Silica as Reinforcing Filler in a Polydimethylsiloxane Elastomer

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Abstract: Silica and sodium silicate solutions were blended into samples of hydroxy-terminated polydimethylsiloxane (PDMS) emulsions, which were then end linked into elastomeric networks. The equilibrium stress-strain isotherms measured in elongation show that silica greatly increased the ultimate properties of the elastomers and were thus effective reinforcing fillers. At high elongation, the reduced stress for the filled elastomer showed downturns due to debonding between polymer and filler, and upturns due to strain-induced crystallization. The energy for rupture (Er) at high filled elastomer was higher than that of the low one.

INTRODUCTION

One of the standard fillers used to reinforce elastomeric materials is silica (SiO$_2$).\textsuperscript{1–3} It has excellent reinforcing capabilities, and there is a great deal of literature on this aspect of its behavior and on a number of its other physical properties as well. The polymer chain ends are terminated with silanol, and the weight-average molecular weights are $2 \times 10^6$ g mol$^{-1}$. Weight-average particle sizes are approximately 0.3 nm.\textsuperscript{24}

The dispersion is prepared by blending the PDMS emulsion with silica (aerosil 130, particle size: 16 nm) and a 45% sodium silicate solution.
The organotin compound is used as a curing catalyst, di-occtyltin-dilaurate (DOTDL). The catalyst reacts in alkaline medium with water-soluble silicate at ambient temperature:

$$ (R'-COO)_2SnR_2 + OH \xrightarrow{\text{OH}} (R'-COO)SnR_2 + RCOO^- $$

(1)

$$ (R'-COO)SnR_2 + Si(OH)_4 \xrightarrow{\text{OH}} (R'-COO)SnR_2 + Si(OH)_3 $$

(2)

$$ (RCOO)SnR_2 + H_2O \xrightarrow{0Si(OH)_3} (RCOO)SnR_2 + OH $$

The formed silastannoxanes are more hydrophobic and therefore migrate to the oil-water interface, where they condense with silanol groups present on the surface of the PDMS emulsion:

$$ CH_3 \xrightarrow{\text{SiOH} + R_2SnOSi(OH)_3} CH_3OOCR $$

$$ CH_3 \xrightarrow{\text{SiOSi(OH)_3} + (R'-COO)SnR_2} CH_3OH $$

(3)

It is assumed that polymers with short, i.e., monomeric or dimeric, terminal silicate groups migrate into the interior of the PDMS emulsion where they cause crosslinking with the oil phase. Polymers with longer terminated silicate groups are solvated by water thereby causing steric and ionic stabilization of PDMS particles at the interface. Vulcanization is thus already terminated prior to the evaporation of water.

The stabilizing effect is destroyed upon evaporation of water, and silica and siloxane molecules now come in close contact with each other. Hydrogen bonding is the last step in the formation of the elastomeric network. The degree of reinforcement for the increasing SiO$_2$ filler contents is determined from equilibrium stress-strain measurements in elongation.$^6$-$^9$

**EXPERIMENTAL**

**Materials**

The PDMS emulsion was purchased (Dow Corning Corp.) as was the catalyst, di-occtyltin-dilaurate (M and T Chem, Inc.), as well as the sodium silicate solution (Fisher Sci., Co.), which was used to adjust the PH. Amorphous silica used to reinforce the elastomer, was blended into PDMS emulsion.

Preparation of elastomer and filled elastomer: The unfilled elastomer of PDMS emulsion was blended with DOTDL and the sodium silicate solution was added to adjust the PH to about 11.

The filled systems were blended with silica according to above procedure. The mixture was cast into a mold and cured for a couple of days. The sheets, which were 1.5mm thick, were pressed with a hand press. After 20 days of curing, test strips approximately 3mm x 50mm, were cut from the sheets.$^6$-$^9$ The compositions of the mixture used are given in Table 1.

**Effect on Swelling**

The weighed strips were placed into a n-heptane until swelling equilibrium was achieved, approximately 4 days. After maximum swelling, the strips were weighed carefully and then dried under vacuum to a constant weight. The volume fraction of polymer ($V_p$) in the swollen

<table>
<thead>
<tr>
<th>Table 1. The Compositions of the Mixture</th>
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<tbody>
<tr>
<td>Sample Ingredient</td>
</tr>
<tr>
<td>PDMS Emulsion</td>
</tr>
<tr>
<td>DOTDL</td>
</tr>
<tr>
<td>Sodium Silicate Solution</td>
</tr>
<tr>
<td>Silica</td>
</tr>
</tbody>
</table>

$^*$R.Q : Required Quantity.
filled systems was then obtained.\textsuperscript{11}

**Stress-Strain Measurements**

Equilibrium stress-strain data were obtained in the usual manner,\textsuperscript{11–13} on the unswollen samples at 25°C.

Measurements were made using a sequence of increasing values of the elongation or relative length, L of the sample, with frequent inclusions of values out of sequence to test for reversibility. Two elastomeric properties were of interest: Nominal stress, given by $f' = f/A'$, where $f$ is the elastic force and $A'$ the undeformed cross-sectional area, and the reduced stress or modulus defined by $(f') = f'/(\alpha - \alpha^2)$, where $\alpha = L/L_0$ is the elongation or relative length of the sample. The measurements were carried out to the rupture points.

**RESULTS AND DISCUSSION**

The degree of swelling is usually expressed in terms of its reciprocal, and the volume fractions ($V_f$) in the filled system are shown in the second column of the Table 2. $V_f$ values increase with increasing SiO$_2$ content which for a high crosslink density means a greater restraint on the network and thus results in lower swelling.\textsuperscript{10} The equilibrium stress-strain isotherms obtained on the network were represented as plots of the modulus versus reciprocal elongation, as suggested by the Mooney-Rivlin equation.\textsuperscript{8,14}

**Table 2. Filler Concentrations and Stress-strain Results**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_f$</th>
<th>$2C_1$ (N mm$^{-3}$)</th>
<th>$2C_2$ (N mm$^{-3}$)</th>
<th>$\alpha'_r$ ($f'/A'_r$)</th>
<th>$10^2 \varepsilon_r$ (J mm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>0.04</td>
<td>0.0025</td>
<td>11.0</td>
<td>0.06</td>
<td>0.30</td>
</tr>
<tr>
<td>S-2</td>
<td>0.08</td>
<td>0.035</td>
<td>0.032</td>
<td>6.0</td>
<td>0.23</td>
</tr>
<tr>
<td>S-3</td>
<td>0.11</td>
<td>0.074</td>
<td>0.062</td>
<td>3.5</td>
<td>0.28</td>
</tr>
<tr>
<td>S-4</td>
<td>0.14</td>
<td>0.08</td>
<td>0.19</td>
<td>6.0</td>
<td>0.63</td>
</tr>
<tr>
<td>S-5</td>
<td>0.17</td>
<td>0.13</td>
<td>0.18</td>
<td>4.5</td>
<td>0.75</td>
</tr>
</tbody>
</table>

$\alpha'_r$ Mooney-Rivlin constants, ultimate properties and energy required for rupture.

\[(f') = 2C_1 + 2C_2 \alpha^{-1} \] (4)

where $2C_1$ and $2C_2$ are constants independent of elongation $\alpha$.

The former is an approximation to the high deformation modulus,\textsuperscript{11} and the latter is a measure of the increase in nonaffineness with increase in elongation.\textsuperscript{12,13}

Typical results for the filled network systems are shown in Figure 1. The curves are approximately linear at moderate elongation. Non-linearity at low elongation is due to strong bonding between polymer and filler for higher filler concentration and at higher elongation is due to strain-induced crystallization.\textsuperscript{15,17} The upturns in $(f')$ arising from the reinforcing

![Fig. 1. Stress-strain isotherms at 25°C for the silica-filled PDMS networks, represented as the dependence of the nominal stress or modulus on reciprocal elongation. The open circles locate the results, obtained using a series of increasing values of elongation, and the filled circles the results obtained out of sequence to test for reversibility. Each curve is labelled with the wt. % filler present in the networks, and the vertical dashed lines locate the rupture points.](image-url)
effects of the fillers are preceded by downturns presumably arising from the straightening and aligning of the network chains in the (oriented) crystallites. The decrease in modulus just prior to the upturns, may indicate that the debonding that is occurring between filler and polymer is complete. Values of the elongation constants $2C_1$ and $2C_2$ obtained from least-squares analysis of the linear portions of the isotherm are given in columns three through four in Table 2.

The modulus greatly increases with an increase in the silica content. For the sample having the largest SiO$_2$ content, the increase in modulus was 13 times larger than that of the unfilled sample. This is similar to the amount of reinforcement obtained from in-situ precipitated SiO$_2$ and TiO$_2$. The same equilibrium stress-strain data are shown as plots of the nominal stress versus elongation in Fig. 2.

The advantage of this representation is that the area under each curve represents the energy $E_r$ required for rupture, which is a standard measure of toughness. Values of the $\alpha_r$, and nominal stress ($f/A^*$), at rupture and $E_r$, obtained from the isotherms, are given in the last five through seven columns in Table 2.

Although $\alpha_r$ is relatively constant in filled systems, both ($f/A^*$) and $E_r$ increase with increasing SiO$_2$ content, as expected.

**CONCLUSION**

The equilibrium stress-strain isotherms measured in elongation show that silica greatly increased the ultimate properties of the elastomers and were thus effective reinforcing fillers. $V_f$ values increase with increasing SiO$_2$ content which for a high crosslink density means a greater restraint on the network and thus results in lower swelling in n-heptane. Non-linearity at low elongation is due to strong bonding between polymer and filler for higher filler concentration and at higher elongation is due to strain-induced crystallization. The energy for rupture($E_r$) at high filled elastomer was higher than that of the low one.

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