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Thermal and Chemical Analyses of Silicone Polymers for Component Engineering Lifetime Assessments

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THERMAL AND CHEMICAL ANALYSES OF SILICONE POLYMERS FOR COMPONENT ENGINEERING LIFETIME ASSESSMENTS.

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Introduction

Accurate predictions of a polymer component's functional lifetime at best are tenuous when one has only relatively short term chemical or mechanical property data to extrapolate. We have analyzed a series of silica-filled siloxanes to determine the chemical and microstructural signatures of aging, and we are incorporating these data into rational methodologies for assessing a component's lifetime measured against as-designed engineering properties. We are monitoring changes in mechanical properties, crystallization kinetics, cross-link density changes, and motional dynamics with a variety of analysis methods: Modulated DSC, Dynamic Mechanical Analysis, and Solid-State Nuclear Magnetic Resonance.

Previous work has shown that the addition of phenyl side groups to polydimethylsiloxane (PDMS) polymer chains reduces the rate and extent of crystallization of the co-polymer compared to that of pure PDMS[1,2]. Crystallization has been observed in copolymer systems up to 6.5 mol % phenyl composition by DSC and up to 8 mol % phenyl by XRD.[1,2] The PDMS-PDPS-silica composite materials studied here are silica reinforced random block copolymers consisting of dimethyl and diphenyl monomer units with 11.2 mol. % polydiphenylsiloxane. Based on this previous work, it is not expected that this material would exhibit crystallization in the polymer network; however, these silicones do, in fact, exhibit crystallization phenomena. This report focuses primarily on our efforts to assess the information content of the crystallization phenomena with respect to aging signatures and mechanisms that may be limiting the functional lifetime of the composite materials.

Experimental

The PDMS-PDPS-silica composite material was a random block copolymer consisting of 90.7 wt.% dimethyl (DMS), 9.0 wt.% diphenyl (DPS), and 0.31 wt.% methyl vinyl (MVS) siloxane monomer units. The polymer was milled with a mixture of 21.6 wt. % fumed silica,

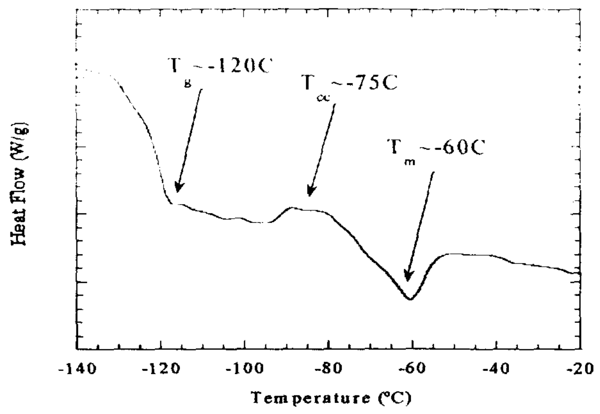

Figure 1. MDSC trace for pristine PDMS-PDPS-silica composites foam. Relevant thermodynamic events are indicated.

4.0 wt. % precipitated silica, and 6.8 wt. % ethoxy-endblocked siloxane processing aid. The resulting gum was then milled with 50 or 60 volume percent of 25-40 mesh prilled urea spheres. Heat was applied to activate the peroxide curing agent in the base gum, after which the urea was washed out with water. Control samples were irradiated for various periods of time in a stainless steel container (volume ~ 2 l) exposed to a ^{60}Co gamma source (E_{avg}~1.2 MeV, 0.5 Mrad/hr). All dosing experiments were performed at the same dose rate.

DMA testing was performed (Rheometrics RMS-800 Dynamic Mechanical Spectrometer, Piscataway, NJ) in parallel plate geometry with a static compression force of 400g. The sample was sheared at a frequency of f=6.3 rad/sec and using a ramp sequence of 20°C from –150°C to 20°C at a rate of 2°C/min. MDSC analyses were performed (TA Instruments, MDSC 2920, New Castle, DE) by cooling the sample at a rate of 6°C/min. to –150°C, followed by heating at 3 °C/min. with a modulation frequency of ± 0.4°C/50 sec. Isothermal x-ray diffraction measurements were done at –85 °C on a Siemens D500 Diffractometer with an Anton Paar TTK Heizregler subambient stage, using a primary beam monochromator.

^{1}H NMR T_2 measurements were performed at 500.13 MHz on a Bruker DRX-500 spectrometer using a HCX 5mm probe. ^{1}H $\pi/2$ excitation pulses of 7 μs and relaxation delays of 10 seconds were used. In all cases, small (0.5 cm x 0.5 cm) squares of foam were cut from the larger foam and set in the portion of a 5 mm NMR tube that would be within the coil volume of the probe.

Results

MDSC analyses, shown in Figure 1, show a glass transition temperature (T_G) at -120°C and a melting point (T_M) at -60°C (ΔH_M~-2.5J/g). The presence of a crystallization phenomena was indicated by the presence of an exothermic peak at –80°C with a heat of cold crystallization (ΔH_C) of ~1.5J/g. DMA data (not shown) showed similar results: The glass transition was evidenced by a drop in G' and a peak in tan δ at –120°C, and crystallization was also evidenced by the peak in G' at –75°C where the formation and melting of the crystalline phase causing an increase in the shear modulus.

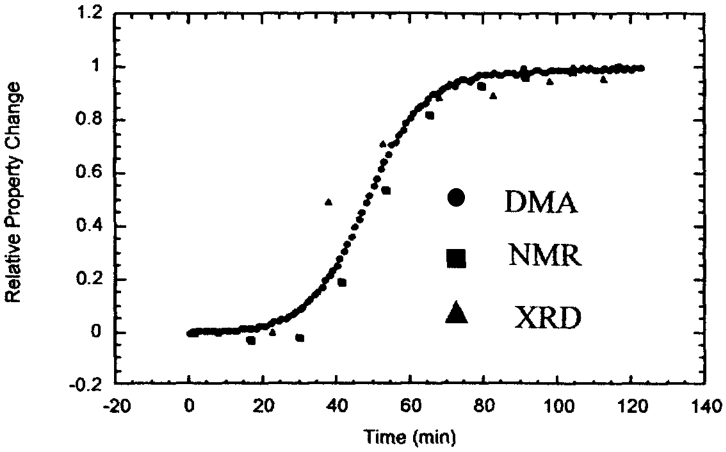

Figure 2. Relative changes in G' (DMA), T_2 (NMR) and %crystallinity (XRD) for foam.

We used low temperature X-ray diffraction to measure the degree of crystallinity in the copolymer composite. This data showed that ~ 15% of the polymer was crystallizing after 2 hours at -85 °C. In order to see how crosslink density might affect the degree of crystallization in these materials, a series of samples with variable crosslink density were prepared and subject to crystallization and the % crystallinity was measured (data not shown). The data show that at sufficiently high crosslink density (~ 1.5X the nominal density studied here), the degree of crystallization after 2 hours at -85 °C began to decrease.

To examine the kinetics of polymer crystallization, isothermal DMA experiments were performed on pristine, variable crosslink density, and irradiated materials. These experiments were performed by rapidly cooling samples to -85 °C and tracking G' as a function of time. We have also investigated the kinetics of crystallization by MDSC, XRD and NMR analysis. Results of ^{1}H relaxation measurements by NMR and the ratio of crystalline peak area to amorphous halo by XRD as a function of time at –85 °C are normalized and plotted along with the DMA data in Figure 2. MDSC could also track the kinetics by changes in ΔH_c with time. The precision of these latter thermal measurements, however, were quite poor and further investigation is ongoing to improve these measurements. The results of our kinetic experiments show that, by all measurement methods, crystallization in the pristine material took place over a 1.8 hour period. We are currently investigating the nature of the slow crystallization kinetics.

Isothermal DMA crystallization kinetic measurements were then performed on materials with variable crosslink density (produced by altering the concentration of vinyl monomer units that produce the crosslinks during the curing process) to assess the variability

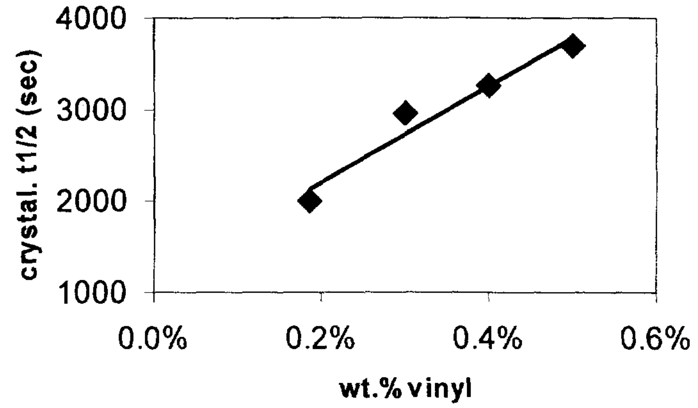

Figure 3. Time to half crystallization as a function of wt.% vinyl monomers (and thus, crosslink density).

of the kinetics with simulated aging signatures. The results of these measurements are shown in Figure 3 and show that as the crosslink density increased, the crystallization kinetics slowed considerably.

In an effort to assess the applicability of measurements of crystallization kinetics to assess changes in actual aged material, we studied the crystallization kinetics for a series of radiatively aged samples. Results from isothermal DMA studies of these samples is shown in Figure 4. For an unirradiated sample, approximately 1.8 hours were required for full crystallization, while a sample dosed to 25 Mrads took 10 hours to crystallize to the same extent. For all model samples, DMA curves suggest that the ultimate amount of crystallization does not change with exposure to radiation, but the time to the onset of crystallization and the rate at which crystallization occur does change. Our results suggest that monitoring crystallization kinetics by MDSC, DMA, NMR or XRD may provide a sensitive method to assess structural changes occurring due to polymer crystallization.

Conclusions

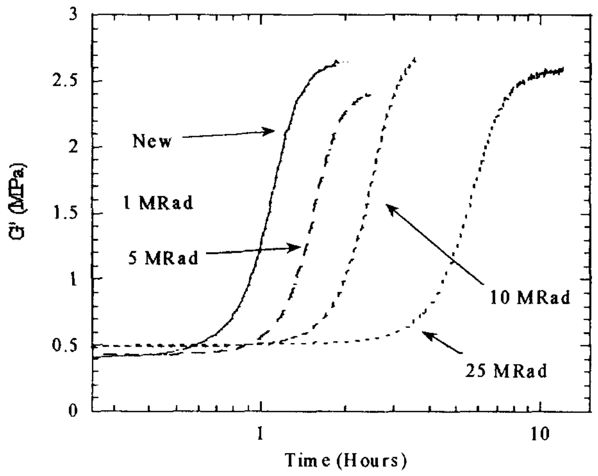

Figure 4. Results of isothermal DMA experiments on gamma-irradiated polymer composite materials.

We have presented preliminary data on crystallization phenomena in PDMS-PDPS-silica composite foam materials. A crystallization event is clearly seen for these materials by DSC, DMA, XRD, and NMR methods despite a concentration of diphenyl monomer units above the threshold at which crystallinity had previously been shown to be precluded[1,2]. The time to crystallization onset and the rate at which the crystallization occurs have been shown to be sensitive to changes in crosslink density induced by artificial aging mechanisms. Naturally aged material also show subtle changes in crystallization behavior. We are still investigating the origins of this phenomenon and investigating the value of such measurements to assess aging signatures for lifetime prediction efforts.

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