Structure and Properties of Precipitated Silica Filled Silicone Rubber

심 상 은

1. Introduction

Studies of the effect of solid fillers in elastomers are of much importance in scientific and engineering points of view. Fillers impart enhanced physical and chemical performances to elastomeric materials. Carbon black and silica are the most frequently used fillers.

Understanding the rheological properties of reinforcing filler-containing composiltes is of great interest since the filler particles enormously change the viscoelastic behaviors of these materials. Filled polymers exhibit a diversity of steady state rheological properties,[1-6] including a shear-thinning (thixotropic) viscosity where the degree of shear thinning increases with filler concentration,[3,4] and an apparent yield stress.[7] Also, understanding the interaction mechanism between the incorporated filler and matrix polymer is a key to exploring the source of reinforcement by the filler. Fumed silica/silicone (polydimethylsiloxane: PDMS) has been the choice for such studies due to the formation of the strong hydrogen bonds between filler particles-matrix and filler-filler particles.[8-12] Due to the strong interaction, the tensile strength of siloxane polymers is increased by a factor as high as 40 by the addition of special silica fillers. This is certainly outstanding compared to a factor of 10 with SBR, NBR, polybutadiene, and polyisoprene and of less than 2 with NR, neoprene, and butyl rubber.[13]

Although precipitated silica in PDMS has been widely utilized[14] in order to achieve moderate reinforcement with a reduced production cost, instead of fumed silica, to the best of our knowledge the rheological characteristics of the system has not been reported. Therefore, the purpose of this work is to investigate the reinforcing capability of precipitated silica in uncured PDMS by means of rheological methods.

2. Experimental

The precipitated silica, Hi-Sil[®] 132 (PPG Industries), was incorporated in PDMS, SE 64 (General Electric Company, Mw = 4.14x10^5 and Mn = 2.34x10^5 g/mol) in the concentration range of 0 to 0.16 volume concentration (0 to 40 phr) by a Moriyama mixer having a chamber capacity of 3 L at room temperature. PDMS was first added in the mixing chamber and softened for 1 minute without filler. Half the amount of filler was added in PDMS

심상은

2002 미국 The University of Akron, 고분자공학과 박사 졸업
2004~ 인하대학교 화학공학과 교수
현재 (전임강사)
실리콘/실리카 System composite
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재료응용
Carbon Nanotube/고분자 composite
Emulsion, Pigment Dispersion
Technology

and after 3 min, the rest was added and mixed for 7 min at room temperature. In order to enhance the dispersion of filler, the silica filled PDMS compounds were further homogenized by a two-roll mill (Dependable Rubber Machinary Co.) at room temperature for 3 minutes. The enhanced dispersion of the filler was confirmed by SEM microphotographs after curing. Vulcanizates of unfilled and precipitated silica filled PDMS were prepared using 0.5 phr dicumyl peroxide (DCP), LUPEROX® 500R (Pennwalt Corp.), was added to compounds on the two-roll mill at 25℃. After mixing, the compounds were pre-cured by a compression molding press (Wabash) in 260 x 260 x 12 mm³ slabs at 170℃ and then post-cured in a ventilated oven at 200℃ for 2 hours. A scanning electron microscopy (SEM: model Hitachi S-2150) was employed.

Bound rubber content (BDR) was measured using benzene ad the solvent in Soxhlet apparatus with a cellulose thimble. A Monsanto Processability Tester (MPT) was used for the rheological study at a steady state. Capillaries of diameter D = 1.51 mm and various length/diameter ratios L/D = 5, 10 and 20 were used. For the measurement of dynamic properties of the compounds, Advanced Polymer Analyzer (APA) 2000 (Alpha Technology®) with biconical die having 20.63 mm radius and 0.125 radian cone angle was employed. The properties were measured in both frequency and strain sweep modes. The temperature settings used for the both MPT and APA were 80, 130, and 180℃.

3. Results and discussion

Figure 1 represents the dependence of fraction of bound rubber on filler concentration. The amount of bound rubber is strongly related to the interaction between filler and matrix polymer, the surface area of the filler, the solubility of the extraction agent, molecular weight of the matrix polymer, the con-

centration of filler in compound, and the extraction time and temperature The bound rubber content is 53.7 % at □ = 0.047 and continuously increases up to 60.0 % at □ = 0.160. In the case of fumed silica. Southwart[15,16] found bound rubber content up to 90 % at filler concentration of □ = 0.06 in PDMS-silica unvulcanized mixes. Vondracek and Schatz reported the bound rubber content in the range of 93-97 %. However, after remilling they found 78-85 % bound rubber.[17] Aranguren and co-workers[18] reported that the concentration of adsorbed PDMS per unit weight of fumed silica was independent of the concentration of the fumed silica in the range of □ = 0.09 to 0.15 (20 - 40 phr). They also calculated the thickness of the layers of adsorbed PDMS as follows:

$$thickness(nm) = \frac{mass\ of\ adsorbed\ polymer\ (g)}{mass\ of\ silica\ (g)} \times \frac{1}{\rho_{polymer}} \times \frac{1}{S_P} \times 1000$$

(1)

where $\rho_{polymer}$ is the density of the bulk PDMS in cm³/g and S_p is the BET surface area of the silica in m²/g.

The thickness of the layer calculated based on the present measurements is given in Table 1. Clearly,
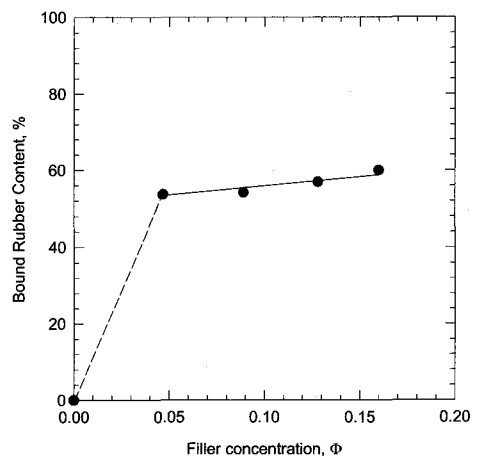

Figure 1. Bound rubber content vs. filler concentration in precipitated silica/PDMS compounds.

Table 1. Thickness of the adsorbed PDMS layer obtained from bound rubber measurement.

Filler Concentration, ϕ	Thickness, nm
0	0
0.05	27.4
0.09	13.8
0.13	9.7
0.16	7.6

the thickness continuously decreases with increasing filler concentration. This might be understood by the existence of aggregates. At higher concentration of filler, more the aggregates are created. Therefore, it is more difficult for polymer chains to penetrate into the filler aggregates resulting in incomplete wetting. Finally, the average layer thickness of adsorbed PMDS would decrease. Swelling of filled vulcanizates is suppressed by the presence of the filler.

From the Kraus constant measurement (to be discussed in the presentation) one can conclude that stronger interaction exists in PDMS-precipitated silica system than in carbon black-rubber systems and weaker interaction than in PDMS-fumed silica system.

Figure 2 shows a representative flow curve for PDMS filled with various amount of precipitated silica measured at several temperatures. The following modified Cross model[19,20] was used to fit the shear viscosity of the unfilled and silica filled PDMS:

$$\eta = \frac{\eta_0(T)}{1 + (\eta_0 \dot{\gamma}/\tau)^{1-n}} \qquad (5)$$

with $\eta_0(T)$ based upon an Arrhenius-type dependence

$$\eta_0(T) = A \exp\left(\frac{T_b}{T}\right) \qquad (6)$$

That is, η_0 denotes the zero-shear-rate viscosity, with T_b being a measure of the temperature sensitivity of viscosity and τ characterizing the shear-stress level at which η is in transition between the Newtonian limit η_0 and the power low reason. The fitting results (lines in Figure 2) of parameters in above equations are given in Table 2. It can be seen that the fitting is very good, indicating that the proposed modified Cross model can well describe the flow behavior of unfilled and precipitated silica filled silicone rubber. In Table 2, it is seen that T_b values, as a measure of sensitivity of material viscosity to temperature, increases as filler concentration increases. This implies that higher activation energy is needed to make PDMS molecules to flow at higher
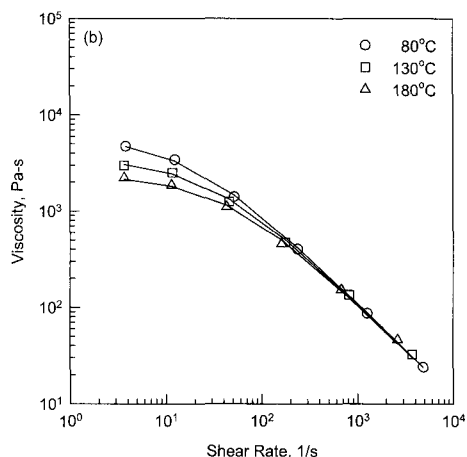
Figure 2. Temperature dependence of PDMS compounds filled with 20 phr of precipitated silica (ϕ = 0.047). Lines are obtained by fitting based on modified Cross model (see text).

Table 2. Fitting parameters for modified Cross model for precipitated silica/PDMS compounds.

Filler Concentration, ϕ	A, Pa·s	T_b, K	τ, Pa	n
0	104.5	1279	22390	0.31
0.047	95.9	1448	99000	0.08
0.089	168.2	1542	78980	0.09
0.128	435.5	1629	84130	0.09
0.160	613.5	1750	94160	0.09

filler content. In addition, n values decreases in filled rubber meaning that filled rubber shows more shear thinning behavior than unfilled rubber in the range of shear rate studied.

Figure 3 depicts comparison of the apparent viscosity versus shear rate obtained using MPT (open symbols) and complex dynamic viscosity versus frequency obtained from APA 2000 (filled symbols) for unfilled and precipitated silica filled PDMS at 80℃. It is noted that the complex viscosity for unfilled PDMS is identical to apparent viscosity at $\omega = \gamma$ indicating that Cox-Merz rule is satisfied.[21] However, with increasing filler concentration, complex dynamic viscosity becomes higher than the apparent viscosity. Cox-Merz rule is no longer valid. This is typically observed in particle filled polymer melts.[22]

At $\square$ = 0.128 and 0.160, the Newtonian region in viscosity is not observed, instead, viscosities are increasing as frequency decreases showing an apparent yielding phenomenon. Yield stress is well observed in fumed silica/PDMS systems due to strong interaction between polymer and filler. One
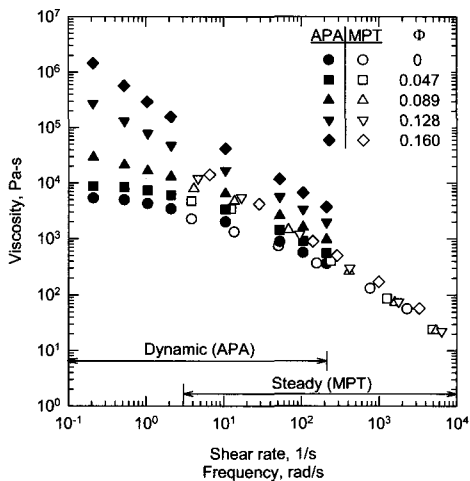

Figure 3. Steady state viscosity (open symbols) and complex dynamic viscosity (solid symbols) of precipitated silica/PDMS compounds at 80℃.
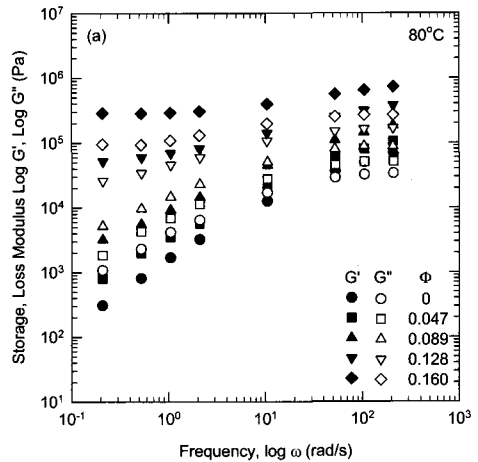

Figure 4. Dynamic modulus of precipitated silica/PDMS compounds at 80℃.

can conclude that precipitated silica imparts similar reinforcement to PDMS as fumed silica[3] albeit it is weaker.

Storage (G') and loss (G") moduli of the precipitated silica/PDMS compounds obtained in frequency sweep mode at several temperatures are displayed in Figure 4. In the range of frequency examined, the compounds exhibit a transition from terminal to rubbery zone. In Figure 4, both storage and loss moduli increase with the frequency with loss moduli being higher than storage moduli at low frequencies at $\square$ = 0.047 and 0.089. At higher frequency, these functions crossover and subsequently the storage moduli become higher than the loss moduli. This observation could be explained by the fact that most of the energy of deformation is dissipated as heat due to increased friction between the filler and polymer chain[23] when their interaction is not strong enough. At higher concentrations ($\square$ $\geq$ 0.128), the storage moduli are higher than the loss moduli at any frequency. This is an indication that once a strong network is generated between filler particles and matrix polymer, the system of interest acts as an elastic solid at low deformation

and G' becomes higher.

More importantly, the storage modulus at filler concentration of □ = 0.128 and 0.160 shows a plateau region with the magnitude of 5×10^4 and 3×10^5 Pa, respectively. This behavior is similar to that of a crosslinked network. It suggests the presence of an effective network of filler particles.[24,25] Upon the formation of network, the connection between the matrix polymer chains and filler, the long-range conformational changes of the polymer molecules is prevented thus, resulting in longer response to the applied strain.

4. Conclusions

The reinforcement of PDMS by means of precipitated silica has been studied in terms of interaction between the filler and matrix. Bound rubber measurement shows that the formation of bound rubber is not significantly dependent on the filler concentration and ranging from 53 to 60%. Compared to ca. 95% of PDMS participated in the formation of bound rubber in fumed silica suspended system, the values suggests that the filler/polymer interaction is weaker in precipitated silica/PDMS system than that in fumed silica/PDMS system. The thickness of the layer of adsorbed PDMS continuously decreases with increasing filler concentration due to the existence of aggregates. However, based on the Kraus constant, C, as an indirect measure of the interaction between filler and matrix, the value for precipitated silica/PDMS system is significantly higher than that of most carbon blacks in various rubbers, which suggests stronger interaction in the compounds studied here.

In rheological study, Newtonian region at low shear rate is observed in unfilled PDMS implying the system follows Cross model behavior rather than close to power law shown for filled system. The sensitivity of viscosity of precipitated silica filled

PDMS to temperature becomes higher as filler concentration increases. The existence of the yield stress at higher filler concentration is seen from the complex dynamic viscosity measurement at low frequency, where the complex viscosity continuously increases and a plateau of the storage modulus is achieved as frequency decreases. As another evidence of an interaction in the system, the storage modulus for high filler concentration of □ = 0.128 and 0.160 shows a plateau region with the magnitude of 5×10^4 and 3×10^5 Pa. It suggests the presence of effective networks of silica particles and silica/PDMS.

Based on the various experimental investigations employed in this study, one could conclude that the interaction of precipitated silica in PDMS is much stronger than that in carbon black filled rubbers but not as strong as in fumed silica/PDMS systems.

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