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The Influence of Filler Morphology and Surface Hydroxyls on Crepe-Hardening of Uncured Silicone Elastomers

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SUMMARY: The shelf stability of uncured silicone elastomers is of fundamental interest to the silicone industry because most formulations are sold in the uncured state for further processing. An increase in viscosity of a filled silicone elastomer with time, called "structuring" or "crepe-hardening," can pose tremendous processing problems. The macroscopic effect of crepe-hardening with time was monitored in terms of its Williams plasticity. Plasticity and its rate of change with time were shown to depend on the fumed silica morphology, fumed silica loading, and the residual surface hydroxyls on the fumed silica after treatment. The microscopic mechanisms of polymer-filler interactions that drive the observed rheological behavior were investigated using proton T_2 relaxation, ^{29}Si NMR cross polarization dynamics, and by monitoring the changes in optical properties with time. It appeared that the dominant mechanism of shelf instability was due to an increase in the thickness of the adsorbed polymer layer. There was no change in the state of dispersion of the filler as the silicone elastomer aged.

Introduction

The nature of polymer-filler interactions has been studied extensively[1-6]. In the silicone industry, research interest in filled systems is driven by the need to design formulations to meet the needs of a wide variety of customers. In addition to meeting the physical property requirements of the end user, an uncured silicone elastomer is intended to retain its processing characteristics until it is milled or extruded. However, it is often observed that the viscosity of highly fumed silica-filled polydimethylsiloxane (PDMS) increases with time; this viscosity increase, known as *structuring* or *crepe-hardening*, is related to shelf stability.

There are a number of factors that can cause the viscosity of a filled PDMS to increase with time. Generally speaking, the properties of fumed silica that drive elastomer reinforcement can also influence the shelf stability of an uncured elastomer. Examples of these properties include specific surface area and filler loading, which together determine polymer-filler contact area; filler morphology (surface structure and particle size distribution (PSD)); and surface

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chemistry. These factors all play essential roles in restricting the motion of the polymer chains[1-3]. The presence of low-molecular weight process aids, the molecular weight of the silicone polymer, and the initial dispersion quality of the fillers are other factors that can influence shelf stability. Efforts have been made to understand the microscopic mechanisms that drive crepe-hardening. DeGroot[5] concluded that as a silicone compound (Mw = 9,000 to 140,000) ages, bridging polymer chains exert an attractive force on the particles, drawing them together and causing the filler to re-agglomerate. However, it was speculated that in high-molecular weight polymers (gums) the viscosity may be too high for the filler to move, so that the observed crepe-hardening is a result of more polymer bridges being formed over time. Cochrane and Lin[6] proposed a microscopic model that utilized nine possible interactions in a filled system. They suggested that the observed increase in network strength with time is due to the free end of a silica-bound polymer molecule becoming attached to an adjacent silica aggregate to form a new type of bond.

The use of proton relaxation NMR to study steady-state adsorption of PDMS onto silica was demonstrated recently by Cosgrove and Turner[7]. In this paper we report the combined use of macroscopic tools such as Williams plasticity to study the bulk dynamics of filled high-molecular weight PDMS with microscopic characterization techniques, such as proton T_2 NMR and cross polarization ^{29}Si NMR in non spinning mode, to investigate the interface of the fumed silica-PDMS network and its effect on elastomer shelf stability.

Experimental Part

The silicone elastomers used for this study consisted of proprietary cold-mixed blends of high-molecular weight (Mw = 740,000-860,000) vinyl-terminated PDMS gums, low-molecular weight siloxane process aids, vinyltriethoxysilane crosslinkers, and fumed silica treated to known surface silanol concentrations. Various treated fumed silicas were used in the formulations, including those having the same BET surface area but different morphologies and blends of high and low surface area fillers to simulate the effect of broad particle size distributions. The mean surface area of each blend of filler was calculated from a linear combination of the primary particle diameters of the component fillers. The resulting compounds were strained through a 150-mesh screen before testing the uncured material.

Williams plasticity (ASTM D926-93) was used to evaluate the effects of filler treatment and morphology on changes in viscosity with time. Compounds were allowed to "wet-in" for 24 hours before plasticity testing was begun. The uncured compounds were freshened by subjecting them to sixteen passes on a two-roll mill to erase any effects of shear history. Samples were tested in triplicate; the test was repeated on unfreshened samples at regular intervals for at least four weeks.

For proton T_2 measurements, the Hahn spin-echo sequence8) was used. The T_2 of samples left undisturbed in NMR tubes was monitored periodically over four weeks. The ^{29}Si NMR CP/MAS was carried out on approximately 200 mg of freshened sample with no air supplied to the rotor for spinning. The samples were run on a Bruker 300 MHz AMX NMR spectrometer equipped with a Doty Scientific 7 mm CP/MAS probe operating at 300.06 MHz proton frequency and 59.7 MHz for ^{29}Si. A standard Hartmann-Hahn cross polarization sequence was performed to generate ^{29}Si magnetization using a 45 kHz spin locking field. For the free induction decay, 256 data points were collected at a spectral width of 20 kHz. The data were then apodized with 30 Hz of Gaussian line broadening, zero-filled, Fourier transformed, phased and baseline corrected with a simple polynomial. A cross polarization contact time of 10 ms was used and 40,000 scans were accumulated at a rate of two seconds per scan (approximately 22 hours total accumulation time). Successive spectra were accumulated over time without disturbing the sample.

Optical measurements were made on a BYK-Gardner Haze-plus® instrument. A uniform film of freshened silicone approximately 2 mm thick was obtained by compression molding between two polyester films. The transmittance, haze and clarity measurements were made at three marked positions within the sample. The spot size was 10-18 mm. Replicate measurements were made periodically at these marked positions over 21 days.

Results and Discussion

A. Macroscopic Phenomena

Williams Plasticity: The plasticity of a silicone elastomer containing 22 wt.% filler had a very weak dependence on the treatment level of the filler; however, the rate of change of plasticity with treatment level was faster at 37 wt.% filler loading, as shown in Figure 1. For an elastomer containing 37 wt.% filler, plasticity increased 250 points in 28 days when the filler was treated to 3.33 OH/nm^2 (evidence of crepe-hardening), whereas plasticity increased only 100 points in 28 days when the filler was treated to 2.99 OH/nm^2. This showed that there exists a threshold of residual surface silanol content and filler loading that will precipitate crepe-hardening.

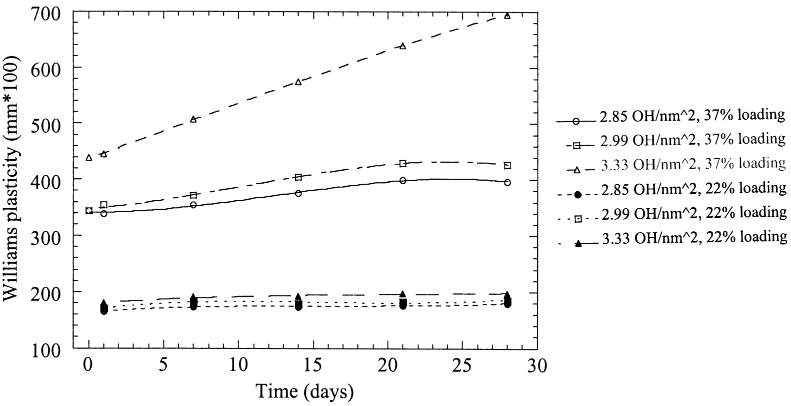

Figure 1: Williams plasticity increase (crepe-hardening) of a silicone elastomer as a function of time, concentration of residual surface silanol groups, and treated fumed silica loading.

There are other factors that influence the initial plasticity and its rate of change. Figure 2 shows the plasticity of four uncured silicone compounds having the same treatment level but different morphologies. The surface areas of HCR#1 and HCR#2 were nominally 200 m^2/g. Blends #1 and #2 were made by combining 200 m^2/g with 90 m^2/g filler and 200 m^2/g with 130 m^2/g filler to produce 175 and 160 m^2/g mean BET surface areas, respectively. The artificially broadened aggregate size distribution allowed us to reduce the initial viscosity (plasticity) in a controlled manner and to study the effect of broad PSD on crepe-hardening. With the introduction of particularly large aggregates in Blend #1, both the initial plasticity and the rate of change of plasticity were significantly reduced. This trend was consistent with the initial and final plasticities of HCR#1 and HCR#2, which had different PSD by transmission electron microscopy (TEM) and atomic force microscopy (AFM).

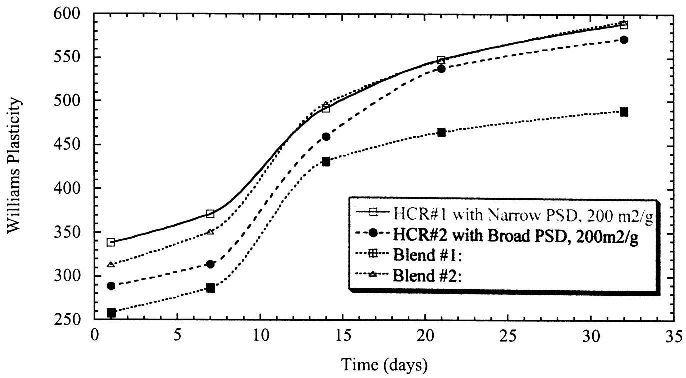

Figure 2: Effect of filler morphology and PSD on crepe-hardening of uncured silicone.

B. Microscopic Phenomena

Optical properties: As discussed by DeGroot[5)] in his study of filled systems, it may be possible for bridging chains to cause filler re-agglomeration as the material ages. If this were the case, one or more of the optical properties (transmittance, haze, or clarity) would change with time as the agglomerates increased in size. Clarity measures light scattered from a sample at less than 2.5° and is a measure of the "see-through" properties of a material. Haze is a measure of light scattering above 2.5°. For this work, an uncured silicone compound was monitored for 21 days. After air bubbles released in the first few days, the optical properties remained fairly constant (standard deviation for transmittance was 0.05-0.2%, for haze was 0.1-0.2%, and for clarity was 0.1-0.2%) even though the crepe-hardening phenomenon was progressing. This suggested that the filler aggregates remained in their initial dispersed state.

Proton T2 Relaxation Behavior: The nuclear magnetic relaxation of protons in the uncured silicone compound depends upon their environment. The motion of the polymer entrained at the polymer-filler interface becomes anisotropic relative to the motion of the bulk polymer. Figure 3 shows the effect of filler morphology and aggregate size distribution on the relaxation of the matrix. The translational diffusion of the neat PDMS was hindered as filler was introduced into the matrix. The occluded volume of the filler as measured by TEM also played a significant role in the anisotropy of the matrix relaxation. At the same treatment level and filler loading, HCR#2, which had a broad PSD and greater occluded area, showed a different relaxation behavior than HCR#1, which had a much narrower PSD. To confirm this observation, a blend of 300 and 90 m^2/g fillers were made such that the mean BET surface area was 200 m^2/g; the blend was then treated to the same residual OH/nm^2 level as the filler used in HCR#2. Figure 3 shows that the relaxation profiles of the compounds made with the naturally and artificially broad PSD's were identical. The T_2 dynamics did not change over the four-week period that the samples were analyzed. This suggested that filler re-agglomeration, which could have changed the net translational diffusion of the polymer, did not occur.

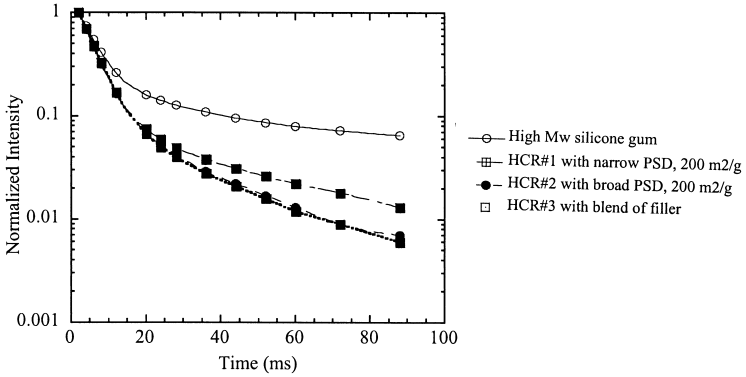

Figure 3: Effect of morphology and PSD on the T_2 relaxation of uncured silicone elastomer.

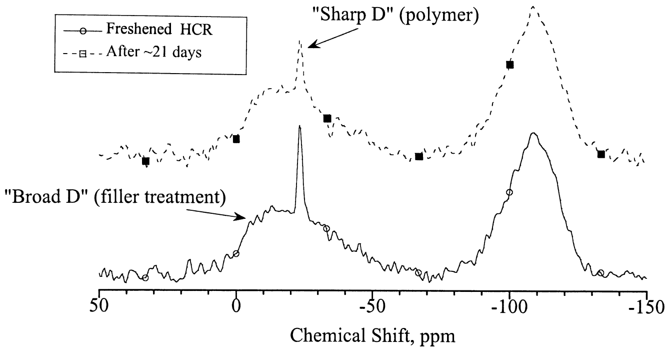

Figure 4: ^{29}Si NMR CP/MAS (non-spinning) of freshened and aged silicone elastomer.

^{29}Si NMR CP/MAS Dynamics: The microscopic mechanism of crepe-hardening was further investigated with non-spinning ^{29}Si NMR CP/MAS. The sample was not spun so that the natural progression of crepe-hardening was not influenced. Figure 4 shows spectra of a freshened sample and of a sample that was aged for 21 days in the NMR tube. A custom macro was used to generate a simulated spectra based on the summation of five lines parameterized by intensity, line shape, line width and chemical shift. Agreement between observation and simulation was excellent. The "sharp D" peak was produced by the free polymer, and the "broad D" peak was produced by octamethyltetracyclosiloxane attached to the filler and by strong hydrogen-bonding of the residual surface silanols with the polymer or process aid. To determine the change in microscopic behavior with time, the peaks were integrated and normalized to Q. Overall, the integral under the "broad D" peak increased 6-7% over a three-week period, which suggested that the influence of the residual surface silanols propagated further into the bulk polymer with time. The increase was not linear due to the random diffusion of the highly mobile low-molecular weight process aid within the strongly adsorbed layer. We propose that the increase in the volume of anisotropic polymer chains influenced by the filler resulted in the increase of the viscosity of the elastomer with time.

Conclusions

We have used several macroscopic and microscopic tools to investigate crepe-hardening of uncured silicone elastomers. Control of filler treatment, filler loading, and filler morphology are important factors in controlling the shelf stability of silicone elastomers. It appears that the dominant mechanism of shelf instability is due to an increase in the thickness of the adsorbed layer of the polymer as evidenced by the influence of these factors. There was no change in the state of dispersion of the filler as the silicone elastomer aged.

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References

1. J.-B. Donnet, A. Voet, *Carbon Black, Physics, Chemistry, and Elastomer Reinforcement*, Marcel Dekker, New York 1976
2. *Reinforcement of Elastomers*, G. Kraus, (Ed.), John S. Wiley & Sons, New York 1965
3. M.-J. Wang, S. Wolf, J.-B. Donnet, *Rubber Chem. Tech.* **64**, 559 (1991)
4. See for example the Silicone Modified Polymers section of the 214th American Chemical Society National Meeting, Dallas, TX, March 28-April 2, 1998
5. J. V. DeGroot, "Rheology of Filled Polydimethysiloxane: Effects of Polymer Bridging," Ph.D. Thesis, University of Minnesota 1994
6. H. Cochrane, C. S. Lin, *Rubber Chem. Tech.* **66**, 48 (1993)
7. T. Cosgrove, M. J. Turner, *Polymer* **38(15)**, 3885 (1997)
8. E. L. Hahn, *Phys. Rev.* **80**, 580 (1950)