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. L-091, Livermore, CA 94550, USA
[b] Department of Chemical and Biomolecular Engineering, University of California at Berkeley, Berkeley, CA 94720, USA

ARTICLE INFO

ABSTRACT

We employ silicon-proton (^{29}Si{^{1}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 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 effects of silica surface hydroxyl modification, interfacial water content, and radiation-induced chemistries are considered responsible for the observed macroscopic behavior of these engineering materials.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The ability to refine and tailor the physical and chemical properties of elastomeric materials has 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 reflect conditions of 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 increasing clear, broadly speaking, that research must turn its focus to understanding the evolution of engineering properties over material lifetimes. The majority of traditional aging research and materials characterization, however, has 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 investigated previously, so direct comparisons to the published data can 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 T (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 μs 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 4 mm MAS probe (Doty, Columbia, SC).

The variation of signal with cross-polarization (CP) contact time 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}:

$$M_x(\tau_{CP}) = \frac{M_\infty}{1 - \frac{T_{HX}}{T_{1\rho}^H}} \lfloor \exp\left(-\frac{\tau_{CP}}{T_{1\rho}^H}\right) - \exp\left(-\frac{\tau_{CP}}{T_{HX}}\right) \rfloor \qquad (1)$$

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.,
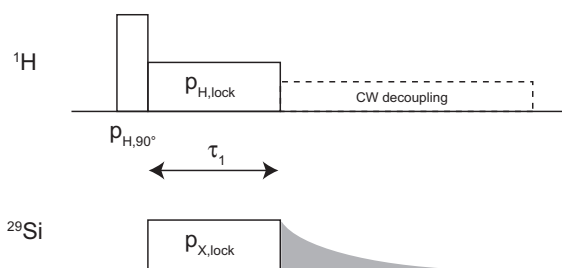

Fig. 1. Pulse sequence for ^{29}Si{^{1}H} cross-polarization. τ_{CP} is the CP contact time and is incremented to measure CP build-up curves. $p_{H,90°}$ is the proton excitation pulse; and $p_{H,lock}$ and $p_{X,lock}$ are the H- and X-channel lock pulses, respectively, matched using the Hartmann-Hahn condition. Continuous wave ^{1}H 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: $p_{H,90°}$ = {$y, y, -y, -y$}; $p_{H,lock}$ = {x}; $p_{X,lock}$ = {$x, x, x, x, y, y, y, y, -x, -x, -x, -y, -y, -y, -y$}; acquire = {$x, x, -x, -x, y, y, -y, -y, -x, -x, x, x, -y, -y, y, y$}.

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 measured separately. In general, 15 values of τ_{CP} ranging from 1 to 100 ms were chosen. For each sample and time point, 59,392 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
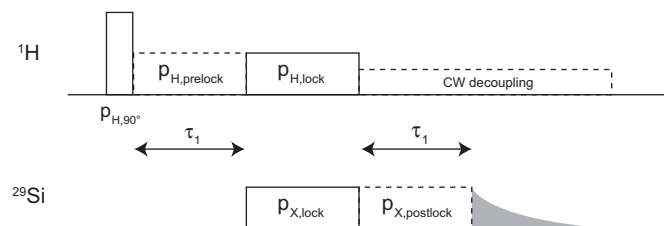

Fig. 2. Pulse sequence for both proton and silicon $T_{1\rho}$ measurement. For the silicon-edited proton $T_{1\rho}$ measurements discussed in the text, use the spin-lock block before CP contact on the proton channel. For CP-assisted silicon $T_{1\rho}$ measurement (for confirmation that $T_{1\rho}^H << T_{1\rho}^{Si}$), use the post-CP contact spin-lock on the ^{29}Si channel. Parameters are as defined in Fig. 1.