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B. P. Mayer, S. C. Chinn, R. S. Maxwell, J. A.
Reimer

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Polymer Degradation and Stability

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**Solid State NMR Investigation of γ -Irradiated Composite Siloxanes:
Probing the Silica/Polysiloxane Interface**

Brian P. Mayer^{a,*}, Sarah C. Chinn^a, Robert S. Maxwell^a, Jeffrey A. Reimer^b

^a *Chemical Sciences Division, Lawrence Livermore National Laboratory, 7000 East Ave.*

Livermore, CA 94550

^b *Department of Chemical and Biomolecular Engineering, University of California at*

Berkeley, Berkeley, CA 94720

LLNL-JRNL-479454

**To whom correspondence should be addressed,*

e-mail: mayer22@llnl.gov

Telephone: +1 925-423-1128

Fax: +1 925-423-9014

Lawrence Livermore National Laboratory

7000 East Ave. L-091

Livermore, CA 94550

Abstract

We employ silicon-proton ($^{29}\text{Si}\{^1\text{H}\}$) cross polarization magic-angle spinning (CP-MAS) to probe directly the interface of a silica-filled polysiloxane elastomer subjected to gamma-radiation. Using a traditional spin-lock CP experiment in conjunction with a silicon-edited proton rotating-frame longitudinal relaxation sequence, the full suite of CP build-up parameters are extracted for all six resolvable silicon chemical shifts. The data, represented by three parameters, T_{HX} , $T_{1\rho}^H$, and M_∞ , are interpreted by means of a model where the simultaneous influence of silica surface hydroxyl modification, interfacial water content, and radiation-induced chemistries is considered responsible for the observed macroscopic behavior of these engineering materials.

Keywords:

cross-polarization

nuclear magnetic resonance

interface

spectroscopy

composite materials

radiation

1. Introduction

The ability to refine and tailor the physical and chemical properties of elastomeric materials have traditionally been provided in large part by the addition of various types of fillers (e.g., organic, inorganic, metallic, porous, etc.) [1]. Although the resultant properties of these composites are governed to some degree by the identity, amount, shape, etc. of their separate constituents, the physical and chemical interactions between filler and polymer are generally the most influential determinant of bulk composite properties. The synergy between physical and chemical interactions at the filler/composite interface is widely regarded to be highly dependent on the types and degree of interaction at the interface [2-4].

It has been well-established that polysiloxane-silica composites experience hydrogen-bonding interactions between chains and silica surface hydroxyl (silanol) groups, and that these interactions dominate the observed changes in material properties relative to pure, bulk siloxanes [5]. These strong interactions have been shown to make more mechanically- and chemically-resistant materials through, for example, melt reinforcement by silica through a larger effective crosslink density [6] and a reduction in the equilibrium degree of swelling [7], respectively. The chemistry of how these interactions change as a function of various “aging” mechanisms remains underexplored.

Thermal, mechanical, chemical, radiological stresses comprise just a small selection of the harsh environments to which siloxane-based materials are subjected. Though design of these materials is often done without significant attention to various aging mechanisms, it is becoming increasingly clear, broadly speaking, that research must turn its focus to understanding property variation/modification over material lifetimes.

The majority of traditional aging research and materials characterization, however, have employed macroscopic, bulk measurements such as tensile testing, elongation-at-break measurements, rheological techniques, etc. that are incapable of providing information about the silica-siloxane interface both directly and selectively. These traditional techniques typically provide only inferences about the chemistries associated with material aging phenomena.

Nuclear magnetic resonance has a rich literature investigating a wide spectrum of multicomponent polymer composites, with particular attention to weak interactions probed over small distances with chemical and dynamic specificity. Examples of recent work on interfacial characterization of polymer-composite materials include a poly(isoprene-*block*-ethylene oxide)-aluminosilicate composite [8], pH effects on a cetyltrimethylammonium bromide-templated silica composite [9], poly(ethylene oxide)-smectite clay (a plate-like mineral) interactions [10], poly(4-vinylpyridine)-colloidal silica composite [11], a 1,4-*cis*-poly(isoprene)-silica composite [12], and materials similar to those studied herein [13]. In addition these studies exploit a common NMR technique: cross-polarization (CP).

In this article, we examine the polymer/filler interface of a silica-poly(siloxane) elastomeric material via CP-MAS (cross polarization magic-angle spinning), focusing on how the composite is modified by exposure to γ -radiation. Our analysis will be compared to what is already known about these systems [14-17], particularly the effects of γ -radiation on fumed silica [18] and polysiloxanes [19-21] alone. We conclude with a model of the polymer/filler interface that is consistent with the competing

softening/stiffening phenomena observed and discussed frequently in previous research [14, 22, 23].

2. Experimental

2.1. Material Preparation. The samples under investigation are identical to irradiated poly(siloxane)-silica composites considered in a large amount of previous work [14, 15, 22, 23]. We used the identical material investigate previously, so that direct comparisons to the published data could be made. They comprise a crosslinked, bimodal siloxane polymer network filled with both precipitated and fumed silica at a cumulative weight fraction of 25.6%. The copolymer is comprised of 90.7 wt% dimethylsiloxane, 9.0 wt% diphenylsiloxane, and 0.3 wt% methylvinylsiloxane (for a subsequent curing reaction) monomer units. 21.6 wt% Cab-O-Sil M7D fumed silica (NuSil Corp., Carpinteria, CA) and 4.0 wt% Hi-Sil 233 precipitated silica (PPG Industries Ind., Pittsburg, PA) were used as the filler materials. After material synthesis, the samples were exposed to various levels of γ irradiation from a ^{60}Co source.

2.2. NMR Methods. The NMR experiments were conducted using an Apollo spectrometer (Tecmag, Houston, TX) with a static magnetic field of 7.03 Tesla (corresponding to a proton Larmor frequency of 299.32 MHz). At this field strength the ^{29}Si Larmor frequency is 59.47 MHz. The proton excitation pulse was 4.0 μsec in length corresponding to a B_1 frequency of 63 kHz. The spin-lock frequencies of both the proton and silicon channels were matched at ca. 50 kHz using kaolinite and searlesite. Searlesite has been previously used to optimize CP experiments when there are two distinct chemical shift ranges, as in the present case [24]. Continuous proton decoupling was

employed at 35 kHz during signal acquisition. Samples were spun at the magic angle at 1.6 kHz using a triple-resonance 4mm MAS probe (Doty, Columbia, SC).

The variation of signal with cross-polarization (CP) contact time CP was obtained using the standard CW spin-lock method seen in Fig. 1. These “build-up curves” were fit to the expression for transverse magnetization, M_x , as a function of build-up time, τ_{CP} :

$$M_x(\tau_{CP}) = \frac{M_\infty}{1 - \frac{T_{HX}}{T_{1\rho}^H}} \left[\exp\left(-\frac{\tau_{CP}}{T_{1\rho}^H}\right) - \exp\left(-\frac{\tau_{CP}}{T_{HX}}\right) \right] \quad (1)$$

where $T_{1\rho}^H$ is the proton spin-lattice relaxation time in the rotating frame, T_{HX} is a parameter characteristic of the proton-silicon dipolar coupling, and M_∞ represents the magnetization that the X spin system can theoretically attain under “ideal” conditions (i.e., strong H - X coupling and the X system decoupled from the effects of any relaxation processes) [25]. In general, elastomeric materials such as those under study presently have CP build-up curves that are dominated only by the proton $T_{1\rho}$; and for each sample this parameter was measured separately via the silicon-edited sequence given in Fig. 2. The benefit of this sequence over the more traditional single resonance 90° -acquire scheme is that one can measure a proton $T_{1\rho}$ value for *each* resolvable silicon resonance. This method becomes necessary when, for example, spin-diffusion does not equilibrate magnetization effectively over the whole proton bath, resulting in different values for $T_{1\rho}^H$ for different ^{29}Si sites (*vide infra*).

The values of τ_{CP} were chosen non-uniformly – more points were selected in the initial rise of CP signal to more accurately fit values of T_{HX} , and less points were chosen at long times because $T_{1\rho}^H$ can be determined more accurately when done measured separately. In general, 15 values of τ_{CP} ranging from 1-100 ms were chosen. For each

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sample and time point, 59392 scans were taken at 4k points/FID. At a recycle delay of 0.6 s, a build-up for one sample took approximately 6 days to measure (see discussion below). Each build-up was normalized for the mass of the sample in the rotor such that populations between samples could be compared directly.

The data were fit using a nonlinear regression toolkit in Mathematica 8.0 (Wolfram Research Inc., Champaign, IL). $T_{1\rho}^H$ values were determined from the silicon-edited spin-lock measurement and so fixed while fitting the CP build-up curves. As the experimental length prohibited additional runs of the entire sample matrix, bounds on experimental error were established using a Monte Carlo-based approach. Three CP build-ups were measured for the 100 kGy sample and the variation of the measured intensities of each peak at each time point was quantified. These “errors” ranged from 4.5% at 0 ms to 12% at 100 ms with a minimum at 0.25% at 30 ms (reflecting the fact that most of the CP build-ups achieved maximum intensity between 10 and 30 ms. A fifth order quadratic was chosen to fit this error vs. time curve and used to alter pseudo-randomly the measured data by weights related to the experimental variability at each time point. This process was done 1500 times for each dosage, and for each individual run, the “data” were fit to Eq. (1). We used only the error from the 100 kGy sample because of the close similarity of the build-ups between different dosages (further simulations supported this action). These fits were stored into a table, and averages and standard deviations were determined from these 1500 simulations for all three CP parameters per total absorbed dosage. The standard deviations of the Monte Carlo results were taken to be a robust estimate of the error associated with the experimentally determined build-up parameters.

3. Results

3.1. ^{29}Si shift assignment. Figure 3 shows the one-dimensional ^{29}Si CP spectrum of the pristine sample at $\tau_{CP} = 12$ ms. The chemical shift scale is externally referenced to the -109 ppm Q_4 silicon shift (see definition below) of fumed silica as reported previously [26]. As can be seen in the figure there are two groups of three overlapping peaks centered at approximately -100 ppm and -20 ppm.

The peaks centered at -100 ppm belong to various silicon sites associated with the fumed silica [26]. The peak at -90.2 is assigned to silicon atoms that have two hydroxyl groups attached, $(\text{Si-O})_2\text{-Si-(OH)}_2$, denoted as Q_2 or *geminal* silicons. The resonance at -100.2 ppm corresponds to silicon atoms with only one -OH group, $(\text{Si-O})_3\text{-Si-OH}$, or Q_3 silicons. Finally the resonance at -109 ppm (to which the data is referenced) belongs to fully-condensed Q_4 silicons, Si-(O-Si)_4 [26].

The second cluster of peaks centered around -20 ppm corresponds to polymer silicon species. The narrow, intense resonance at -19.4 ppm is due to more mobile polymer species associated with the bulk (i.e., relatively far from the silica surface). This assignment is based on chemical shift data for PDMS melts and solutions discussed in previous spectroscopic investigations [13]. The remaining two peaks are shifted downfield and are broader with full-linewidths-at-half-maximum (FLHM) an order of magnitude larger than the mobile polymer resonance. We will refer to these peaks as “poly1” and “poly2”, referring to the more intense (at -16.2 ppm) and less intense (at -9.2 ppm) peaks, respectively. A summary of chemical shifts, relative intensities, and FLHM

are found in Table 1. Note that the chemical shifts of the resonances do not change upon irradiation, so they are only reported for the unirradiated case.

3.2. CP build-up curves. Fig. 4 shows sample CP build-up curves for the 100 kGy and 500 kGy samples. The qualitative similarity of the curves associated with the build-up of any given ^{29}Si site highlights the necessity of fitting Eq. (1) to the data. Table 2 shows the results of the data-fitting procedure: M_∞ , T_{HX} , and $T_{1\rho}^H$ values are tabulated for all six peaks for each sample as a function of cumulative absorbed dose. Each build-up curve is described well by a single set of the M_∞ , T_{HX} , and $T_{1\rho}^H$ parameters.

For a given τ_{CP} , relative peak intensities cannot intrinsically be considered a quantitative measure of their relative populations, as they are dictated by the particulars of the CP processes of each silicon resonance. This is seen for example when considering the intensities of the Q₃ and Q₄ peaks given in Table 2 and Fig. 4. The Q₄ peak is surprisingly small considering the relatively low ratio of Q₃ to Q₄ sites present in fumed silica even despite the primary silica particle size being quite small (~5-25 nm in diameter). The low Q₄ intensity is in fact due to a considerably weaker proton-Q₄ silicon dipolar interaction, owing to a lack of proximate hydroxyl species that participate in the CP process. These facts highlight the importance of obtaining high-quality data so that population information can be extracted.

4. Discussion

4.1. M_∞ : populations. Table 2 contains for all resonances the dosage dependence of M_∞ , the parameter that represents the amount of silicon (at a given chemical shift) that can theoretically participate in the cross-polarization process. For the Q₄ sites, this parameter is relatively constant over the whole range, indicating that the size

of the Q₄ CP population does not change markedly upon irradiation. This observation is not unexpected since the mass fraction of silica should not change between samples, and significant conversion into other silica sites is unexpected. Also, as far as the CP process is concerned, core Si atoms should not be affected greatly since they exist in a domain relatively deficient in protons.

Referring to the lower half of **Figure 5** there exists for the Q₃ sites a small but noticeable increase in this population from 0 to 10 kGy. This observation is accompanied by a decrease in M_∞ of the Q₂ sites. This change is approximately equal and opposite ($\Delta M_\infty \approx 1.6 \pm 0.4$) suggesting that low levels of radiation convert Q₂ into Q₃ sites. Such a conversion is consistent with a model wherein a single silanol moiety in a geminal hydroxyl group is cleaved from the silica surface (Q₂ \rightarrow Q₃ conversion), as has been argued previously for irradiated fumed silica.¹⁸

The polymer M_∞ data given in the upper half of Fig. 5 show upon irradiation there is a decrease in M_∞ values for both the poly1 and poly2 populations at low dosages. Note that there exists a concomitant increase in the “mobile” polymer population (Table 2). We suggest these data are consistent with the destruction/interconversion of silanol groups (as discussed above), wherein the reduction in available hydrogen bonding sites precipitates a “release” of the polymer from the surface of the silica. Finally, we note that above 10 kGy, the sums over polymer- and silica-specific M_∞ values reveal that while a roughly constant overall number of protons participate in the CP process, they interconvert between various ²⁹Si types (e.g., Q₂ \leftrightarrow Q₃ or poly1 \leftrightarrow mobile). Between 0 and 10 kGy, however, there exists a decrease in the overall polymer population, reflecting the notion of polymer release at the surface. We would expect that a fraction of these

released polymer chains now exhibit dynamics more like the surrounding polymer matrix, unassociated with the inorganic filler, and do not participate effectively in the CP process.

4.2. T_{HX} : surface interaction. Fig. 6 details the changes in the silicon-proton coupling (T_{HX}). For dosages up to 50 kGy there is an increase in T_{HX} for both the Q₂ and Q₃ silica sites. The derived values shown in Fig. 6 are consistent with those reported previously (1.5 ± 0.2 and 3.1 ± 0.4 ms, respectively, for the Q₂ and Q₃ sites) [26]. Larger T_{HX} values indicate weaker dipolar couplings owing to increased internuclear distances, more molecular mobility, or a combination of the two. It has been established for some time that there exists a network of hydrogen-bonded silanols (of both Q₂ and Q₃ nature) on the surface of various silica materials [26-28]. This hydrogen-bonded network restricts the motion of what would otherwise be freely rotating, isolated, hydroxyl groups. We surmise that upon irradiation with high-energy γ -rays, the hydrogen-bonded surface silanol network is modified to form a variety of compounds such as H₂O, H₂, reactive ions, or radical species. The removal of these silanols weakens the overall effect of the hydrogen-bonding network, allowing more motion around the Si-O axis for the remaining (now perhaps isolated) silanols. This enhanced mobility (i.e., the greater degree of motional averaging of the dipolar interaction) and reduced surface proton density (as reflected in M_∞ values) would account for the observed increase in the values of T_{HX} .

The T_{HX} data for the polymer show the values to be largely constant for all resonances though there exists an observed decrease for the poly1 population between 0 and 10 kGy. We speculate that a stronger association between surface protons and polymer silicon nuclei would account for the decrease in polymer T_{HX} values: the now weakened surface hydrogen-bonding network creates more opportunity for stronger

associations between silica hydroxyls and surface-adjacent polymer chains (i.e., a reduced competitive effect).

The strong similarity of respective poly1/Q₃ and poly2/Q₂ T_{HX} values suggests some sort of correlation between silicon atoms associated with the silica and with the polymer. This association is also mirrored in the similarities of M_{∞} for the poly1/Q₃ and poly2/Q₂ pairs. We hypothesize that these groups are strongly associated with each other and thereby envision a scenario where poly2 silicon nuclei belong to groups that are involved in hydrogen-bonding adsorption events with geminal silanols, and where the poly1 silicon atoms are associated with Q₃, or *vicinal* silanols. It is important to note that a poly1 or poly2 designation does not correspond to an entire polymer chain but to a small subunit of monomers that is strongly affected by the adsorption event. It would stand to reason, then, that along a single polymer chain there can be multiple segments that behave like poly1 and poly2 sites or that behave as mobile segments (as in, e.g., loop or end-chain structures).

4.3. $T_{1\rho}^H$: proton mobility. $T_{1\rho}^H$ is well known as a measure of micro- to millisecond scale dynamics associated with concerted motion of polymer chain segments [26]. Modest-to-strong dipolar coupling amongst protons in polymers usually results in a single value of $T_{1\rho}^H$, where the dipolar coupling leads to *spin diffusion* [25,29]. In the present study we employed the silicon-edited $T_{1\rho}^H$ measurement (Fig. 2) so that derived values are obtained while minimizing proton spin diffusion processes.

Though the values for $T_{1\rho}^H$ of the Q₄, Q₃, and poly1 domains are quite similar (see Table 2 and Fig. 7), we must consider the reasons for the significant relative decrease in $T_{1\rho}^H$ for the poly2 and Q₂ sites. Though geminal and vicinal silanols are relatively well

distributed in fumed silica, we surmise that spin diffusion must be quite weak for there to be such a disparity in Q₂ and Q₃ $T_{1\rho}^H$ values. This might be possible if there exist large “pools” of Q₂ and Q₃-type silanols. This possibility has been addressed previously by Chuang et al. wherein they assert that even the surface of fumed silica (which is generally disordered due to its formation at high temperatures) can be thought of as being at least partially similar to that of crystalline β -cristobalite [30]. Specifically, the (100) face of this quartz phase has been shown to bear characteristics similar to Q₂ domains on the fumed silica surface. Local domains of (100)-type structural order on fumed silica, then, could be large enough to prevent significant spin diffusion from Q₂ sites that would otherwise lead to a single $T_{1\rho}^H$ value. Other work also concluded that there are different spin diffusion rates for both silanol species, where the Q₂ hydroxyls spin exchange more rapidly as a consequence of stronger hydrogen bonding interactions [26]. Considering the different spin diffusion rates, the possible lack of efficient diffusion between silanol types, and the surface structure arguments considered above it is reasonable that there exists multiple $T_{1\rho}^H$ values for various ²⁹Si sites.

An important observation whose impacts on derived $T_{1\rho}^H$ values (and, indeed, all CP parameters discussed presently) should be considered is that of the relatively low signal intensities of the poly1 and Q₂ peaks. Both resonances are partially masked by those of neighboring peaks (poly2 and Q₃), and the CP dynamics of these more intense peaks might be expected to have some impact on those parameters derived for the low intensity silicon-containing species. If there indeed exists this “bleed through” of information from more intense peaks, one would expect it to artificially alter values of $T_{1\rho}^H$, M_∞ , and T_{HX} and perhaps obfuscate trends in data for the poly1 and Q₂ sites. Refer

to, for example, $T_{1\rho}^H$ data of Q₂ sites; the lack of clear trend coupled with enhanced “error bars” might result from such an issue. That there exist, though, distinct values (and, in some cases, trends; e.g. refer to $T_{1\rho}^H$ of poly1 sites or M_∞ of Q₂ sites) for the low intensity peaks despite the possible influence of populations and parameter values for other silicon species confirms that the poly1 and Q₂ are indeed distinct entities from the perspective of CP dynamics. While the results may not be completely quantitatively reliable, we trust the derived trends and estimate that the extracted parameters are no larger than an additional 10 - 15% (as additional Monte Carlo experiments suggest).

Micro- to millisecond time-scale dynamics have been investigated in previous publications by employing transverse relaxation (T_2) experiments from which residual dipolar couplings (RDCs) were derived [14, 22, 23]. In those experiments trends that mimicked rheological data were observed: a softening (increased T_2) at low dosages followed by an overall stiffening (decreased T_2) from 50 to 500 kGy. For example, Fig. 8 represents the relative change in RDC magnitude with cumulative radiation dosage [22]. Generally speaking, a decrease in the RDC magnitude relates directly to a increase in segmental motion of polymer chains [14, 17, 22, 23]. We clearly see this same behavior in Figure 7 for the Q₃, poly1, and poly2 sites' values of $T_{1\rho}^H$. At 10 kGy there is a significant increase in $T_{1\rho}^H$ for the poly1 and poly2 components pointing to increased mobility at these kilohertz frequencies. Following this dosage, there is an equally significant decrease in $T_{1\rho}^H$ up to 500 kGy, however, the M_∞ data rules out the possibility of additional/regenerated silanol groups on the silica surface. Previous work indicates that a reduction in interfacial water (through desiccation, radiation, etc.) reduces the screening of electrostatic interactions between the polymer and the silica surface.

Computational studies of these materials show significant decreases in both polymer-surface distance and chain mobility upon removal of water from the interface [31]. The observed decrease in segmental mobility was shown to result from stronger interactions with the silica surface. This stronger surface association, then, would cause the reduction in polymer segmental motion reflected in the observed decrease in $T_{1\rho}^H$. The observed behavior mirrors exactly the observation from the T_{HX} data, which indicates a stronger association of polymer chains with the silica surface through, presumably, a reduction of surface hydrogen-bonding networks in favor of interactions between the polymer and individual silanol groups.

Studies on the irradiation of polysiloxanes in the melt have observed competing phenomena: namely, chain scissioning and cross-linking [32]. Under a variety of conditions, it has been shown that cross-linking dominates as a result of reaction between a variety of radical species, specifically $-\text{Si}\cdot$ and $-\text{CH}_2\cdot$ [32, 33]. These moieties can react to form a variety of bridges between chains (mostly involving one or two $-\text{CH}_2-$ groups or oxygen atoms), or can form more complex structures such as heterocyclic “end-loops” (i.e., cross-linking along the same chain) [34]. It has been known that irradiation of silica can incite radiation-induced band gap excitation wherein the generation of a hole/electron pair involves the conversion of matrix O^{2-} sites into O^- sites [35]. At low dosages there is a sharp increase in the concentration of trapped O^- within the silica matrix, but at higher doses, these defects saturate and reactive species can migrate to and subsequently “active” the silica surface. In pure silica, researchers have observed the reaction of these active sites with physisorbed water or silanol groups to liberate H_2 or H_2O [36, 37]. In the presence of other chemical species (e.g., polymer),

even more complex silica surface chemistry is possible including radiolysis of water, hydrogen peroxide generation, radical chemistries, etc. [21, 34, 38, 39] The presence of radical species in both the silica and polymer domains in conjunction with their mutual proximity therefore force us to consider the possibility of cross-linking with the surface at dosages well above 50 kGy. This cross-linking would subsequently restrict strongly the conformational space of the chain segment near the linkage, slowing its mobility and resulting in a decrease in the value of $T_{1\rho}^H$. As a final note, it should be pointed out that the values of $T_{1\rho}^H$ for the mobile phase are slightly larger at 250 and 500 kGy. This increase in $T_{1\rho}^H$ may be a result of well-documented oxidative, radiation-induced chain scissioning. The resultant chains having a lower average molecular weight would be expected to exhibit enhanced mobility and hence be described by large rotating frame spin-lattice relaxation time constants.

5. Conclusions

This section serves to concisely summarize the data discussed in detail above. We begin by considering phenomena at low dosages then conclude with high dosage observations.

5.1. Under 50 kGy. At low levels of radiation there is a conversion of Q₂ geminal silanols into Q₃ species. The strength of the hydrogen-bonding network associated with these surface hydroxyls decreases because the average distance between hydroxyl protons increases. The interactions between silanols (and their associated physisorbed water) and the polymer chain also weakens, and chains are subsequently released from the surface. This weakened H-bonding network increases the local mobility of chain segments along the polymer backbone to the degree where they behave

like the mobile polymer segments. As Q₄ are buried within the silica core, they remain relatively unaffected by radiation (insofar as the $^{29}\text{Si}\{^1\text{H}\}$ CP dynamics are concerned).

5.2. Above 50 kGy. Above 50 kGy a significant reduction in Coulombic screening between the polymer and the silica filler strongly reduces the segmental dynamics of the polymer as chain segments approach and interact with the silica surface. It is also possible that reactive radical species present in the system cause polymer to covalently attach to the silica surface. The poly1 chain segments appear to associate strongly with surface Q₃ groups. The same can be said for Q₂ and poly2 sites given a strong correlation in their respective CP dynamics. Overall there is little dependence of relative population on dosage as parameterized by M_∞ .

5.3. Further work. Much of the above conclusions on the effects on γ -radiation on siloxane-silica composites were derived from the proposal that chain segments called poly1 were highly correlated (i.e., adsorbed) to vicinal, Q₃ silanol sites on the silica surface. Similarly, Q₂ silanols were associated with poly2 segments of polymer. These assignments were based on strong correlations in extracted parameters derived from $^{29}\text{Si}\{^1\text{H}\}$ cross-polarization build-up curves. Though other observations (e.g., relative line-widths and ^{29}Si chemical shift phenomena) help to support this assumption, further evidence of the domain correlations would be helpful. Current work now focuses firmly establishing evidence of proximities of various ^1H and ^{29}Si environments through both homonuclear and heteronuclear two-dimensional solid-state NMR techniques.

6. Acknowledgements

Abbreviated Title: SS-NMR of γ -Irradiated Siloxane Elastomers

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Table 1. Populations, shifts, and line-widths extracted for the six peaks present in the $^{29}\text{Si}\{^1\text{H}\}$ spectrum of the unirradiated sample at $\tau_{CP} = 12$ ms (see Figure 3).

site	rel. inten. (a.u.)	chem. shift (ppm)	FLHM (ppm)
Q ₂	0.08 ± 0.02	-90.2 ± 0.1	2.9 ± 0.2
Q ₃	0.38 ± 0.03	-100.2 ± 0.1	3.6 ± 0.2
Q ₄	0.65 ± 0.05	-109.0 ± 0.2	4.2 ± 0.2
mobile	0.27 ± 0.03	-19.4 ± 0.2	0.9 ± 0.3
poly1	0.40 ± 0.02	-16.2 ± 0.1	3.0 ± 0.2
poly2	0.14 ± 0.03	-9.2 ± 0.2	5.0 ± 0.3

Table 2. Extracted values for the M_∞ , T_{HX} , and $T_{1\rho}^H$ parameters as a function of radiation dosage using CP build-up data and Eq. (1). Note that the values of $T_{1\rho}$ corresponds to that of the protons; silicon $T_{1\rho}$ values are not given. “Errors” are generated from Monte Carlo simulations taking into account experimentally measured variation in intensity measurements.

poly1				Q3		
dosage	M_∞ (a.u.)	T_{HX} (ms)	$T_{1\rho}^H$ (ms)	M_∞	T_{HX}	$T_{1\rho}^H$
0 (kGy)	7.2 (0.9)	4.7 (0.3)	39 (3.9)	4.9 (0.5)	3.1 (0.2)	48 (4.0)
10	4.9 (0.5)	2.5 (0.3)	67 (4.1)	6.5 (0.7)	3.7 (0.2)	52 (4.9)
50	5.2 (0.7)	2.7 (0.3)	53 (4.5)	6.8 (0.7)	4.0 (0.2)	57 (3.1)
100	5.1 (0.4)	2.9 (0.4)	55 (2.5)	6.5 (0.5)	3.7 (0.5)	56 (2.7)
250	4.1 (0.3)	3.0 (0.1)	44 (4.3)	6.9 (0.7)	3.7 (0.2)	40 (2.9)
500	4.5 (0.8)	4.5 (0.5)	35 (2.1)	6.5 (0.5)	3.6 (0.3)	40 (4.2)
poly2				Q2		
dosage	M_∞	T_{HX}	$T_{1\rho}^H$	M_∞	T_{HX}	$T_{1\rho}^H$
0	3.4 (0.3)	3.7 (0.8)	12 (3.4)	1.7 (0.5)	1.5 (0.2)	25 (5.5)
10	1.0 (0.4)	3.5 (1.0)	30 (3.2)	0.5 (0.4)	2.0 (0.2)	28 (3.8)
50	1.4 (0.3)	3.1 (0.6)	21 (3.5)	0.6 (0.5)	3.0 (0.2)	21 (5.2)
100	1.2 (0.8)	3.5 (0.5)	14 (3.0)	0.6 (0.2)	3.1 (0.4)	31 (7.1)
250	1.2 (0.4)	2.4 (0.7)	13 (4.3)	0.7 (0.2)	2.9 (0.2)	27 (3.0)
500	1.0 (0.2)	5.2 (0.8)	19 (3.6)	0.6 (0.4)	3.0 (0.2)	22 (4.2)
Mobile				Q4		
dosage	M_∞	T_{HX}	$T_{1\rho}^H$	M_∞	T_{HX}	$T_{1\rho}^H$
0	5.7 (0.6)	14.5 (1.4)	67 (5.0)	15.3 (0.5)	8.3 (0.5)	45 (2.7)
10	5.9 (1.0)	12.5 (1.4)	62 (3.2)	14.4 (1.0)	8.5 (0.6)	43 (5.2)
50	5.2 (1.6)	13.4 (1.5)	61 (4.6)	14.9 (1.2)	8.7 (1.0)	47 (7.7)
100	8.0 (1.8)	14.6 (2.1)	47 (5.4)	15.0 (1.1)	8.4 (1.2)	48 (3.6)
250	6.8 (1.4)	12.5 (2.3)	52 (2.6)	14.0 (1.0)	8.5 (1.3)	44 (5.6)
500	6.1 (1.1)	12.7 (3.2)	60 (4.2)	16.2 (1.2)	11.0 (1.5)	42 (3.6)

Figure Captions.

Figure 1.

Pulse sequence for $^{29}\text{Si}\{^1\text{H}\}$ cross-polarization. τ_{CP} is the CP contact time and is incremented to measure CP build-up curves. $p_{\text{H},90^\circ}$ is the proton excitation pulse; and $p_{\text{H},\text{lock}}$ and $p_{\text{X},\text{lock}}$ are the H- and X-channel lock pulses, respectively, matched using the Hartmann-Hahn condition. Continuous wave ^1H decoupling is optional though may be necessary especially if proton density is high or coupling to silicon nuclei is strong. Phase cycling is as follows: $p_{\text{H},90^\circ} = \{y, y, -y, -y\}$; $p_{\text{H},\text{lock}} = \{x\}$; $p_{\text{X},\text{lock}} = \{x, x, x, x, y, y, y, y, -x, -x, -x, -x, -y, -y, -y, -y\}$; acquire = $\{x, x, -x, -x, y, y, -y, -y, -x, -x, x, x, -y, -y, y, y\}$.

Figure 2.

Pulse sequence for both proton and silicon $T_{1\rho}$ measurement. For the silicon-edited proton $T_{1\rho}$ measurements discussed in the text, use the spin-lock block before CP contact on the proton channel. For CP-assisted silicon $T_{1\rho}$ measurement (for confirmation that $T_{1\rho}^{\text{H}} \ll T_{1\rho}^{\text{Si}}$), use the post-CP contact spin-lock on the ^{29}Si channel. Parameters are as defined in Figure 1.

Figure 3.

$^{29}\text{Si}\{^1\text{H}\}$ spectrum of the pristine sample at a contact time $\tau_{CP} = 12$ ms. The chemical shift scale is externally referenced to the Q₄ shift of fumed silica. Overlaid on the data are Gaussian peak fits of each peak except the narrow, mobile polymer peak. No post-processing has been done to the data save zeroth-order phase correction.

Figure 4.

A comparison of the CP build-up curves obtained for the 100 and 500 kGy samples. The curves in black plot Eq. (1) using the values from Table 2.

Figure 5.

M_∞ as a function of dosage. This parameter quantifies the relative populations of ^{29}Si CP participants. The top graph shows the parameter derived from the polymer data. The bottom graph highlights the silica populations.

Figure 6.

T_{HX} dependence on dosage. This parameter represents the strength of the dipolar interaction between the ^{29}Si nucleus and proximate protons. The top graph shows the parameter derived from the polymer data. The bottom graph highlights the silica populations.

Figure 7.

Proton $T_{1\rho}$ as a function of dosage. This parameter quantifies the decay of the CP build-up and can be thought of roughly as a measure of molecular mobility. The top graph shows the parameter derived from the polymer data. The bottom graph highlights the silica populations.

Figure 8.

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Observed dependence of a reduced RDC (relative to unirradiated case), D^* , on total dosage. D^* is defined as $(D_{\text{res}} - D_{\text{res},0})/D_{\text{res},0}$ as defined previously. The dashed line indicates the nominal, unirradiated material. Negative values of D^* represent a larger degree of chain mobility relative to the unirradiated material, and positive values represent decreased mobility. Data shown for three magnetic field strengths, 20, 65, and 200 MHz. Taken from [23].