Preprint
UCRL-JC-135979

Radiation Induced Structural and Motional Changes Occurring in Silica Filled Silicone Polymer Foams as Probed by Multinuclear NMR

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This article was submitted to
American Chemical Society National Meeting, San Francisco, CA,
March 26-30, 2000

October 14, 1999

U.S. Department of Energy
Lawrence
Livermore
National
Laboratory

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Introduction

The aging of polymeric composite materials through factors such as thermal and mechanical stresses, environment, radiation, and chemical attack can affect the length of time for which a given material can maintain its engineering performance. Iterative interactions and cumulative reactions may result in the material or device reaching a critical age where its properties fail unexpectedly and catastrophically. The mechanical property changes associated with multi-mechanism aging may be subtle, and may not necessarily change linearly as a function of time in service. Since such linear relationships are often used in lifetime predictions, there is a fundamental need to develop and employ spectroscopic methods to investigate the structural and motional changes that occur in these organic-inorganic materials as a result of aging in chemically, thermally, or radioactively harsh environments.

Silica filled polydimethylsiloxane (PDMS) composite systems are of technological interest due to their chemical and environmental resilience. Silica is usually chosen as the filler phase due to the significant reinforcement of the composite material through hydrogen bonding between the polymer chains and the surface silanol groups on the filler. Unfilled PDMS is known to crosslink when exposed to high-energy radiation. The presence of a silica filler phase, which has a higher electron density than the polymer matrix, has been proposed to result in an increased incidence of crosslinking or scission due to a backscatter of the incident radiation.[1]

Cohen-Addad has used ^{1}H relaxation times to characterized cross-link density in unirradiated filled PDMS and Charlesby has reported ^{1}H relaxation studies of irradiation induced changes in unfilled PDMS systems of average molecular weights up to 1 MDalton.[2,3] However, no specific studies have been reported on aging of silica-filled PDMS based polymers systems. To this end we have applied Nuclear Magnetic Resonance (NMR) methods to gain insight into the processes that are contributing to mechanical failure of silica filled polydimethylsiloxane (PDMS) based cushions. The studies so far have concentrated on (A) ^{1}H, ^{13}C, and ^{29}Si Magic Angle Spinning (MAS) measurements of chemical speciation from chemical shifts, and (B) ^{1}H relaxation measurements.

Experimental

Materials. The materials tested were a copolymer of polydimethylsiloxane and polydiphenylsiloxane, crosslinked by a vinyl monomer/vinyl-specific catalyst system. The percentages of each monomer unit in the base rubber are 90.7% PDMS, 9.0% PDPS, and 0.31% polymethylvinylsiloxane. The resultant rubber was then milled with a mixture of fumed and precipitated filler (21.6 and 4.0 wt%, respectively), and 6.8 wt% of an ethoxy enblocked siloxane as a processing aid. The composite was studied in foamed form made by processing the filled polymer with prilled urea, which was subsequently washed out. The investigated foams exhibited 60 percent porosity. Samples were irradiated in a stainless steel container (V ~ 2 liters) that was exposed to a Co^{60} source (1.2 MeV, 0.5Mrad/hr) for various periods of time. All experiments were performed at the same dose rate.

Solvent Swelling. The silicone samples were submerged in 600 ml of stirred toluene solution in a sealed Teflon container. The swollen weight was recorded periodically until an equilibrium weight was obtained. 150 ml of concentrated NH_4OH (~28%) then was added directly to the toluene solution. The samples again were weighed periodically until equilibrium was reached with the toluene/NH_4OH mixture. The samples were dried overnight in a vacuum oven at ambient temperature or for 7 days in air and reweighed for the final dry weight. Molecular weight between crosslinks (M_x) and crosslink density (CD) were then calculated using the Flory and French equations.[4] A correction was made for the weight gain due to filling of the pore space by the solvent. Each determination involved duplicate measurements of six samples of the same sample lot.

NMR. ^{29}Si NMR experiments were performed on a Chemagnetics CMX-300 spectrometer using a Chemagnetics 7.5mm CPMAS probe at 59.6MHz. ^{13}C NMR experiments were performed on a Chemagnetics CMX-300 spectrometer using a Bruker 7mm CPMAS probe tuned to 75.25MHz. ^{1}H relaxation NMR experiments were performed on a Chemagnetics CMX-300 spectrometer at 300.14MHz using a Bruker wide-line variable temperature H-X probe and on a Bruker Avance 500MHz spectrometer using a HCX, triple resonance probe. ^{1}H MAS experiments were performed at 300MHz using the decouple channel of a Bruker 7mm CPMAS probe. T_2 relaxation times were measured using a 90- τ-180- τ echo sequence and T_1 relaxation times were measured using an inversion recovery sequence. Temperatures were controlled with a Bruker VT unit and temperatures could be held to with in ±2 °C of the target temperature for up to 4hrs.

Results and Discussion

MAS studies. The non-spinning ^{13}C, ^{29}Si, and ^{1}H NMR spectra (not shown) of all three nuclei are characterized by resonances that are narrower than one would expect for spins in static environments. This is due to the fact that the polymers are well above T_g at room temperature and can be characterized by a high degree of motion. This motion provides a mechanism to attenuate the anisotropic interactions that typically broaden NMR spectra of solid materials. However, the resolution obtainable at static conditions is far from high enough to observe all structural species. As a result, our initial studies used MAS to remove the residual anisotropic interactions present and provide the highest possible resolution. Unfortunately, no chemical or structural changes have been directly observed by MAS methods for materials γ-irradiated up to 50Mrad. This suggests that the changes occurring are subtle

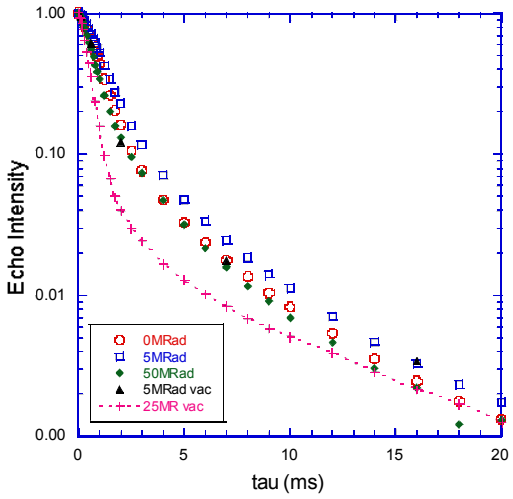

Figure 1. ^{1}H Spin-echo NMR decay curves for γ-irradiated silica-filled silicone foams.

and occur at a frequency of less than approximately 1% of the monomer units. It is also possible that structural changes are occurring at the cross-linking vinyl species. Since these sites are unobservable in all NMR experiments, any changes in these functionalities are also unobservable.

Relaxation studies. ^{1}H spin-lattice relaxation times (T_1) remained constant within experimental error at 1.15±0.05 sec for all samples at ambient temperature. Though the ^{1}H T_1s of the present samples are lower than the T_1's reported for low and high molecular weight PDMS linear polymers subjected to γ-irradiation, the invariance of T_1 with irradiation is reproduced.[3] The invariance of the ^{1}H spin-lattice relaxation times to dose rates lower than 50Mrad is a consequence of the only minor effects of any additional cross-linking and entanglements on the rapid motion of the methyl groups around the Si-C, C3, axis.

Spin-echo decay curves were characterized by two relaxation times that dominated at short and long taus, respectively:

$$M(t) = X_s \exp(-tau/T_{2s}) + X_L \exp(-tau/T_{2L}) \quad \{1\}$$

Where X_s and X_L represent the mole fractions of spins undergoing transverse relaxation with the short (T_{2S}) and long (T_{2L}) relaxation times. In

agreement with Charlesby[3] and Cohen-Addad,[2] we assign the two different relaxation times to protons in environments with a large degree of network structure (T_{2s}) and free, low molecular weight polymer chains (T_{2L}). The large differences in the two relaxation times reflect the large difference in molecular mobilities of the two regions of the polymer system. The values for the relaxation times and mole fractions are tabulated in Table 1 are plotted as a function of dose in figures 2 in air and in vacuum. In general, the short relaxation times average around 1ms, while long relaxation times average about 460 ms. X_L averaged about 0.06. The short transverse relaxation times found in this study are, in general, one to two orders of magnitude less than the transverse relaxation times found for high molecular weight linear PDMS polymers. We attribute this difference to the larger degree of cross-linking in these polymers due to the presence of the vinyl cross-linking agents and the cross-linking due to the interaction with the silica filler.

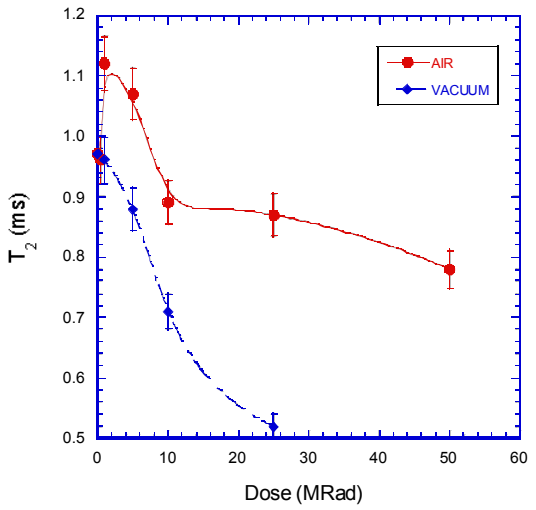

Figure 2. T_2 vs. dose for silica filled silicone polymer samples. Closed circles are samples irradiated in air and closed diamonds are samples irradiated in vacuum.

As shown in figure 2, as the cumulative dose increased for samples irradiated in air, the transverse relaxation times first increased to a maximum of 1.12 ms at 5 Mrad and then decreased to 0.84 ms at 50 Mrad. For samples irradiated in vacuum, the T_2 steadily decreased with dose to 0.52 ms at 25 Mrad. The mole fraction of low molecular weight polymer was characterized by trends similar to those seen for T_{2s}. The X_L for samples irradiated in air with less than or equal to 10Mrad was seen to increase and then to decrease upon further irradiation. For samples irradiated in vacuum, the free chain fraction steadily decreases over the range of irradiation exposure.

Previous work has shown that the motional processes of methyl groups attached to long PDMS chains that contribute to relaxation processes can be characterized by slow, random motion of the C3 axis as the chain undergoes rotational and translational motions. (The rapid rotations of the methyl groups around the C3 axis occur too rapidly to significantly contribute.) The transverse nuclear magnetization resulting from such random motions has been shown to be governed by the residual dipolar couplings produced by time fluctuations in the angle the C3 axis makes with the static magnetic field.[2] Though explicit modeling of motional mechanisms would be prohibitively difficult due to the highly complex distributions of motional processes occurring in this complex system, qualitative correlations can be made between the changes in relaxation times and the morphological changes occurring upon γ-irradiation. As changes occur in the polymer matrix, such as cross-linking, that reduces the degrees of motional freedom of the PDMS chains, T_2 would be expected to decrease. As processes occur which increase the flexibility of the chains, T_2 would increase.

Consequently, the experimental observations for samples irradiate in air noted above are consistent with an initial structural relaxation of the lattice. This is due to either chain scission or a disruption of the hydrogen bonding between the polymer and silica filler. Since chain scission has not been found to be a significant contribution to γ-irradiation induced damage in linear PDMS polymers,[1,3] the initial increase in T_{2s} is likely due to the latter explanation. At doses higher than 5Mrad, the T_2 data suggests that the changes in the polymer morphology are characterized by a hardening of the lattice due to continued crosslinking of the polymer network. For samples irradiated in vacuum, no initial increase in T_{2s} is seen. This suggests that the mechanisms of morphological changes be dominated by cross-linking in the polymer network and/or at the polymer/silica interface. In is unclear what process may be contributing to the increase in short molecular weight chains. Possible explanations include the liberation of short chains adsorbed to the silica surface and chain scission occurring as a result of irradiation.

Table 1. Transverse Relaxation Times and Mole Fractions for γ-irradiated Foams.

Dose (Mrad)	Atmos.	T_{2s}(ms) (± 0.02)	X_L (±0.005)	T_{2L} (ms) (± 0.15)	M_x (kDal.)
0	na	0.97	0.062	4.75	28.6
0.5	air	0.96	0.063	4.78	29.2
1	air	1.12	0.079	4.80	30.0
5	air	1.07	0.087	4.76	40.9
10	air	0.89	0.091	4.45	32.9
25	air	0.87	0.083	4.12	33.5
50	air	0.78	0.056	4.60	22.9
1	vac.	0.96	0.052	6.33	24.9
5	vac.	0.88	0.046	6.33	20.0
10	vac.	0.71	0.031	6.33	11.4
25	vac.	0.52	0.020	6.33	7.15

Conclusions

We have measured changes in cross-link density and average molecular weight for a series of γ-irradiated silica filled siloxane polymers by solid state NMR relaxation times. ^{1}H transverse relaxation times, T_2, have been shown to be sensitive probes of changes in slow, cooperative motions occurring in the siloxane chain dynamics as a consequence of the γ-irradiation. Preliminary studies suggest that the transverse relaxation time is linearly dependent on the cross-link density in these filled PDMS systems, in agreement with previous work on unfilled PDMS systems.[3] For samples irradiated in air, siloxane polymer cross-linking was observed to be proceeded by an initial disruption of the hydrogen bond interaction between the polymer backbone and the silica silanol groups at the interface. Stiffening due to radiation induced cross-linking then dominates the polymer chain motions at dosages above 10Mrad. Samples irradiated in vacuum undergo increases in polymer cross-linking only, with no apparent relaxation in the silica-polymer interaction. The work reported here shows that detailed characterization of the relaxation processes of the various nuclei in the siloxane polymers under static conditions has the potential to provide detailed insight into changes in the mechanisms and energetics of motional processes brought about by polymer aging processes.

Acknowledgement. Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

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