

Reduction of Offensive Odor from Natural Rubber by Odor-Reducing Substances

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ABSTRACT: A number of chemicals including carbon black, chitosan, benzalkonium chloride, sodium dodecyl sulfate, cyclodextrin, and zeolite13x were tested as odor-reducing fillers. The rationale is based on the concept of using odor absorbents/adsorbents for which both physical adsorption and chemical adsorption play an important role in odor reduction. The fillers were incorporated into highly odorous natural rubber (STR20 and RSS5) by physical mixing prior to sulfur vulcanization. As identified by gas chromatography and gas chromatography/mass spectrometry, the unpleasant odor mainly originates from low molecular weight volatile fatty acids. The quantity of acetic acid, a representative of odor molecule, can be significantly reduced in the presence of chitosan and zeolite13x. Although

carbon black and cyclodextrin exhibited a tendency to reduce the odor, they were not as effective as zeolite13x and chitosan. On the other hand, commercial surfactants such as benzalkonium chloride and sodium dodecyl sulfate cannot serve as odor-reducing substances because of their limited thermal stability. An olfactometry test confirmed that chitosan and carbon black are good odor-reducing agents. Chitosan and carbon black showed a reinforcing effect on vulcanized rubber, whereas the surfactant deteriorated the strength of the rubber composite. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2253–2260, 2004

Key words: odor; odor reduction; natural rubber; composites; fillers

INTRODUCTION

Despite the fact that synthetic rubbers have become very competitive in the world rubber market, a demand for natural rubber in some applications remains appreciably high as a consequence of its superior elasticity, resilience, and heat-transfer properties. Offensive odor emitted from natural rubber products and from natural rubber raw material during drying, storage, mastification, and curing has been recognized as a long-standing, unsolved problem for natural rubber manufacturers and consumers. Low molecular weight volatile fatty acids were identified as major odorous components according to an indirect analysis of exhausted gas emitted from natural rubber factories.^{1–2} Systematic identification of odorous contents of different-graded solid natural rubber by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) by using headspace as a direct sampling technique later confirmed that low molecular weight

volatile fatty acids are the major cause of offensive odor.³ Additionally, the strength and the characteristics of the odor strongly depended upon the rubber quality and the drying process. Approximately 50 compounds having molecular weights in the range of 40–200 amu were identified. They were classified into four groups ranging from low to high polarity: aliphatic and aromatic hydrocarbons, derivatives containing nitrogen or sulfur, aldehydes and ketones, and volatile fatty acids. Ethylamine, benzylhydrazine, and low molecular weight fatty acids such as acetic acid, propionic acid, isobutyric acid, butyric acid, isovaleric acid, and valeric acid were discovered in most of the samples. It is believed that incomplete degradation during storage and thermal degradation during the processing of nonrubber components (carbohydrates, proteins, and lipids) are responsible for generating the offensive odor.

Little attention has been directed to the elimination of the unpleasant smell from natural rubber. The treatment of air released from natural rubber factories by water scrubber systems is the only indirect approach currently used.^{1–2} The method of reducing offensive odor from the material is in fact to change the bad odor to be more pleasant by masking and/or reducing the odor intensity to a more acceptable level. Based on

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a simple concept of employing odor absorbents or odor adsorbents, a physical mixing of several substances, which are expected to potentially reduce the unpleasant odor in natural rubber, is proposed. In general, an odor absorbent is a material that captures and retains odor molecules in its interior, while an odor adsorbent retains odor molecules on its surface. A number of materials are tested as odor-reducing fillers: carbon black, cyclodextrin, zeolite13x, chitosan, sodium dodecyl sulfate, and benzalkonium chloride. It was reported recently that carbon black works efficiently as odor-adsorbing filler in some polymer composites used as vapor detectors.⁴⁻⁵ It was found that the vapor detector produced sensitive detection of various organic acids and relatively little response to nonacidic organic vapors. Cyclodextrin has been used in textile applications as a deodorant for unpleasant body odor in the form of unsaturated aldehydes.⁶ Although a number of publications have addressed the reduction of odor from volatile organic compounds by using zeolites,⁷⁻¹¹ to the best of our knowledge, none have addressed the use of chitosan for the same purpose. The deodorizing effects of some anionic and cationic ion-exchange resins on lower fatty acids, ammonia, and odor of feces have been previously demonstrated.¹² Benzalkonium chloride, in particular, exhibits an antimicrobial property.¹³ It should then be capable of preventing odor formation that can be accelerated in the presence of microorganisms. STR20 and RSS5 are chosen as representatives of highly odorous natural rubber. Both GC and GC-MS are used as tools to monitor the volatile components of odor through the course of the studies. An olfactometry test is used to measure qualitatively the efficacy of odor reduction. Mechanical properties of vulcanized natural rubber composites, namely tensile properties and hardness, are investigated to evaluate the effect of these compounds on cure rubber properties.

EXPERIMENTAL

Materials

Standard Thai Rubber 20 (STR 20) and Ribbed smoke sheet 5 (RSS 5) were kindly supplied by Teck Bee Hang Co., Ltd. (Rayong, Thailand) and Mitthai Nakorn Co., Ltd. (Nakorn Srithummaraj, Thailand), respectively. STR20 is mainly produced from cup lumps, which are coagulum of fresh latex in collecting cups, standing for some time after tapping, by crumb processing and washing by continuous water spraying before being dried in an oven at a temperature of 50–60°C for 3–4 days. The dried rubber crumbs are then pressed into rubber bales. RSS5 is obtained as a rubber sheet after smoking at a temperature of 50–60°C for 3–4 days in a smokehouse. The sheet is prepared by coagulating fresh latex

TABLE I
Formulas for Rubber Compounding

| Ingredient | Quantity of mix (phr) |
|-----------------------|-----------------------|
| Natural rubber sample | 100 |
| Sulfur | 3.5 |
| Zinc oxide | 6.0 |
| Steric acid | 0.5 |
| TMTD | 0.5 |
| Odor-reducing agent | 1.5 or 5.0 |

with formic acid. The coagulum is passed through a series of squeeze and wash rolls before being subjected to smoking.

All standard carboxylic acids were purchased from Merck (Darmstadt, Germany) and used as received. Activated carbon powder (Fluka, Buchs, Switzerland), benzalkonium chloride (Fluka), β -cyclodextrin (Aldrich, Milwaukee, WI), chitosan (Seafresh, Bangkok, Thailand; $M_w = 700,000$), sodium dodecyl sulfate (APS Ajax Finechem, Bangkok, Thailand) were reagent grade and used as received. Zinc oxide (DYNA Trade Co., Ltd., Bangkok, Thailand), sulfur (DYNA Trade Co., Ltd.), tetramethyl thiuram disulfide (Sunny World Co., Ltd., Bangkok, Thailand), and stearic acid [Imperial (Thai) Co., Ltd., Bangkok, Thailand], and zeolite13x (Estern Cegate, Bangkok, Thailand) were commercial grade.

Methods

Preparation of vulcanized rubber filled with odor-reducing substances

Sodium dodecyl sulfate, benzalkonium chloride, chitosan, carbon black, zeolite13x, and cyclodextrin were used as odor-reducing substances. By using a two-roll mill, 1.5 or 5.0 phr of the odor-reducing substance was mixed with natural rubber samples (STR20 or RSS5) along with other additives. The formulation of rubber compound is illustrated in Table I. Vulcanized rubber sheets were prepared by compression molding of compounded rubbers at 150°C for 4–5 min.

Determination of volatile organic contents by gas chromatography and gas chromatography/mass spectrometry

Methyl valerate (1 μ L) was added into all rubber samples as an internal standard. The volatile components were collected from air above vulcanized rubber samples (10–15 g) that were trapped in 100-mL vials and preheated at 60°C for 2 h. A known volume of gas was withdrawn by a gas-tight syringe before being injected into the column for GC and GC/MS analysis. Five replicate samples for each condition were analyzed weekly for a period of 5 weeks. To avoid the

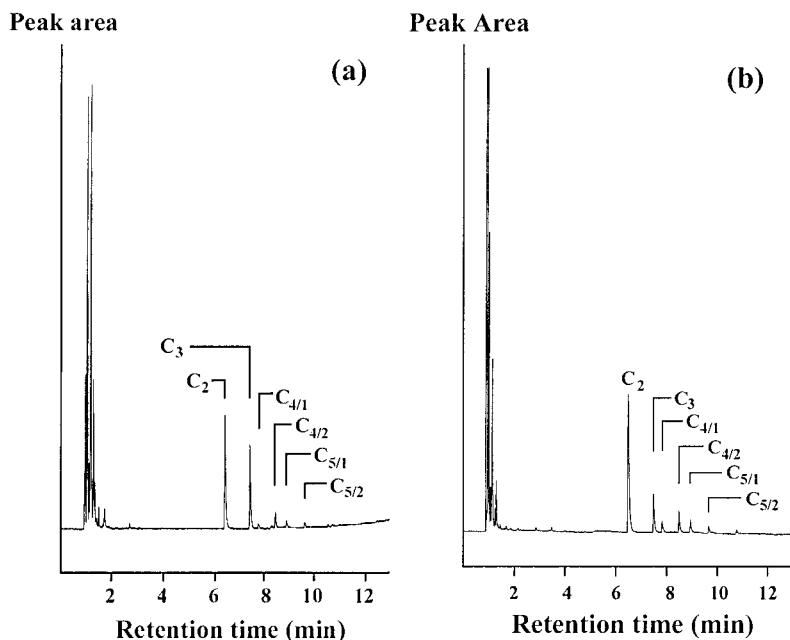


Figure 1 GC chromatograms of odor components of (a) STR20 and (b) RSS5.

leakage of volatile components through the hole that was punched by the syringe needle, a new rubber septum was rapidly replaced after each sampling.

A Hewlett-Packard (HP) Model 6890 gas chromatograph was used with a flame ionization detector (FID) and a HP-20M capillary column (0.2 mm \times 25.0 m; coated with 0.2- μ m film of polyethylene glycol). The column temperature was held at 35°C for 2 min and programmed to 150°C at a rate of 10°C/min for all runs. The injector and detector temperatures were installed at 200°C. Helium and nitrogen were used as the carrier gas and make-up gas, respectively, at the flow rate of 2.00 mL/min.

A gas chromatograph/mass spectrometer, Finigan MAT GCQ[®], was used with a ZBWAX capillary column (0.32 mm \times 30 m; coated with 0.25- μ m film of polyethylene glycol). The column temperature was held at 35°C for 6 min and programmed at the rate of 10°C/min to 180°C and held for 5 min. The injector temperature was 200°C. The transfer line temperature was 240°C. Helium was used as the carrier gas at a velocity of 50 cm/s. The mass range was 40–200 amu. The electron multiplier voltage was set at 1550 V with the ion source temperature of 200°C.

Olfactometry test

Twenty persons (10 men and 10 women) having ages in the range of 20–35 years were subjected to the olfactometry testing. Vulcanized rubber samples (STR20 and RSS5) with and without odor-reducing substances were prepared according to the previously described method. To generate references for odor testing, various amounts of original rubber samples

were filled in 250-mL bottles. References 1–5 ranging from low to high odor intensity were made by filling 1, 5, 10, 15, and 20 g of rubbers in 250-mL bottles,

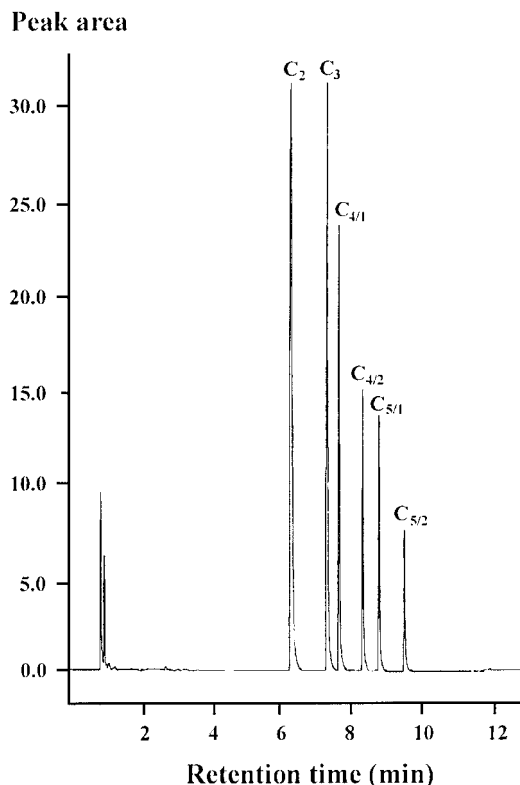


Figure 2 GC chromatogram of mixed standard carboxylic acids: acetic acid (C_2), propionic acid (C_3), isobutyric acid ($C_{4/1}$), butyric acid ($C_{4/2}$), isovaleric acid ($C_{5/1}$), and valeric acid ($C_{5/2}$).

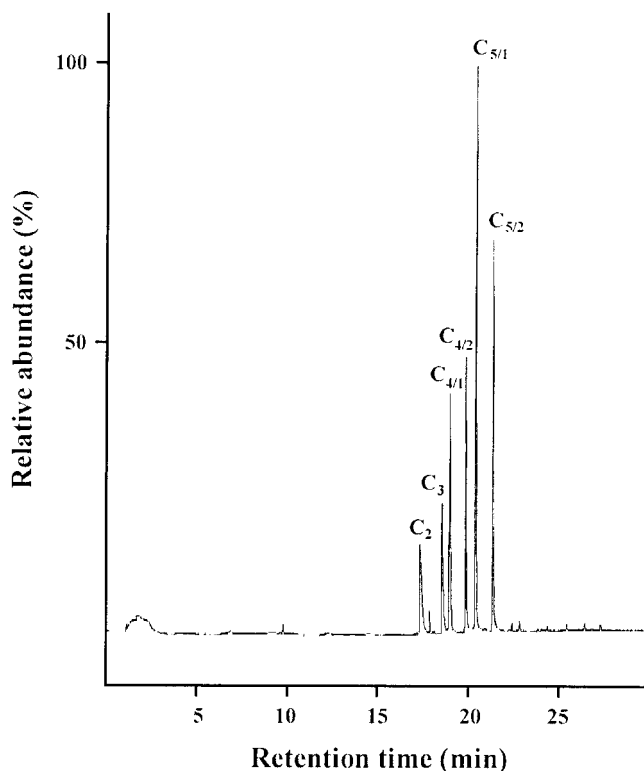


Figure 3 GC/MS chromatogram of mixed standard carboxylic acids: acetic acid (C_2), propionic acid (C_3), isobutyric acid ($C_{4/1}$), butyric acid ($C_{4/2}$), isovaleric acid ($C_{5/1}$), and valeric acid ($C_{5/2}$).

respectively. The odor of 10 g of vulcanized rubber mixed with each odor-reducing substance in a 250-mL bottle was compared with each reference. Each person specified the reference number that gave lower or equal odor intensity as compared to the vulcanized rubber mixed with each odor-reducing substance. The results of the olfactometry test were reported as a percentage of people who chose each reference. Every person had to smell the odor of coffee beans prior to each comparison to erase the previous experience from the former odor comparison and to minimize odor confusion.

Mechanical testing

Tensile strength and elongation at break were determined in accordance with ASTM D412-C. The vulcanized rubber sheets were cut into dumbbell shapes. The tests were carried out by using Automated Materials Testing System 6.05 Model 1011 (Instron Corp., Series IX, USA) at a crosshead speed of 500 mm/min. The hardness of vulcanized rubber sheets was analyzed according to ASTM D 2240 by using Shore Type A Durometer Hardness System.

RESULTS AND DISCUSSION

Determination of volatile organic contents from odorous rubbers

STR20 and RSS5, both manufactured in Thailand, were chosen because they are the most odorous rubbers in their classes. Both of them possess a very intense smell; the former is generally prepared from field-grade materials such as lumps and scraps that are low in quality, whereas the latter is a coagulated sheet treated with smoking. Upon optimum conditions for GC analysis by using HP-20M, there were two groups of peaks appearing in both chromatograms, as shown in Figure 1, obtained from analysis of STR20 and RSS5. The peaks having retention time beyond 6 min were well resolved. Major peaks were later verified by GC and GC/MS analysis of standard carboxylic acids as low molecular weight volatile fatty acids: acetic acid (C_2), propionic acid (C_3), isobutyric

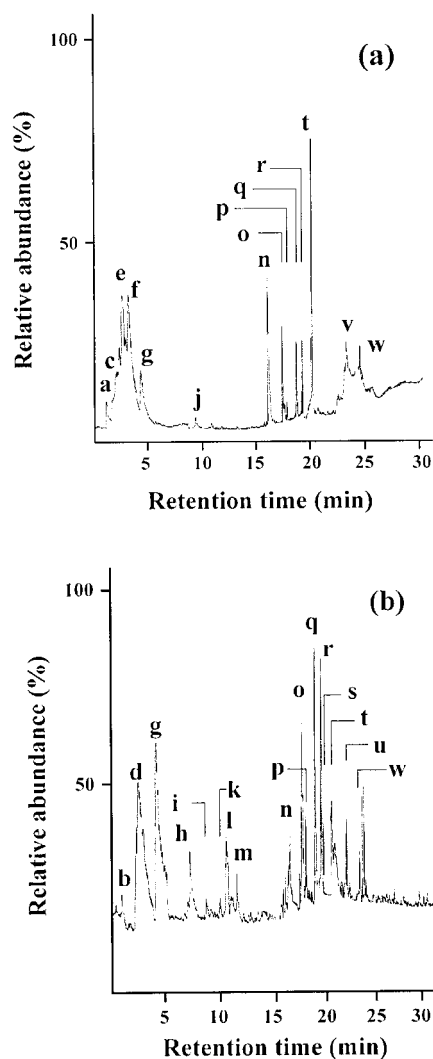


Figure 4 GC/MS chromatograms of odor components of (a) STR20 and (b) RSS5.

TABLE II
The Components of Odor from STR20 and RSS5 as Identified by GC/MS

| Symbol | Chemical component | M_w (amu) | Retention time (min) | STR20 | RSS5 |
|--------|---------------------------|-------------|----------------------|-------|------|
| a | Ethylamine | 45 | 1.10 | ✓ | |
| b | Thiophene | 85 | 1.44 | | ✓ |
| c | Pentanal | 86 | 2.16 | ✓ | |
| d | Propanal | 58 | 2.25 | | ✓ |
| e | 2-Pentanone | 88 | 2.32 | ✓ | |
| f | Hexanone | 100 | 3.02 | ✓ | |
| g | Benzylhydrazine | 122 | 4.15 | ✓ | ✓ |
| h | Ethylbenzene | 106 | 7.26 | | ✓ |
| i | 1,4-Dimethylbenzene | 106 | 8.47 | | ✓ |
| j | Heptanone | 114 | 9.24 | ✓ | |
| k | <i>o</i> -Xylene | 106 | 10.15 | | ✓ |
| l | <i>tert</i> -Butylbenzene | 106 | 10.53 | | ✓ |
| m | 1,2,4-Trimethylbenzene | 106 | 11.51 | | ✓ |
| n | Acetic acid | 60 | 16.25 | ✓ | ✓ |
| o | Propionic acid | 74 | 17.40 | ✓ | ✓ |
| p | Isobutyric acid | 88 | 18.03 | ✓ | ✓ |
| q | Butyric acid | 88 | 18.58 | ✓ | ✓ |
| r | Isovaleric acid | 102 | 19.30 | ✓ | ✓ |
| s | Naphthalene | 128 | 20.01 | | ✓ |
| t | Valeric acid | 102 | 20.26 | ✓ | ✓ |
| u | Phenol | 94 | 22.66 | | ✓ |
| v | Heptanoic acid | 130 | 23.36 | ✓ | |
| w | <i>p</i> -Cresol | 108 | 24.36 | ✓ | ✓ |

acid ($C_{4/1}$), butyric acid ($C_{4/2}$), isovaleric acid ($C_{5/1}$), and valeric acid ($C_{5/2}$), as shown in Figures 2 and 3. The components eluted out prior to 6 min remained inseparable. By using ZBWAX for GC/MS, the peak resolution was slightly improved. GC-MS chromatograms of STR20 and RSS5 are illustrated in Figure 4. Summarized in Table II are peak assignments of volatile components of STR20 and RSS5. Each peak is labeled as a–w, ranging from short to long retention times. Benzylhydrazine (g) and low molecular weight volatile fatty acids (n–r, t) were discovered in both samples. The peaks having retention times below 6 min in GC-MS included carbonyl compounds in the form of aldehydes [i.e.; pentanal (c), propanal (d), or ketones, i.e., 2-pentanone (e), hexanone (f), and heptanone (j)]. Some nitrogen-containing compounds such as ethylamine (a) and benzylhydrazine (g) were found along with a sulfur-containing compound in the form of thiophene (b). The distinguishably smokier smell of RSS5, compared with STR20, can be explained as a result of the existence of various aromatic compounds such as ethylbenzene (h), 1,4-dimethylbenzene (i), *o*-xylene (k), *tert*-butylbenzene (l), 1,2,4-trimethylbenzene (m), and *p*-cresol (w).

Reduction of offensive odor

Low molecular weight volatile fatty acids seem to be the major causes of the pungent and rancid smell of both STR20 and RSS5. We selected acetic acid, the

compound exhibiting the highest peak intensity in both samples, as an indicator of odor intensity. The reduction of odor was monitored by following the peak corresponding to acetic acid (retention time = 6.43) by using GC analysis. To determine the capacity of odor reduction as a function of storage time, vulcanized rubber samples filled with each odor-reducing substance were analyzed weekly in comparison with the unfilled vulcanized rubber samples. It should be emphasized that it was rather difficult to quantify the exact amount of acetic acid due to inevitable limitations of the headspace sampling technique used in this particular case. Thus, the method of adding an internal standard was modified and applied to facilitate a semiquantitative analysis. A known quantity of methyl valerate used as an internal standard was added directly into sample bottles together with solid vulcanized rubber. It was assumed that roughly every bottle contained the same concentration of methyl valerate in the gas phase to begin with. The relative quantity of acetic acid was assessed by comparing its peak intensity with that of methyl valerate, with a retention time of 1.82. Throughout the period of 5 weeks, the peak intensity of methyl valerate remained relatively constant in all bottles, implying that it did not react with either the odor-reducing substance or the rubber. This also suggests that there was no measurable loss of volatile contents. This outcome helped in simplifying the data manipulation step. The relative amount of acetic acid can then be monitored

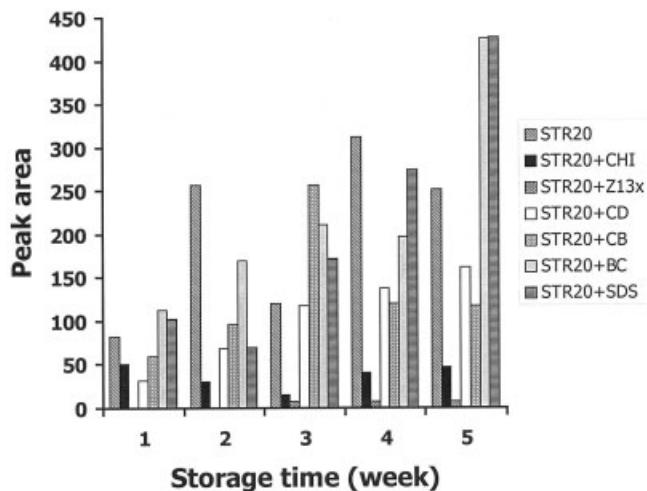


Figure 5 Average peak area of acetic acid from vulcanized STR20 filled with odor-reducing substances as characterized by GC.

directly from its peak area. Each peak area was an average from five bottles. Standard deviations of peak area data were extremely low (<2–5%), suggesting that results were quite consistent and statistically reliable. It was also found that the incubation at 60°C for 2 h is necessarily long enough for the amount of volatile components to reach the equilibrium value. The amount of odor-reducing substance incorporated was 5 phr for chitosan (CHI), zeolite13x (Z13x), carbon black (CB), and cyclodextrin (CD) and 1.5 phr for benzalkonium chloride (BC), and sodium dodecyl sulfate (SDS).

Despite the fluctuation of the peak area of acetic acid from the original STR20 (Fig. 5) and RSS5 (Fig. 6), zeolite13x and chitosan seemed to be very effective

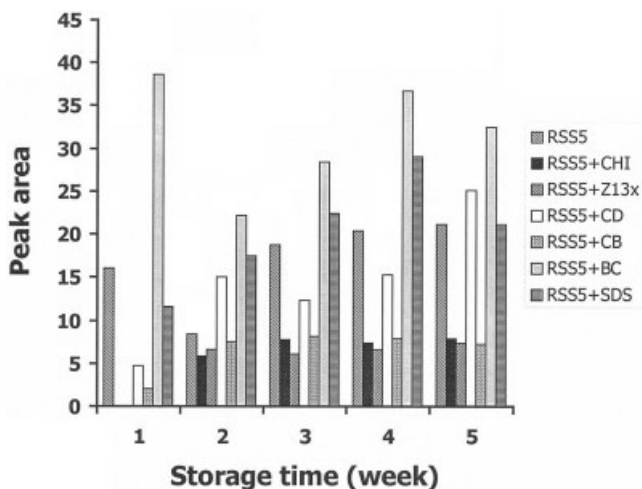


Figure 6 Average peak area of acetic acid from vulcanized RSS5 filled with odor-reducing substances as characterized by GC.

odor-reducing substances. More than 90% of the peak area disappeared within a period of 5 weeks for the case of STR20. Interestingly, the peak areas of acetic acid from rubber samples filled with zeolite13x and chitosan approached approximately the same minimum value (5–8) regardless of the difference of the original peak area; STR20 released a substantially higher quantity of acetic acid than RSS5 did. The ability of zeolite13x to reduce odor may be attributed to its suitable pore size (inner pore of 15 Å, outer pore of 7 Å) that can accommodate a molecule of acetic acid.¹⁴ The presence of amino groups renders chitosan another promising odor adsorbent. When free amino groups in the structure of chitosan become positively charged, they can form bonds with negatively charged functional groups such as carboxyl groups.¹⁵ It is quite unlikely to regard the electrostatic attraction between opposite charges as the key interaction in the solid state where the pH cannot be correctly identified. Hydrogen bonding and amide bonding between amino groups of chitosan and carboxyl groups of acetic acid are perhaps the dominant interactions that can lead to the desirable odor reduction. A minimum of 5 phr of zeolite13x and chitosan is required to achieve this effective odor reduction. Odor-reduction efficiency was not improved when larger amounts of substances were incorporated.

We initially hypothesized that as a cationic surfactant as well as an antimicrobial agent, benzalkonium chloride should be able to interact with low molecular weight volatile fatty acids, the major odorous components. However, the result turns out to be the opposite. Not only is it unable to reduce the amount of acetic acid (used as a representative odorous component in this work), but it also tends to release more of the acid as the samples were kept for a longer period of time. It is plausible that benzalkonium chloride was partially degraded during high-temperature vulcanization and/or fermented anaerobically into odorous molecules in the presence of some microorganisms along with moisture in the bottles and slowly released during storage. The same explanation is also valid for SDS. We did not encounter the problem due to deg-

TABLE III
Results of Olfactometry Test of Vulcanized STR20 Filled with Odor-Reducing Substances

| Odor-reducing substance | Percentage of olfactometry test | | | | |
|-------------------------|---------------------------------|--------|--------|--------|--------|
| | Ref. 1 | Ref. 2 | Ref. 3 | Ref. 4 | Ref. 5 |
| Sodium dodecyl sulfate | 60 | 20 | 10 | 10 | 0 |
| Chitosan | 40 | 40 | 20 | 0 | 0 |
| Carbon black | 60 | 40 | 0 | 0 | 0 |
| Cyclodextrin | 20 | 20 | 20 | 20 | 20 |
| Benzalkonium chloride | 10 | 40 | 10 | 10 | 30 |
| Zeolite13x | 20 | 50 | 30 | 10 | 0 |

TABLE IV
Results of Olfactometry Test of Vulcanized RSS5
Filled with Odor-Reducing Substances

| Odor-reducing substance | Percentage of olfactometry test | | | | |
|-------------------------|---------------------------------|--------|--------|--------|--------|
| | Ref. 1 | Ref. 2 | Ref. 3 | Ref. 4 | Ref. 5 |
| Sodium dodecyl sulfate | 40 | 20 | 20 | 20 | 0 |
| Chitosan | 40 | 40 | 20 | 0 | 0 |
| Carbon black | 40 | 40 | 20 | 0 | 0 |
| Cyclodextrin | 40 | 30 | 30 | 0 | 0 |
| Benzalkonium chloride | 20 | 10 | 10 | 30 | 20 |
| Zeolite13x | 20 | 50 | 20 | 10 | 0 |

radiation in the cases of zeolite13x, cyclodextrin, carbon black, and chitosan.

Due to its highly porous structure with a large surface area, carbon black is known to adsorb many organic chemicals that are often responsible for taste, odor, and color problems.¹⁶ It is anticipated to physically adsorb acetic acid and consequently promote odor reduction. The cyclodextrin used in this study consists of seven D-glucopyranosyl units (β) connected by α -(1,4)-glycosidic linkages. It is in the form of a toroid with the upper (larger) and lower (smaller) opening carrying secondary and primary hydroxyl groups, respectively. The interior is hydrophobic having a pore diameter of 6–7 Å. The hydroxyl groups are expected to bind with carboxyl groups of acetic acid through hydrogen bonding. Carbon black and cyclodextrin had a good tendency to reduce odor but are not as effective as zeolite13x and chitosan. A reasonable explanation may be that nonspecific physisorption by carbon black and adsorption through hydrogen bonding by cyclodextrin are not sufficiently strong to hold acetic acid molecules as opposed to absorption into the porous structure of zeolite13x and electrostatic attraction and hydrogen bonding associated with amide linkage with chitosan.

People sense odors through their noses because the odor molecule fits into a molecular receptor in their noses. It turns out that any similar chemical fitting into the slot of the receptor will be perceived as a similar smell, even though the chemical is different.¹⁷ Besides the chromatographic evidence, the effectiveness of odor reduction should be best judged by human

testers. Although the olfactometry test is highly subjective, it should be capable of justifying whether or not the offensive odor mainly originates from low molecular weight volatile fatty acids, especially acetic acid, as identified by chromatographic data. It should be noted that only 5–10 well-trained persons are generally required for the test. Because of the lack of well-trained persons for testing the odor quality, the tests were preliminary and adapted from the concept of dilution olfactometry. As many as 20 persons participated in the test to assure statistically reliable data. For each test, each person chose the reference whose odor intensity was higher than or equal to that of the sample. The results were then reported as percentages of the number of persons who selected each reference (Tables III and IV). The higher the reference number chosen, the lower the odor-reducing efficiency.

The trends are somewhat similar to those of the chromatographic data. Carbon black and chitosan are evidently the most effective odor-reducing agents. The majority (80–100%) verified that the odor intensities of both vulcanized STR20 and RSS5 filled with carbon black and chitosan were less than or equal to reference 2 (5 g/250 mL). The remainder thought that the odor intensity did not exceed reference 3 (10 g/250 mL). The ability of cyclodextrin to reduce offensive odor was, however, inconclusive; each reference was equally selected for the case of STR20, while 70% of persons agreed that the odor intensity of vulcanized RSS5 filled with cyclodextrin was less than or equal to reference 2 (5 g/250 mL). In contrast with the results deduced from GC analysis, SDS seemed to be as effective as zeolite13x in reducing the offensive odor. Again, it can be confirmed that benzalkonium chloride was the least efficient odor-reducing substance. Although the olfactometry test only partly agrees with the chromatographic indication of odor reduction, it is generally in qualitative agreement and provides supportive evidence, indicating the success of this approach.

Mechanical properties

For practical purposes, a good odor-reducing substance should be capable of reducing offensive odor

TABLE V
Tensile Properties and Hardness of Vulcanized STR20 Filled with Odor-Reducing Substances

| Odor-reducing substance | Tensile stress at maximum load (MPa) | Tensile strain at maximum load (%) | Tensile modulus (M300) (MPa) | Hardness |
|-------------------------|--------------------------------------|------------------------------------|------------------------------|----------|
| Unfilled | 22.49 ± 1.01 | 730.00 ± 44.80 | 1.98 ± 0.12 | 40.0 |
| Zeolite13x | 22.11 ± 0.58 | 736.93 ± 52.81 | 2.41 ± 0.15 | 43.7 |
| Chitosan | 21.06 ± 1.24 | 656.60 ± 21.22 | 2.74 ± 0.15 | 46.1 |
| Carbon black | 21.47 ± 0.71 | 737.63 ± 50.45 | 2.33 ± 0.18 | 41.7 |
| Sodium dodecyl sulfate | 12.40 ± 1.47 | 991.40 ± 32.37 | 1.61 ± 0.11 | 37.9 |

TABLE VI
Tensile Properties and Hardness of Vulcanized RSS5 Filled with Odor-Reducing Substances

| Odor-reducing substance | Tensile stress at maximum load (MPa) | Tensile strain at maximum load (%) | Tensile modulus (M300) (MPa) | Hardness |
|-------------------------|--------------------------------------|------------------------------------|------------------------------|----------|
| Unfilled | 23.33 ± 1.81 | 713.90 ± 55.80 | 2.33 ± 0.29 | 40.2 |
| Zeolite13x | 23.65 ± 1.55 | 764.37 ± 56.17 | 2.02 ± 0.24 | 40.2 |
| Chitosan | 21.74 ± 0.49 | 712.90 ± 13.23 | 2.41 ± 0.16 | 44.4 |
| Carbon black | 22.03 ± 0.99 | 715.45 ± 6.87 | 2.57 ± 0.08 | 40.8 |
| Sodium dodecyl sulfate | 11.34 ± 2.04 | 774.40 ± 82.99 | 1.46 ± 0.30 | 34.9 |

while maintaining the basic mechanical integrity of the vulcanized rubber. Mechanical testing was performed on vulcanized rubber filled with substances exhibiting promising odor-reducing characteristics according to GC analysis as well as the olfactometry test. The substances were chitosan, zeolite13x, carbon black, and sodium dodecyl sulfate. As shown in Tables V and VI, the tensile stress at maximum load of filled vulcanized rubber was not affected much in comparison with the unfilled rubber, except when filled with SDS. This outcome suggested that the vulcanized rubber became more ductile when SDS was added even though only 1.5 phr of the filler was incorporated. The data in both tables also highlight the strain at maximum load, which is significantly enhanced, and the subsequent reduction of tensile modulus for the rubbers filled with SDS. Chitosan, carbon black, and zeolite13x exhibited reinforcing effects on vulcanized rubber (especially in the case of STR20), which can be seen from the slight improvement of the tensile modulus. Such a relatively low filler loading (1.5 or 5 phr) was sufficient to influence the hardness to a certain extent. The vulcanized rubber was apparently tougher in the presence of chitosan but was softer in the presence of SDS.

CONCLUSION

The simple concept to reduce offensive odor from natural rubber by physical mixing of some substances during vulcanization proved to be feasible. According to the GC analysis and olfactometry test, the unpleasant odor from STR20 and RSS5 can be significantly reduced in the presence of chitosan, zeolite13x, and carbon black. Benzalkonium chloride and SDS did not exhibit the desired odor-reducing properties as a consequence of their thermal degradation during vulcanization. The ability to adsorb physically and/or chemically with the volatile fatty acids as well as their reinforcing effect indicates that chitosan and carbon black are strong candidates for odor reduction of natural rubber.

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