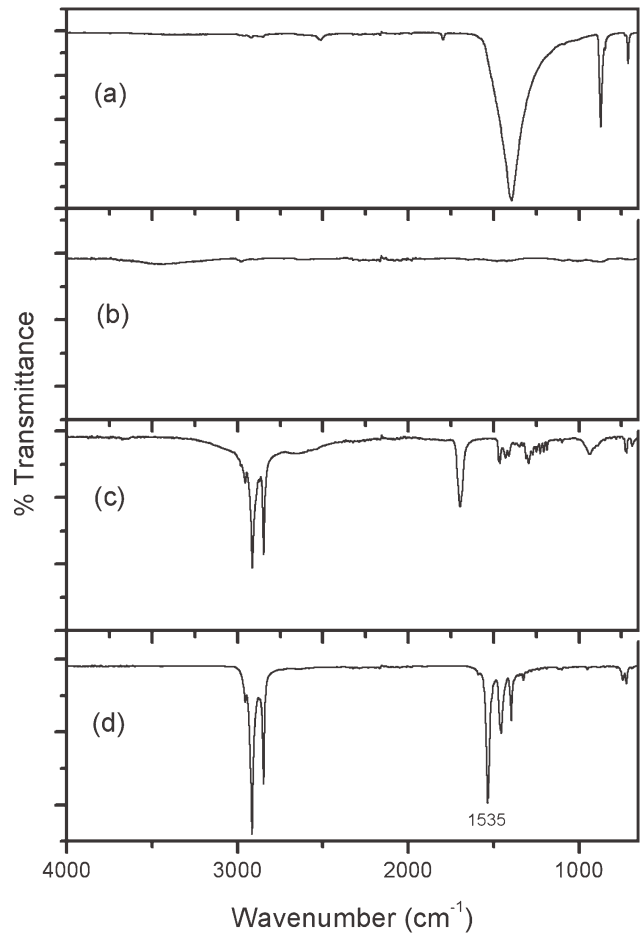

Figure 4 ATR-FTIR spectra of calcium carbonate ($CaCO_3$) (a), zinc oxide (ZnO) (b), stearic acid (c), and zinc stearate (d).

additives in the sample, the bloomed material should be one of the organic additives. Calcium carbonate, zinc oxide, stearic acid, and zinc stearate were chosen as the candicate materials. Calcium carbonate is the reinforcing filler; zinc oxide is the cure activator of sulfur cure system; stearic acid is also the cure activator; and zinc stearate is the reaction product of zinc oxide and stearic acid. The candicate materials were analyzed with ATR-FTIR and the spectra were compared to those of the aged samples. Figure 4 illustrates the ATR-FTIR spectra of the four candicate chemicals. The peak at 1535 cm^{-1} was zinc stearate. The ATR-FTIR spectra of the aged samples were not matched with those of the candicates. This means that the accumulated materials were not the additives remaining in the sample and the whitening phenomenon caused by the humid aging cannot be explained with the simple blooming of the organic materials remaining in the specimen.

A possible cause of the whitening phenomenon may be the formation of new materials and their accumulation on the sample surface. Various metal cations exist in humid air and tap water. The metal cations can react with fatty acids such as stearic acid to form metal salts of fatty acids.[31] Stearic acid might exist in the sample because the EPDM article had sulfur cure system. Stearic acid might also migrate to the surface. Sodium (Na^{+}) and calcium (Ca^{2+}) cations may exist in humid air and tap water. Sodium stearate and calcium stearate were analyzed

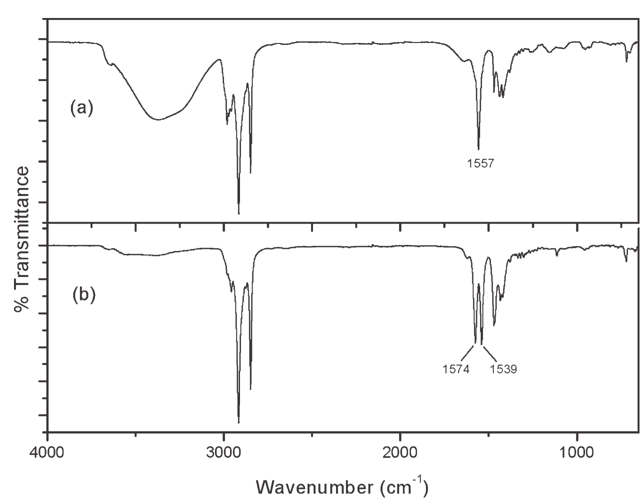

Figure 5 ATR-FTIR spectra of sodium stearate (a) and calcium stearate (b).

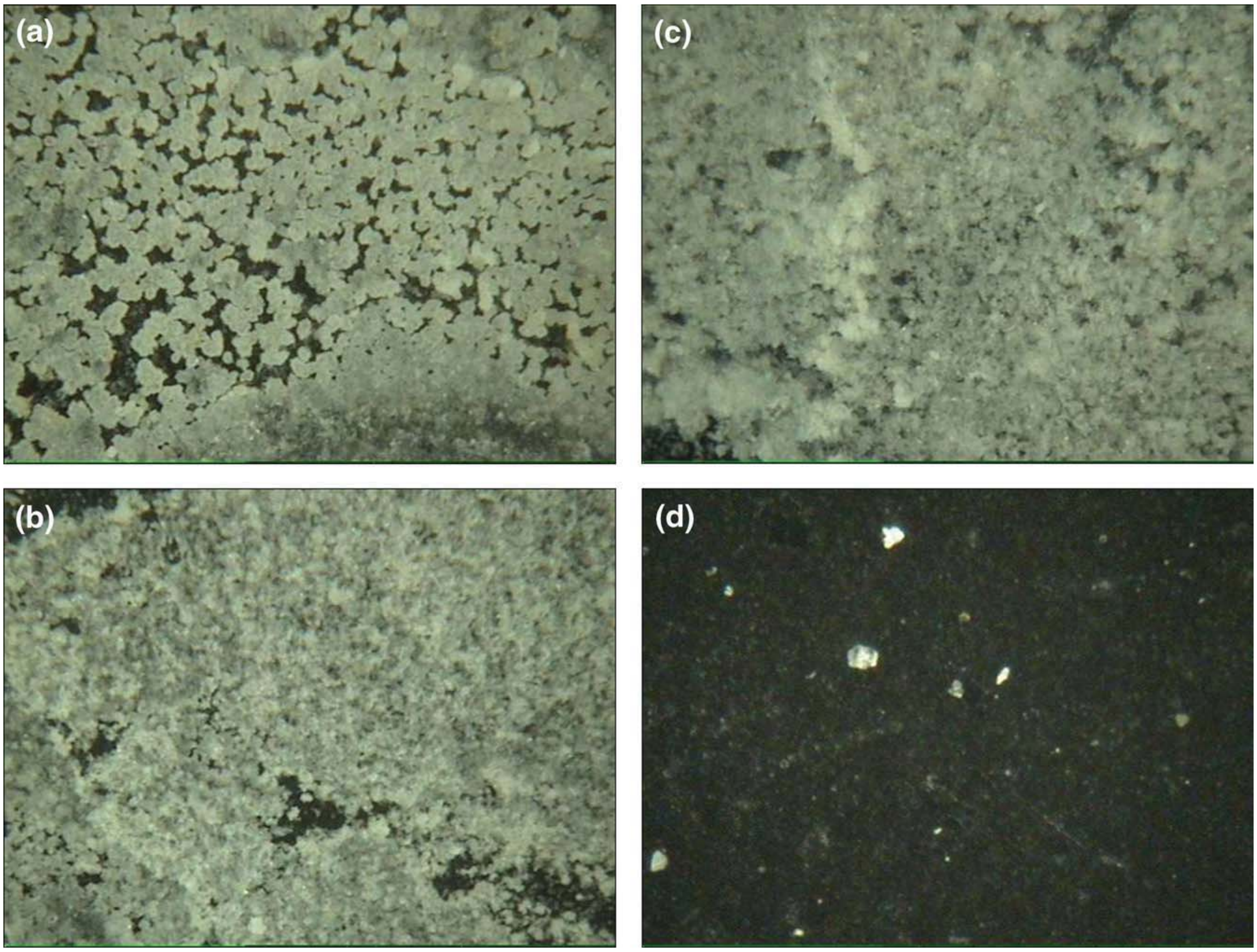

Figure 6 Magnified images (×300) of the aged model EPDM composite surfaces of the compound 1(Talc) (a), 2($CaCO_3$) (b), 3(Clay) (c), and 4(Resole) (d).

with ATR-FTIR. Figure 5 shows their ATR-FTIR spectra. The ATR-FTIR spectrum of sodium stearate displayed the peak around 1500 cm^{-1}, however, only one peak at 1557 cm^{-1} was observed. Hence, the ATR-FTIR spectrum of sodium stearate was not matched with the aged samples. The ATR-FTIR

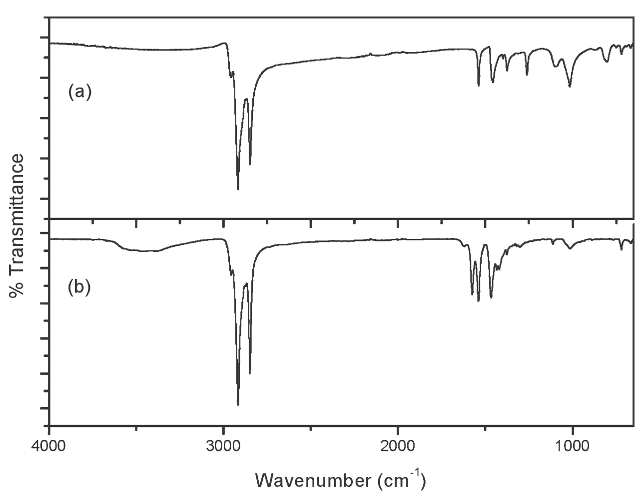

Figure 7 ATR-FTIR spectra of the model EPDM composite 1(Talc) surface before (a) and after (b) aging in 90°C tap water for 7 days.

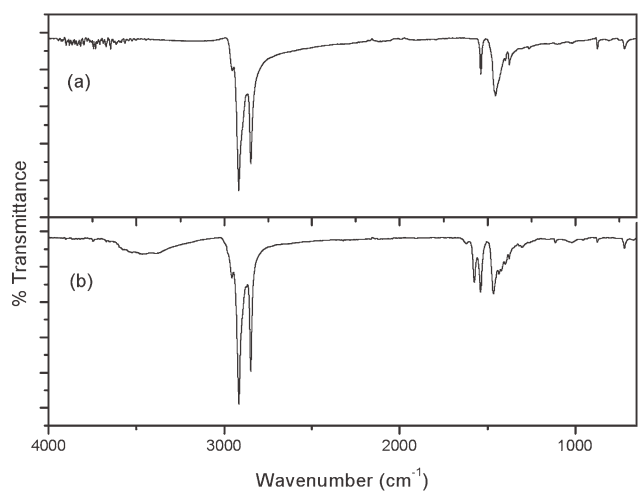

Figure 8 ATR-FTIR spectra of the model EPDM composite 2($CaCO_3$) surface before (a) and after (b) aging in 90°C tap water for 7 days.

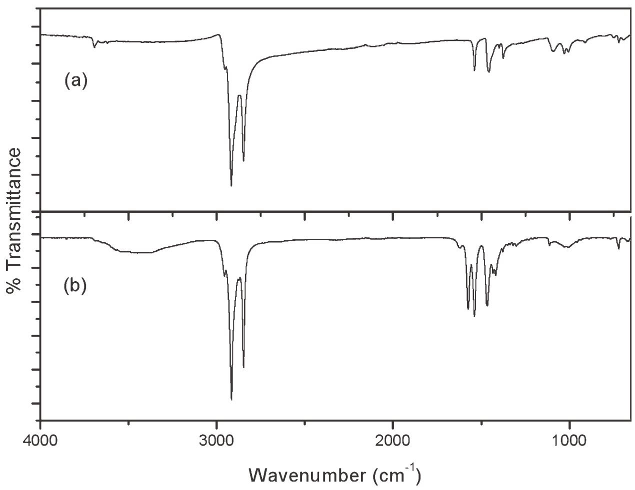

Figure 9 ATR-FTIR spectra of the model EPDM composite 3(Clay) surface before (a) and after (b) aging in 90°C tap water for 7 days.

spectrum of calcium stearate displayed the peaks at 1539 and 1574 cm^{-1}, and the whole spectrum was consistent with those of the aged sample surfaces. This indicates that the material accumulated on the aged EPDM article was calcium stearate. Besides calcium stearate, another possible bloomed material is calcium palmitate because stearic acid for industrial use contains palmitic acid. Furthermore, the IR spectra of calcium stearate and calcium palmitate are not distinguished. Thus, the whitening mechanism was the formation and accumulation on the surface of calcium stearate formed by reaction between calcium cation (Ca^{2+}) in humid air (or tap water) and stearic acid on the sample surface. Calcium stearate is not soluble in water (its solubility product, $K_{sp} = 3.61 \times 10^{-15}$).[32] Thus, calcium stearate formed on the sample surface was not dissolved in water and was accumulated on the specimen surface to cause the whitening. Calcium stearate is not also soluble in organic solvents. Due to that, the GC/MS TIC chromatogram did not show the bloomed materials.

Analysis of the aged model EPDM composites

To verify the reason of whitening, four model EPDM composites reinforced with both carbon black and inorganic filler were prepared. Three model samples had sulfur cure systems and one had non-sulfur cure system (resole cure system). The sulfur-cured samples contained stearic acid, whereas the resole-cured one did not contain stearic acid. Three sulfur-cured samples contained different inorganic filler of talc, calcium carbonate, or clay to investigate the influence of inorganic fillers on the whitening phenomenon. The detail formulation was listed in Table I. The model EPDM composites were aged in 90°C tap water for 7 days. Figure 6 shows the magnified images of the aged sample surfaces of the compounds 1(Talc), 2($CaCO_3$), 3(Clay), and 4(Resole). The model EPDM 1(Talc), 2($CaCO_3$), and 3(Clay) surfaces were covered by thick white films or spots, whereas the model EPDM 4(Resole) surface was still black. All of the sulfur-cured model EPDM composite surfaces changed to white irrespective of the filler systems, but the color of the resole-cured one did not change. Thus, the whitening phenomenon only occurred in the sulfur-cured EPDM composites because of stearic acid. The bloomed surfaces were analyzed with ATR-FTIR and the spectra are shown in Figures 7–9. The unaged sample surfaces did not show the peaks of calcium stearate at 1539 and 1574 cm^{-1}. ATR-FTIR spectra of all the aged sulfur-cured model EPDM samples irrespective of the filler systems clearly displayed the calcium stearate peaks at 1539 and 1574 cm^{-1}. Figure 10 displayed ATR-FTIR spectra of the unaged and aged surfaces of the model EPDM 4(Resole), which did not show a big difference. We verified the reason for the whitening of sulfur-cured EPDM composites by humid aging. The whitening mechanism was the formation and accumulation of calcium stearate which was produced by the reaction of Ca^{2+} with stearic acid. The Ca^{2+} came from the humid air or the tap water, while the stearic acid came from the sulfur-cured EPDM composite.

To avoid the whitening phenomenon in sulfur-cured EPDM articles, fatty acids including stearic acid must not be used for the manufacturing of EPDM articles. However, it is not easy to avoid use of fatty acids because it is one of common additives of rubber articles. In general, fatty acids have been widely used for manufacture of EPDM articles as sulfur cure activator, softener, or lubricant.

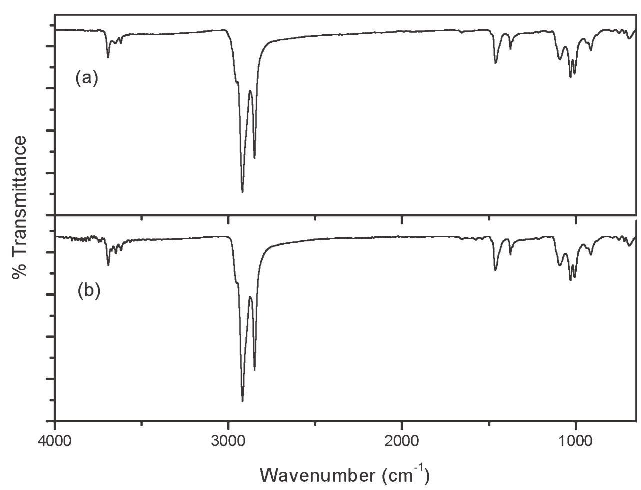

Figure 10 ATR-FTIR spectra of the model EPDM composite 4(Resole) surface before (a) and after (b) aging in 90°C tap water for 7 days.

CONCLUSIONS

The sulfur-cured EPDM composites were aged in humid air and tap water. The black sample surfaces changed to white. The bloomed surfaces were analyzed with ATR-FTIR and the material which causes the whitening was found to be calcium stearate. The calcium stearate was formed by reaction between calcium cation (Ca^{2+}) and stearic acid. The Ca^{2+} came from the humid air or the water, while the stearic acid came from the sulfur-cured EPDM article.

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