Collection and Identification of Organic Materials Accumulated on a Rubber Composite

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Received 8 July 2006; accepted 5 November 2006
DOI 10.1002/app.25781
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Rubber composites are composed of rubber(s), reinforcing filler(s), crosslinking agents, antidegradants, and processing aids. Organic materials with low molecular weight can migrate to the surface of the rubber composite and get accumulated on the surface. The bloomed materials make the appearance worse and contaminate the surroundings. It is not easy to collect successfully the bloomed materials without damage to the sample. The collecting methods of scratching with a polished glass, heating with an iron, scrubbing with solvent-soaked cellulose tissue, and scrubbing with solvent-soaked melamine foam were compared. The collected materials were analyzed using gas chromatography/mass spectrometry (GC/MS). The scrubbing with solvent-soaked melanine foam or with solvent-soaked cellulose tissue was found to be recommendable. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1260–1264, 2007

Key words: blooming; rubber composite; collection and identification; solvent-soaked melanine foam; GC/MS

INTRODUCTION

In general, a rubber composite is composed of rubber(s), reinforcing filler(s), curatives, antidegradants, and processing aids. The antidegradants, processing aids, and residues of curatives migrate to the surface of a rubber composite and get deposited on the surface. This is called blooming. Blooming in a rubber article may occur when an additive with low solubility is used in excess.[1,2] For example, a material dissolved in a rubber composite at a high mixing temperature becomes supersaturated as the stock cools down. Because of the concentration gradient between the layer immediately beneath the surface and the bulk of the rubber, further blooming will occur at the surface until the concentration of the component reaches the solubility limit through the rubber article. A component below its solubility limit will not bloom.

Koczorwska and coworkers[3,4] studied the solubility limits of sulfur, oil, and zinc stearate in rubber compounds. The principal reason about blooming is the solubilities of organic materials in a rubber composite. Commonly used rubbers such as natural rubber (NR), polybutadiene (BR), and styrene-butadiene copolymer (SBR) are less polar, whereas antidegradants such as *p*-phenylenediamines and cure accelerators such as benzothiazole sulfenamides are more polar materials. Thus, solubilities of the polar ingredients in a rubber compound are very low and the solubility of wax used as an antidegradant is also very low. The major blooming materials are antidegradants, wax, and fatty acids since their molecular sizes are not big. Blooming phenomena of wax, antidegradants, and fatty acids were studied by several researchers.[5–7]

It is not easy to collect successfully the bloomed materials without damage to the rubber articles. In the present work, analyses of bloomed materials, including collection and identification, were studied. Scratching with a polished glass, heating with an iron, scrubbing with solvent-soaked cellulose tissue, and scrubbing with solvent-soaked melamine foam were employed as collection methods of the bloomed materials. The collected materials were dissolved in solvent and analyzed using gas chromatography/mass spectrometry (GC/MS). Experiments were performed using model and real samples.

EXPERIMENTAL

Carbon black-filled styrene-butadiene rubber (SBR) vulcanizate was employed as a rubber article. The SBR vulcanizate was composed of SBR1502 (100.0 phr), N220 (carbon black, 50.0 phr), ZnO (2.0 phr), stearic acid (2.0 phr), *N*-phenyl-*N*′-(1,3-dimethylbutyl)-*p*-phenylenediamine (HPPD, antidegradant, 2.0 phr), wax (2.0 phr), *N*-tert-butyl-2-benzothiazole sulfenamide (TBBS, cure accelerator, 1.4 phr), and sulfur

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Contract grant sponsor: Ministry of Commerce, Industry, and Energy of Korea; contract grant number: grant no. 10016800.

Journal of Applied Polymer Science, Vol. 104, 1260–1264 (2007)

(1.4 phr). Acetone, *n*-hexane, and THF were purchased from Aldrich and used as solvents.

Model sample was prepared as follows. First, organic materials remained in the rubber vulcanizate were extracted using THF for 5 days and *n*-hexane for 2 days and drying at room temperature for 5 days to prepare an organic material-free rubber specimen. Second, target blooming materials were dissolved in solvent. HPPD, wax, and stearic acid were employed as target blooming materials. HPPD and stearic acid of 5 mg were dissolved in acetone of 1 mL and wax of 2 mg was dissolved in *n*-hexane of 1 mL. Third, the solution of 5 μL was dropped on the model rubber specimen five times. Finally, the solvent was evaporated. Four collecting methods, scratching with a polished glass, heating with an iron, scrubbing with solvent-soaked cellulose tissue (Kleensite lens cleansing paper of Graf-Apsco Co.), and scrubbing with solvent-soaked melamine-formaldehyde resin foam (melamine foam, Basotect of BASF Co.; its bulk density is about 0.01 g/cm^3), were employed (Fig. 1).

The collected materials were dissolved in solvent of acetone or *n*-hexane of 200 μL. Analysis of the gathered materials was performed with GC/MS. GC/MS chromatograms and mass spectra of the collected materials were acquired with 6890*N*/5987 GC/MS of Agilent Co. DP-5MS capillary column (length 30m) was used. Injector temperature of the GC was 200°C. The GC oven temperature program was as follows: (1) The initial temperature was 150°C and kept for 3 min. (2) The temperature was then increased from 150 to 300°C at a rate of 10°C/min.

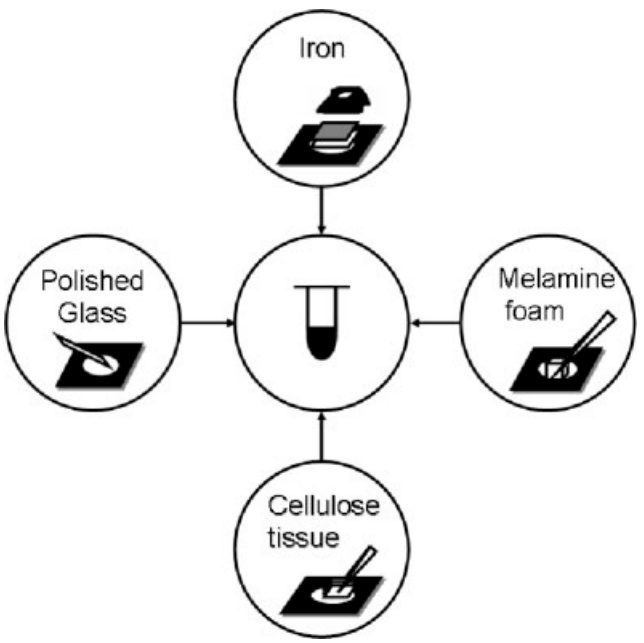

Figure 1 Methods to collect organic materials bloomed on a rubber article.

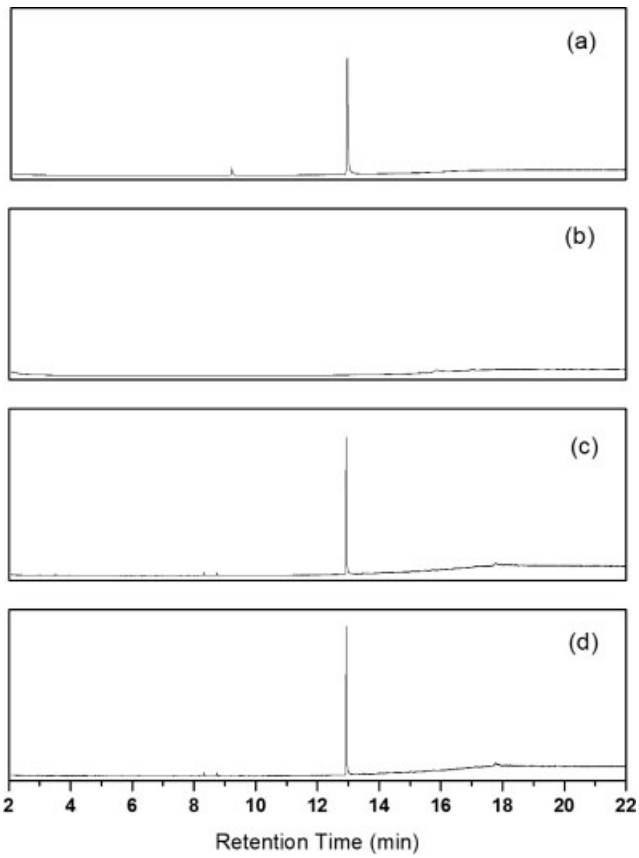

Figure 2 GC/MS chromatograms of the materials collected from the model sample surface using HPPD solution in acetone. The collecting methods are (a) scratching with polished glass, (b) heating with iron, (c) scrubbing with acetone-soaked cellulose tissue, and (d) scrubbing with acetone-soaked melamine foam.

RESULTS AND DISCUSSION

First of all, using the model sample of HPPD, the four collecting methods, scratching with a polished glass, heating with an iron, scrubbing with solvent-soaked cellulose tissue, and scrubbing with solvent-soaked melamine foam, were compared. Figure 2 shows the GC/MS chromatograms of the gathered materials using the four collecting methods. The simplest collecting method is a scratching method using a knife or glass. The rubber specimen surface on which HPPD was deposited by dropping the HPPD solution was scratched several times with a polished glass and the gathered materials were dissolved in acetone to analyze with GC/MS. The GC/MS chromatogram of the gathered material using the polished glass shows the HPPD as shown in Figure 2(a). However, this method was found to be useful only when the layer of bloomed materials was thick. The second method is a heat transfer with an iron. Filtering paper or cellulose tissue was placed on the HPPD-accumulated surface and was scrubbed several times with a hot iron to transfer the bloomed materials from the rubber

specimen to the filtering paper or cellulose tissue by heating. The filtering paper or cellulose tissue was put in acetone and analyzed with GC/MS. The results were illustrated in Figure 2(b). The GC/MS chromatogram of the gathered material using the heat transfer method did not show any peaks. The heating method with an iron at first was expected to be one of the efficient methods. Guittard and coworkers[8] reported for analysis by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS) of native glycophospholipids after development on thin layer chromatographic plates and after heat transfer using an iron from the plates to the polymer membranes. But this method was not found to be useful. This may be due to the dissolution of bloomed HPPD into the rubber specimen by heating. The bloomed materials on the rubber article surface is redissolved into the rubber specimen when heat is applied on the rubber article surface.

The other methods are using solvent-soaked cellulose tissue and solvent-soaked melamine foam. Cellulose tissue of 4 × 4 cm^2 was folded to 1 × 1 cm^2 and soaked in acetone. The HPPD-deposited surface was scrubbed several times with the acetone-soaked cellulose tissue. The cellulose tissue was put in acetone to analyze with GC/MS. Melamine foam is a very light and open-cell material and has been used for acoustical and thermal insulation. Melanime foam of 0.5–1.0 cm^3 was cut and soaked in acetone. The HPPD-accumulated surface was scrubbed with the acetone-soaked melamine foam several times. The melamine foam was put in acetone to analyze with GC/MS. Figure 2(c,d) show the GC/MS chromatograms of the collected HPPD using acetone-soaked cellulose tissue and melamine foam, respectively. The two methods show good results. We have also used THF-soaked cellulose and THF-soaked melamine foam to collect the bloomed materials on the rubber specimen since THF is a good solvent for rubber chemicals. The method using THF was failed because THF get transferred into the rubber specimen and swelled it.

The two methods of solvent-soaked cellulose tissue and solvent-soaked melamine foam to collect wax and stearic acid accumulated on the rubber specimen

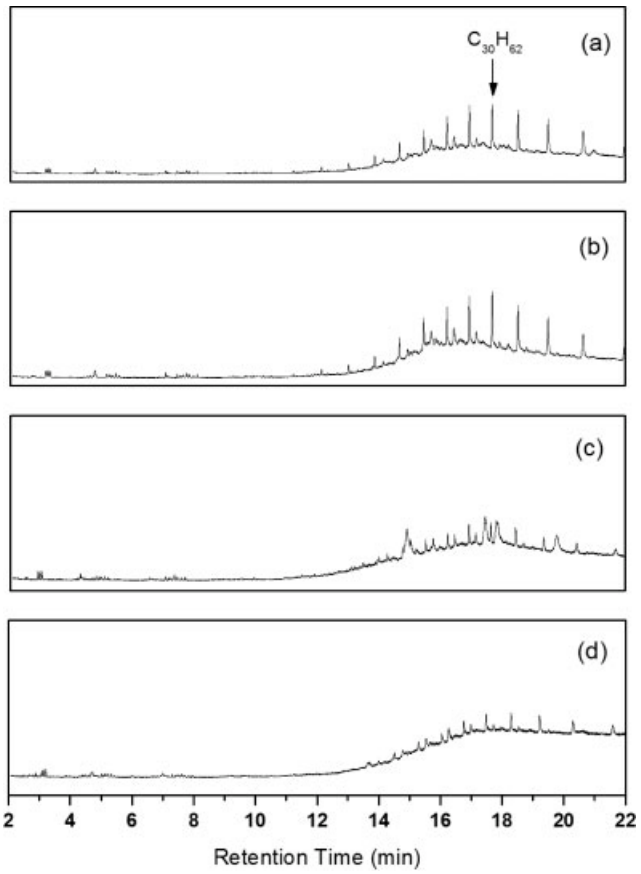

Figure 3 GC/MS chromatograms of the materials collected from the model sample surface using wax solution in *n*-hexane. The collecting methods are (a) scrubbing with *n*-hexane-soaked cellulose tissue, (b) scrubbing with *n*-hexane-soaked melamine foam, (c) scrubbing with acetone-soaked cellulose tissue, and (d) scrubbing with acetone-soaked melamine foam.

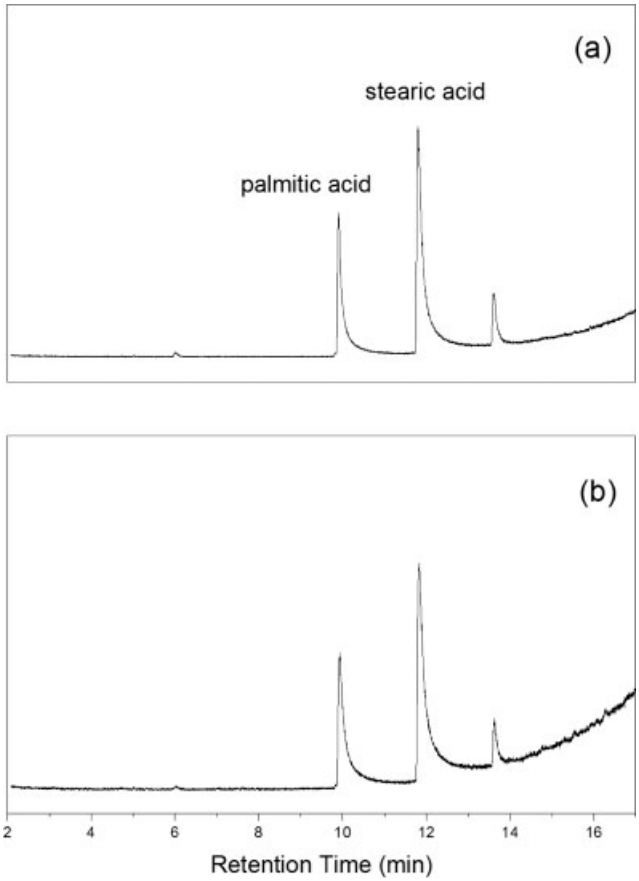

Figure 4 GC/MS chromatograms of the materials collected from the model sample surface using fatty acids solution in acetone. The collecting methods are (a) scrubbing with acetone-soaked cellulose tissue and (b) scrubbing with acetone-soaked melamine foam.

were compared. Two solvents (*n*-hexane and acetone) were used for collection of the accumulated wax. Figure 3 shows the GC/MS chromatograms of the collected wax. Wax used in a rubber compound has a molecular weight distribution of C_nH_{2n+2}. The GC/MS chromatograms of the collected wax with *n*-hexane-soaked cellulose and *n*-hexane-soaked melamine foam show a clear molecular weight distribution of C_nH_{2n+2} as shown in Figure 3(a,b). The GC/MS chromatograms of the collected wax with acetone-soaked cellulose tissue and acetone-soaked melamine foam, however, do not show clear peaks as shown in Figure 3(c,d). This implies that selection of the solvent is very important. Wax is more soluble in *n*-hexane than acetone. The stearic acid ($CH_3(CH_2)_{16}CO_2H$) used in a rubber industry is not a pure material. Stearic acid is a mix of fatty acids, including palmitic acid ($CH_3(CH_2)_{14}CO_2H$) and eicosanoic acid

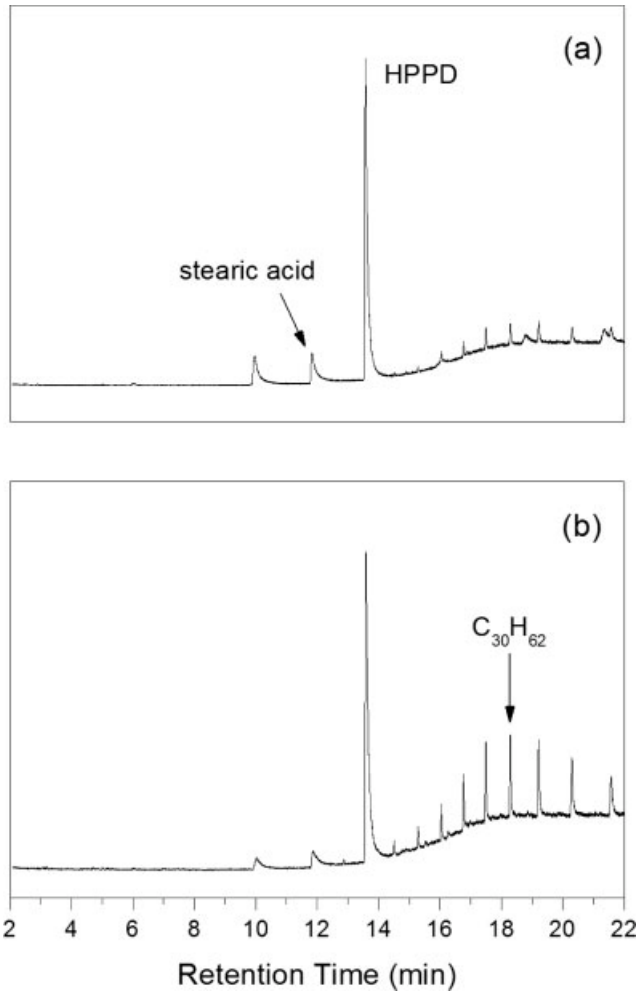

Figure 5 GC/MS chromatograms of the materials collected from the model sample surface using mixed solution of HPPD, wax, and fatty acids in acetone. The collecting methods are (a) scrubbing with acetone-soaked melamine foam and (b) scrubbing with *n*-hexane-soaked melamine foam.

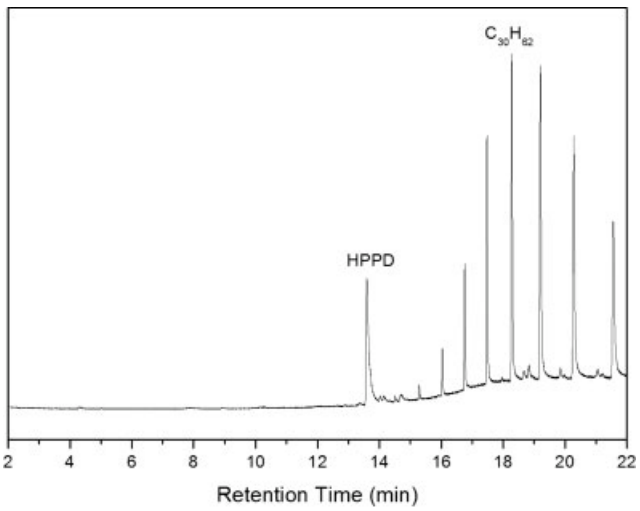

Figure 6 GC/MS chromatograms of the materials collected from the SBR vulcanizate surface aged for 3 months at room temperature. The bloomed materials were collected by scrubbing with acetone-soaked melamine foam.

($CH_3(CH_2)_{18}CO_2H$) as well as stearic acid. The accumulated fatty acids were collected with the acetone-soaked cellulose tissue and acetone-soaked melamine foam. The GC/MS chromatograms of the collected fatty acids show peaks of palmitic acid, stearic acid, and eicosanoic acid as shown in Figure 4.

In comparison with the two collecting methods using the solvent-soaked cellulose tissue and solvent-soaked melamine foam, it was found that amount of the collected materials by one scrub using the solvent-soaked melamine foam was more than that using the solvent-soaked cellulose tissue. The melamine foam is also easier to extract the solution remained in it than the cellulose tissue. Thus, we can say that the melamine foam is more convenient than the cellulose tissue and also more effective to collect the bloomed materials on a rubber specimen.

HPPD, wax, and fatty acids were dissolved together in acetone and the solution was dropped on the rubber specimen to prepare the model bloomed materials. The bloomed materials were gathered with the acetone- or *n*-hexane-soaked melamine foam. The gathered materials were analyzed with GC/MS. The GC/MS chromatogram of the acetone-soaked melamine foam shows clear peaks of the fatty acids and HPPD but the peaks of wax are not clear as shown in Figure 5(a). The GC/MS chromatogram of the *n*-hexane-soaked melamine foam shows clear peaks of the HPPD and wax but the peaks of fatty acids are not clear as shown in Figure 5(b). This is due to the solubility difference between the two solvents.

The SBR vulcanizate composed of SBR1502, N220, ZnO, fatty acids, HPPD, wax, TBBS, and sulfur was aged at room temperature for 3 months. Some materials were bloomed on the surface. The bloomed mate-

rials were collected with the acetone-soaked melamine foam and analyzed with GC/MS. Figure 6 shows the peaks of HPPD and wax. The other organic materials such as fatty acid, TBBS, and sulfur were not detected or trace. The fatty acids react with zinc oxide and curatives in the rubber compound during the mixing and curing processes to form zinc complexes.[9,10] The zinc complexes in the rubber composites rarely migrate to the surface since their size is big. TBBS and sulfur participate in crosslinking reactions to form sulfur crosslinks, zinc complexes, and pendent sulfide groups terminated by an accelerator residue.[11–13] Thus, amounts of TBBS and sulfur remained in the rubber specimen are very small and the bloomed chemicals are almost nil. The peaks for the wax were observed clearly since the wax was more accumulated than the other materials because of the less volatile property.

CONCLUSIONS

Bloomed materials on a rubber article was collected using four collecting methods, scratching with a polished glass, heating with an iron, scrubbing with solvent-soaked cellulose tissue, and scrubbing with solvent-soaked melamine foam, and the gathered materials were dissolved in solvent and were analyzed with GC/MS. The scratching method using a polished glass was useful only when the accumulated materials were thick and the heating method using an iron was not useful. The scrubbing method using solvent-soaked cellulose tissue or solvent-soaked melamine foam is recommendable. Especially the method using melamine foam is more covenient and efficient. The selection of the solvent is very important.

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