

# Compounding of Poly(dimethyl siloxane) to Reduce Tack in Natural Rubber

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**ABSTRACT:** Tack in natural rubber latex was reduced by compounding poly(dimethyl siloxane) (PDMS) emulsion in concentrated latex. Sheet and dipped film surfaces were examined with Fourier transform infrared spectroscopy using attenuated total reflection (FTIR-ATR) and by contact angle measurements. Autohesive tack and tensile properties were also determined. For both sheet and dipped film, FTIR-ATR showed that the PDMS concentration was higher at the glass surface than at the air surface. The contact angle of ethylene glycol on the rubber decreased with increasing PDMS content. Autohesive tack for sheet and dipped film also decreased with increasing PDMS amount; however, annealing for 1 week at 70°C in air did cause tack to rise in the sheets. The rubber surface could be made nonadhesive by addition of sufficient PDMS. PDMS caused a decrease in tensile strength for the sheet, especially after annealing; however, PDMS did not cause a substantial decrease in percentage elongation for the sheets, except at relatively high PDMS contents. The tensile strength and percentage elongation for dipped film was not affected by PDMS over the much more limited PDMS concentration range studied. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 519–526, 2001

**Key words:** tack; natural rubber; autohesion; poly(dimethyl siloxane)

## INTRODUCTION

Natural rubber (NR) is used in applications such as tires, shoes, and dipped products (gloves, condoms, baby soothers, etc.). Latex gloves were first introduced by William Halstead in 1890.<sup>1</sup> Natural rubber latex gloves are widely used to protect the skin of healthcare workers from harmful antiseptics. Latex gloves are almost always the first line of defense against infectious disease and provide an effective, protective barrier for both the healthcare professional and the patient.

Vulcanizates obtained from NR exhibit tack and, thus, not only sticky surfaces but also high surface friction. Tack is the ability of two materials to resist separation after bringing their surfaces into contact for a short time under light pressure.<sup>2,3</sup> Autohesion or autohesive tack<sup>3</sup> is a term used to describe tack between two surfaces having the same chemical identity. Autohesion is not required for some applications of NR and, in fact, is undesirable in medical gloves. Prior attempts have employed various approaches to reduce tack in rubber gloves such as coating with corn starch powder,<sup>4</sup> compounding with silicone oil,<sup>5,6</sup> halogenation of the natural rubber,<sup>6–10</sup> and polymeric coatings.<sup>11,12</sup> Each approach has disadvantages. Cornstarch powder has the unfortunate tendency to contaminate other surfaces, and

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**Table I Formulation for Vulcanized Rubber Sheet and Dipped Film<sup>a</sup>**

| Material <sup>b</sup>        | Compounded Natural Rubber Latex <sup>b</sup> |                |                |                |                |
|------------------------------|--|----------------|----------------|----------------|----------------|
|                              | CPD  | CSE 5          | CSE 10         | CSE 15         | CSE 20         |
| 60% NRL                      | 100  | 100            | 100            | 100            | 100            |
| 10% KOH                      | 0.2  | 0.2            | 0.2            | 0.2            | 0.2            |
| 35% PDMS                     | 0  | 5              | 10             | 15             | 20             |
| 50% S                        | 0.65   | 0.65           | 0.65           | 0.65           | 0.65           |
| 50% W-L                      | 0.60   | 0.60           | 0.60           | 0.60           | 0.60           |
| 50% ZEDC                     | 0.70   | 0.70           | 0.70           | 0.70           | 0.70           |
| 50% ZnO                      | 1.00   | 1.00           | 1.00           | 1.00           | 1.00           |
| 40% SDBC                     | 0.12   | 0.12           | 0.12           | 0.12           | 0.12           |
| Distilled water <sup>c</sup> | Add to 32% TSC                               | Add to 32% TSC | Add to 32% TSC | Add to 32% TSC | Add to 32% TSC |

<sup>a</sup> Each entry represents the weight of each component.

<sup>b</sup> CPD = pure compounded rubber vulcanizate; CSE = PDMS-compounded rubber vulcanizate; NRL = natural rubber latex; S = sulfur; W-L = wingstay-L (antioxidant); ZEDC = zinc diethyldithiocarbamate; SDBC = sodium dibutyldithiocarbamate; and TSC = total solid content.

<sup>c</sup> Samples for dipped film had added distilled water to get 40 wt % of total solids content.

many users have an allergic reaction to the powder. A worldwide increase in reported allergic reactions to medical products containing natural rubber latex has been reported since the early 1990s.<sup>1</sup> Silicone oil tends to bloom to the surface and give gloves an oily feel. Although halogenated rubber has a permanent slippery surface, the glove is more vulnerable to oxidation and discoloration. Finally, a polymeric coating adds working time and significant cost to manufacture.

The objective of this study was to reduce tack in NR by compounding poly(dimethyl siloxane) (PDMS) in concentrated natural rubber latex. Two types of samples were prepared, rubber sheet and dipped film. These samples were characterized by attenuated total reflectance infrared spectroscopy and contact angle measurement. Effects of PDMS content on autohesive tack determined by 180° peel test and tensile properties were investigated. The effects of aging on adhesive and tensile properties were also studied.

## EXPERIMENTAL

### Materials

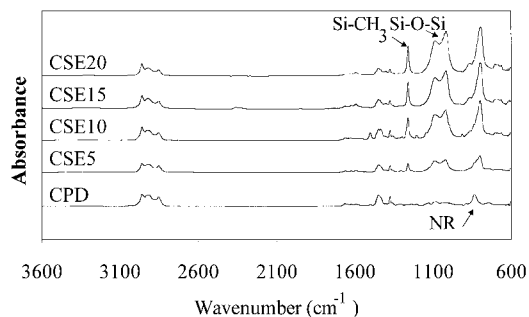
Concentrated natural rubber latex with 60% dry rubber content (DRC; Rubber Research Institute of Thailand) was compounded with PDMS as silicone emulsion [365, 35% Dimethicone National Formulary having a density of 0.99 g/cm<sup>3</sup>; Dow Corning (Thailand) Ltd.]. Sulfur was used as the vulcanizing agent. A coagulant solution of 35% calcium nitrate was used in the dipping process.

Sulfur, calcium nitrate, and other ingredients listed in Table I were supplied by the Rubber Research Institute of Thailand. For contact angle measurements, ethylene glycol (obtained from Lab-Scan Analytical Science and Baker Analyzed Reagent Co., Ltd.) was used as the liquid phase. Ethylene glycol was fractionally distilled at 200°C under nitrogen gas and stored under nitrogen gas before use.

### Preparation of Rubber Samples

Samples were prepared in two forms, sheets and dipped films. Compounded natural rubber latex (CNRL) was formed by thoroughly mixing each material in the amounts shown in Table I, and then maturing for about 3 days. For spectroscopic studies and contact angle measurements, sheet samples were prepared by pouring 1.2 g into a glass petri dish (15 × 60 mm). They were dried at 60°C and vulcanized at 100°C for 10 min prior to surface characterization. For peel and tensile tests, 150- and 65-g samples of CNRL were poured onto glass plates of 9 × 12 and 6 × 6 in., respectively. The thickness of all sheet samples was approximately the same, to minimize any issues with respect to drying time and so forth. Sheets were dried at room temperature and vulcanized at 100°C for 10 min.

For the dipping process, a clean glass tube (the former) was immersed into 35% calcium nitrate, allowed to dry at room temperature, and then immersed into CNRL for 15 s. Dipped films (0.18–0.20 mm) were substantially thinner than sheets



**Figure 1** FTIR-ATR spectra of vulcanized rubber sheets with and without PDMS exposed to glass petri dish (inside).

(0.88–1.00 mm) and thus drying times were considerably shorter. The dipped films were also vulcanized at 100°C for 10 min.

Samples were aged by annealing in an oven at 70°C for 7 days in air.

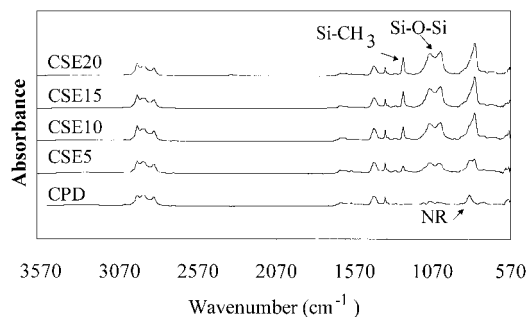
### Characterization

Both sheets and dipped films were examined with a Fourier transform spectrometer (Bruker Equinox 55 with DTGS detector) equipped with attenuated total reflection (FTIR-ATR). Zinc selenide crystal (refractive index 2.4) was used to give a total of 16 reflections; for this geometry and angle (45°) the approximate penetration depth was 1.6 microns at 1000  $\text{cm}^{-1}$ . Contact angle measurements were performed using a 20- $\mu\text{L}$  ethylene glycol drop, photographed by Nikon FM2 camera after 3 min of contact. The image was scanned into a computer and the angle was measured by using Photoshop version 5.0. Three drops were measured and the average value was reported.

Thermogravimetry (TG; PERKIN ELMER 7) and scanning electron microscope with electron dispersive detector (SEM-EDS; JEOL 6400 with LINK ISIS) were applied to investigate the degradation of the samples. Samples were heated from 50 to 850°C at a rate of 20°C/min.

To perform a T-peel test, two pieces of rubber samples were backed with cotton cloth and then compressed at 30 and 1.5 tons, respectively, for 10 min. The width of the samples was 25 mm, whereas the gauge lengths were 80 and 25 mm for sheet and dipped films, respectively. A Lloyd LR5K (JJ Lloyd) was used to measure force at a crosshead speed of 254 mm/min. Aging was performed before the material was pressed together.

Tensile tests were performed following ASTM D638 with a dogbone-shaped specimen. The Lloyd LR5K tensiometer was used at a crosshead speed of 500 mm/min and a gauge length of 25 mm.



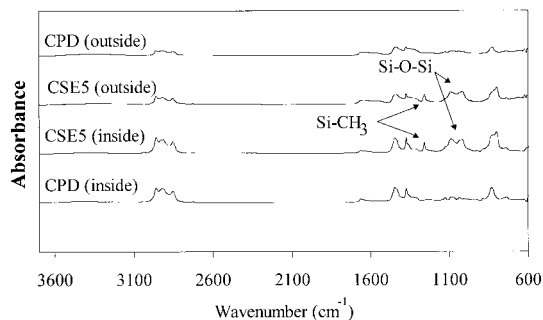
**Figure 2** FTIR-ATR spectra of vulcanized rubber sheets with and without PDMS exposed to air (outside).

## RESULTS AND DISCUSSION

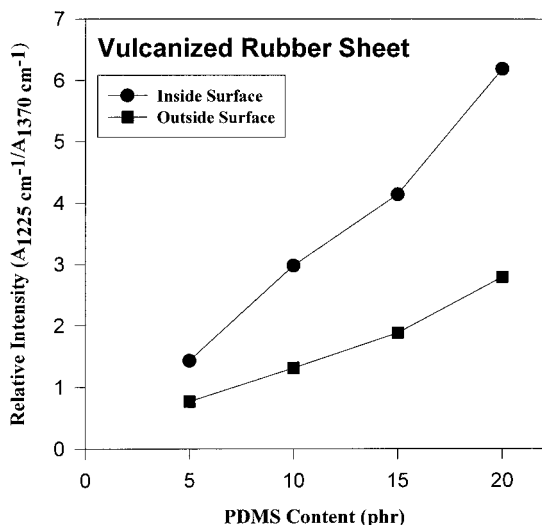
### Spectroscopic Study

Both sides of the rubber surface were characterized by FTIR-ATR. Only the region between 600 and 2000  $\text{cm}^{-1}$  is shown, given that the higher wavenumber region of the mid-IR spectra contained no useful information. The two peaks between 1000 and 1100  $\text{cm}^{-1}$  and the one peak at 1225  $\text{cm}^{-1}$  are assigned to Si-O and Si-CH<sub>3</sub> bonds, respectively. Figure 1 shows the inside spectra for the sheet, that is, the surface exposed to the glass petri dish, whereas Figure 2 shows the spectra for the sheet exposed to air. Figure 3 shows spectra for both the inside and outside surfaces of the dipped film.

The surface excess was characterized semi-quantitatively by comparing the peak area at about 1225  $\text{cm}^{-1}$  to the peak area at 1370  $\text{cm}^{-1}$ , characteristic of the C-H bending mode in the methyl group. The results for the rubber sheets are shown graphically in Figure 4. The concentration of PDMS is higher on the inside surface than that on the outside surface, presumably because of the strong affinity of PDMS to glass. Both con-



**Figure 3** FTIR-ATR spectra of vulcanized rubber-dipped films with 5 phr PDMS and without PDMS for both inside and outside surfaces.



**Figure 4** Relative intensity of FTIR-ATR absorption bands for vulcanized rubber sheets with and without PDMS.

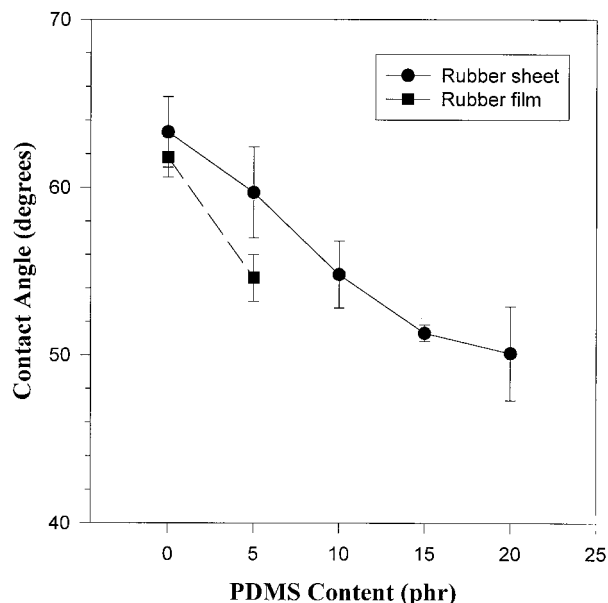
centrations are linear with the PDMS bulk concentration, indicating that coverages are not near saturation. Unfortunately, the relative absorption coefficients of the two bands are not known, so the absolute amount of PDMS at the surface cannot be determined; however, the inside most likely has an excess of PDMS at the surface. Thus, the inside surface of the rubber piece was chosen for the later study of surface adhesion.

### Contact Angle Measurement

Static contact angles shown in Figure 5 were determined by using drops of ethylene glycol placed on the inside of the rubber sample surfaces. For both sheets and dipped films, the contact angle decreased with increasing PDMS bulk content, indicating that the amount of PDMS at the surface increased, consistent with FTIR-ATR results. Usually, a more slippery surface shows a higher contact angle than a high-friction surface; however, this generalization depends on the chosen liquid for contact angle measurement. In this case, the decrease of contact angle is attributed to the adhesion between hydroxyl groups of ethylene glycol and oxygen atoms in PDMS.

### T-Peel Test and Aging Effect

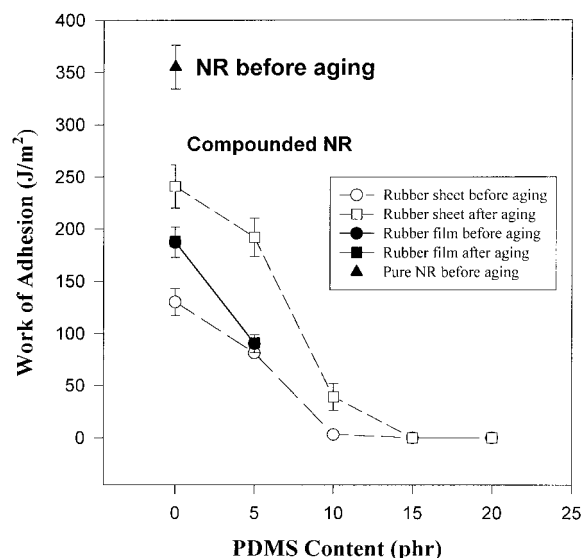
The autohesive tack for the inside surfaces was determined by T-peel test. Results before and after aging are shown for sheets and dipped films in Figure 6. The pure NR sheets show very high autohesion; after vulcanization, a significant re-



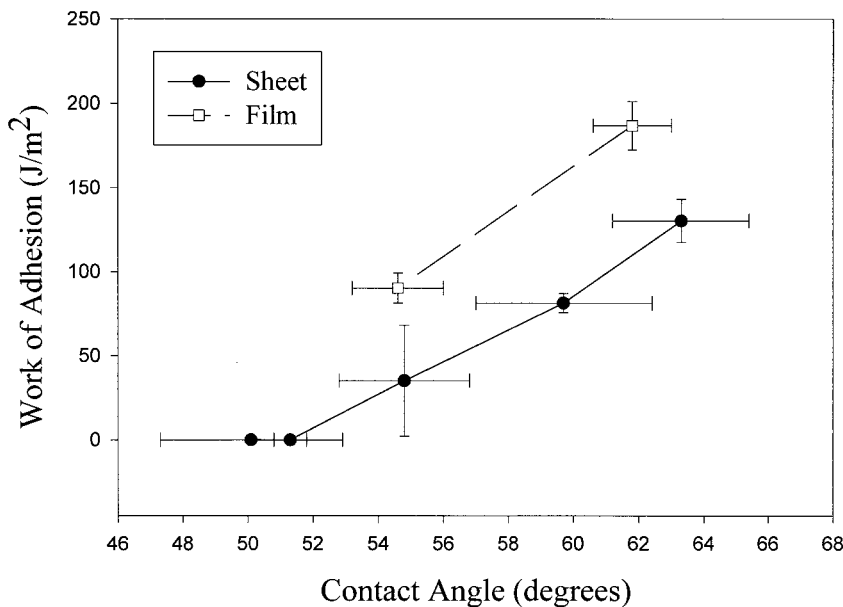
**Figure 5** Contact angle of the inside surfaces of vulcanized rubber sheets at various PDMS contents.

duction in adhesion occurs primarily as a result of crosslinking, which limits molecular motion.<sup>8,13</sup> When the silicone emulsion was added to the compounded NR, adhesion energy was reduced substantially, as shown in Figure 6.

Figure 7 replots the data in Figure 6 in a different form and shows that the work of adhesion in the dipped film shows higher peel strength



**Figure 6** Work of adhesion versus PDMS content for the vulcanized rubber sheets (open symbols) and dipped films (filled symbols) before and after aging (the filled symbols are overlapped).



**Figure 7** The relationship between work of adhesion and contact angle for the vulcanized rubber sheets and dipped films before aging.

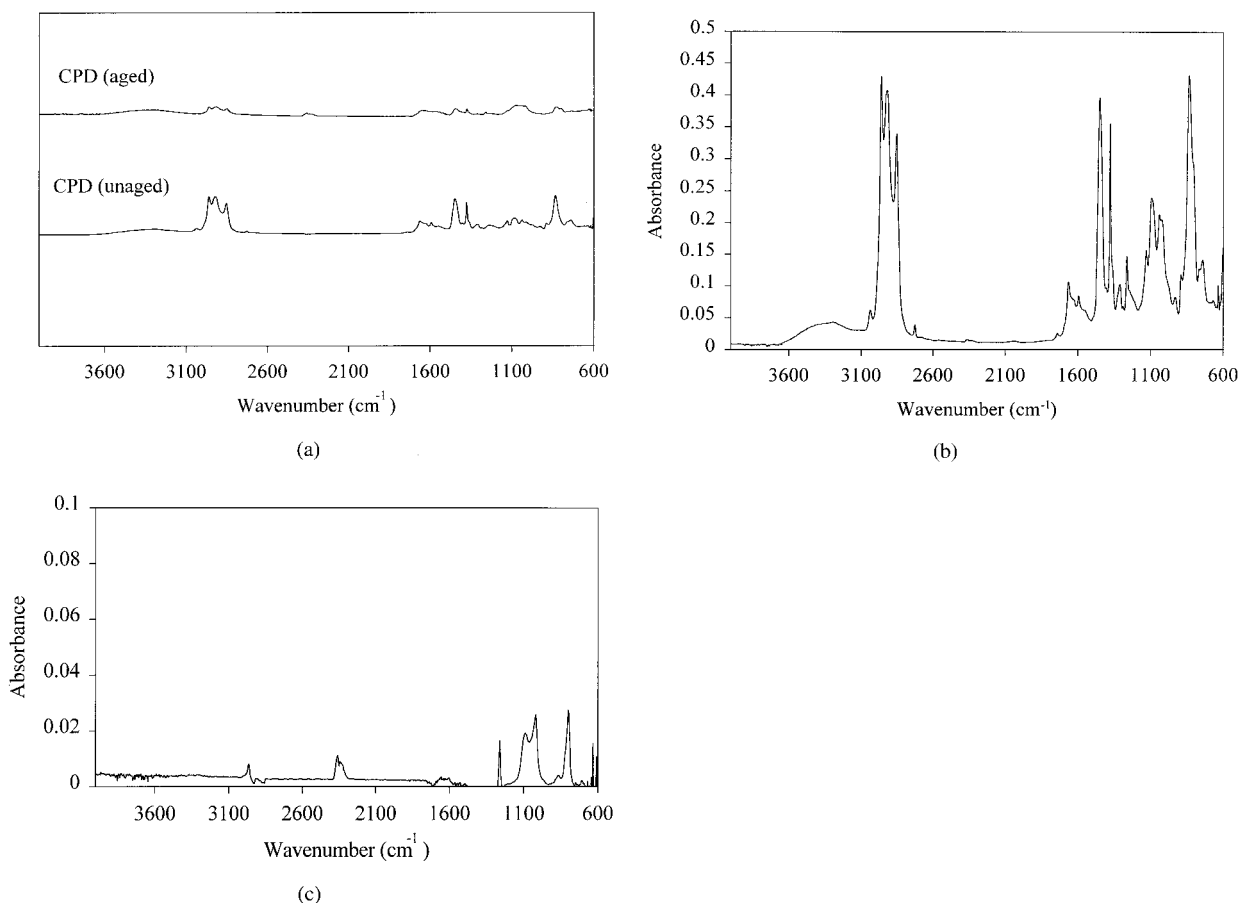
than the sheet film, even when the contact angles are equivalent. Generally, adhesion depends on thickness; the thinner film exhibits higher peel strength because it is more prone to plastic deformation and stretching.<sup>14</sup> However, the adhesions of compounded rubber with 5 parts per hundred (phr) silicone emulsion are almost identical for both sheet and film. In other words, film adhesion is comparable with sheet adhesion because there is a much larger drop of adhesion for the rubber film after the addition of PDMS. The reason for this agreement is that substantially more PDMS is at the interface in the film versus that in the sheet, as clearly demonstrated by the much larger reduction in contact angle in the film. Clearly, PDMS can reduce tack in the film more efficiently than in the sheet. However, even in the sheet PDMS is quite effective in reducing tack; only 5 phr of the silicone emulsion was necessary to lower the surface adhesion by half and only 10 phr silicone was necessary to totally eliminate tack in the sheet.

The effect of aging was surprising. The work of separation for CPD, CSE5, and CSE10 rose significantly after aging, but no peel load was detected at higher PDMS contents, even after aging. One possibility to explain the increase of adhesion upon aging is that NR is oxidized under these conditions, and oxidation forms functional groups that increase tack. Because PDMS is not oxidized, the effect of aging was reduced or eliminated at

high PDMS contents as a consequence of increased PDMS contents at the surface. However, aging did not cause any new absorption bands of oxygen-containing moieties to appear in ATR-IR spectra shown in Figure 8(a)–(c), indicating that oxidation was probably not the cause of any increase in work of separation with aging. To confirm our rejection of an oxidation effect, thermogravimetry was applied to investigate the decomposition of aged and unaged samples. As illustrated in Figure 9, aged and unaged CPD and CSE5 show the same thermograms and there was no oxidation trace at 70°C. This experiment supports the conclusion that oxidation did not occur and was not the reason for the increase in the work of separation.

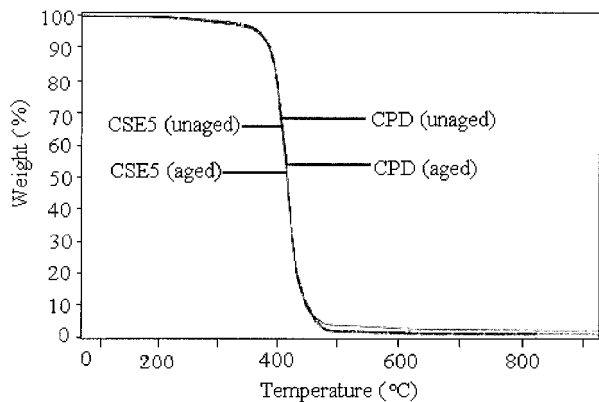
Surface elemental analysis obtained from SEM with energy-dispersive spectroscopy is shown in Tables II and III for unaged and aged compounded sheets with and without PDMS. After aging there was a reduction in both sulfur and oxygen content at the surface for the rubber with no PDMS. This result suggests a diffusion of uncrosslinked hydrocarbon molecules to the surface of the rubber. Thus, one explanation for the increase in work of adhesion with aging is that mobile rubber segments/molecules (e.g., small rubber molecules or other unsaturated hydrocarbon ingredients) provide high surface energy and good adhesion. In the case of rubber with 5 phr PDMS emulsion, the results reveal that after ag-

Absorbance



**Figure 8** FTIR-ATR spectra for the inside surface of the vulcanized rubber sheets (CPD) (a) before and after aging, (b) with 5 phr PDMS (CSE5) before aging, and (c) with 5 phr PDMS (CSE5) after aging.

ing the amount of PDMS at the surface increased substantially. In the case where PDMS was blended with rubber, PDMS that diffused to the



**Figure 9** Thermograms of the vulcanized rubber sheets without PDMS (CPD) and with 5 phr PDMS (CSE5) before and after aging.

surface interfered with the mobile hydrocarbons, and the increase of adhesion with aging was reduced. When more PDMS was added (10 phr), enough PDMS molecules were present at the surface to totally suppress the increase of adhesion after aging.

For the dipped film, the work of adhesion did not change after aging presumably because diffu-

**Table II** Elemental Content of Unaged and Aged Rubber Sheets from SEM

| Element | Unaged CPD  |            | Aged CPD    |            |
|---------|-------------|------------|-------------|------------|
|         | Element (%) | Atomic (%) | Element (%) | Atomic (%) |
| C       | 58.96       | 66.42      | 63.76       | 70.54      |
| O       | 37.51       | 31.73      | 33.92       | 28.17      |
| Na      | 2.08        | 1.22       | 1.99        | 1.15       |
| S       | 0.21        | 0.09       | 0.05        | 0.02       |

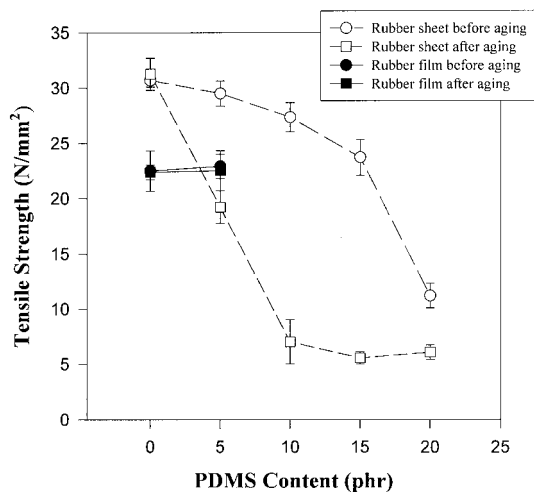
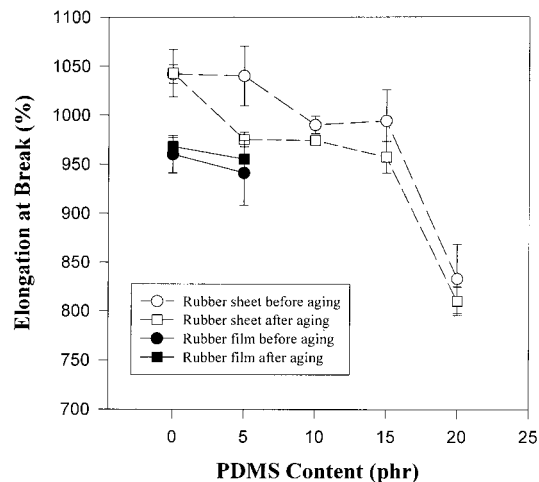
**Table III** Element Content of Unaged and Aged CSE5 from SEM

| Element | Unaged CSE5 |            | Aged CSE5   |            |
|---------|-------------|------------|-------------|------------|
|         | Element (%) | Atomic (%) | Element (%) | Atomic (%) |
| C       | 70.04       | 75.76      | 65.09       | 71.52      |
| O       | 29.66       | 24.09      | 33.89       | 27.96      |
| Si      | 0.19        | 0.09       | 0.29        | 0.13       |
| Na      | 0.10        | 0.06       | 0.57        | 0.32       |
| S       | 0           | 0          | 0.11        | 0.04       |

sion of PDMS and hydrocarbon molecules to the film surface is completed during the curing step. This finding is beneficial for the glove industry because PDMS-compounded NR gloves should have tack properties that do not vary with time.

### Tensile Test

As demonstrated by Figure 10, PDMS decreased the tensile strength for aged and unaged sheets. The dipped film has lower strength than the sheets because of the smaller rubber content. Most dramatically, the tensile strength of aged sheets with PDMS decreases considerably compared to that of the unaged sheets. Aging probably forced more phase mixing between the PDMS molecules and the bulk rubber phase, and the rubber was softened and weakened. Unlike the case for the rubber sheet, tensile strength was not

**Figure 10** Effect of PDMS content on tensile strength for the vulcanized rubber sheets and dipped films before and after aging.**Figure 11** Effect of PDMS content on elongation at break for the vulcanized rubber sheets and dipped films before and after aging.

strongly affected after aging for the dipped film. This result suggests that diffusion and phase mixing were complete for the dipped film during the curing step, which agrees with the results from the work of adhesion.

Figure 11 shows the elongation at break of rubber sheets and dipped films before and after aging. Elongation at break of the rubber sheet decreases only slightly, except at very high PDMS contents. In other words, elongation at break is not very sensitive to a plasticizing effect caused by PDMS. Elongation at break is almost unaffected by aging.

### CONCLUSIONS

1. From spectroscopic studies, PDMS is found on both sides of the rubber surface, that is, the surface facing glass and the surface facing air. The surface facing glass has significantly more (almost twofold) PDMS than the surface facing air.
2. Autohesive tack decreased as PDMS content increased, consistent with contact angle measurements. At 15% phr PDMS emulsion, the autohesive tack in the sheet was essentially zero. Moreover, PDMS was more effective at reducing tack in film samples than in sheet samples.
3. Tensile strength decreased substantially with increasing PDMS amount. The tensile strength was even smaller after aging, presumably as a result of more mixing of

PDMS with the bulk rubber. The elongation at break decreased slightly, except at very high PDMS contents where the elongation at break decreased substantially.

4. Aging causes diffusion of mobile hydrocarbons and PDMS to the surface in sheets. At lower levels of PDMS, an increase in tack with aging occurs, whereas at high PDMS contents no increase in tack with aging was found. Oxidation attributed to aging was not observed. An aging effect on the film is hardly noticeable.

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