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Probing degradation in complex engineering silicones by ^{1}H multiple quantum NMR

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ABSTRACT

Static ^{1}H Multiple Quantum Nuclear Magnetic Resonance (MQ NMR) has recently been shown to provide detailed insight into the nextwork structure of pristine silicon based polymer systems. The MQ NMR method characterizes the residual dipolar couplings of the silicon chains that depend on the average molecular weight between physical or chemical constraints. Recently, we have employed MQ NMR methods to characterize the changes in network structure in a series of complex silicone materials subject to numerous degradation mechanisms, including thermal, radiative, and desiccative. For thermal degradation, MQ NMR shows that a combination of crosslinking due to post-curing reactions as well as random chain scissioning reactions occurs. For radiative degradation, the primary mechanisms are via crosslinking both in the network and at the interface between the polymer and the inorganic filler. For samples stored in highly desiccating environments, MQ NMR shows that the average segmental dynamics are slowed due to increased interactions between the filler and the network polymer chains.

INTRODUCTION

Silica filled polydimethylsiloxane composite systems have a wide

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variety of important commercial and technological applications [1]. This is in no small part due to their chemical and thermal stability and the tailoribility of mechanical properties. This tailoribility is a result of the wide range of structural architectures possible, including the degree and type of crosslinking, the molecular weight between crosslinks, the number of elastically ineffective chains (loops, dangling chain ends, sol-fraction) as well as filler content and surface properties [2-5]. However, due to the complexity of the network structure and the poorly characterized interface between the polymer and the filler, quantitatively characterizing changes in these structures with time is difficult.

Nuclear magnetic resonance (NMR) has been used to characterize chemical speciation changes occurring in both soluble and insoluble fractions of silicone polymers for decades [6-9]. One of the most common strategies for characterizing the effects of aging on these materials has been correlating changes in the T_2 relaxation times measured by spin-echo methods to changes in crosslink density of the bulk polymer. In fact, these methods have been developed to an extent that they are used in production applications with low resolution, portable relaxometers [10-12]. Unfortunately, spin-echo based methods are subject to a number of systematic errors which lead to over estimated changes in crosslink density, in chain order parameters, or in some cases completely incorrect trends [13].

Static ^{1}H Multiple Quantum (MQ) NMR spectroscopy, on the other hand, has shown the ability to more reliably quantitatively characterize elastomer network structure and heterogeneities [14-19]. ^{1}H MQ NMR methods allow for the measurement of absolute residual dipolar couplings ($<\Omega_d>$) and segmental/cooperative dynamics without interference from magnetic susceptibility and field gradients which complicate relaxation measurements [13, 14, 20,21] It has previously been shown that the residual dipolar couplings are directly related to the dynamic order parameter, S_b, and the crosslink density (1/N) [9]:

$$S_b = \frac{1}{P_2(\cos\alpha)} \frac{\langle\Omega_d\rangle}{\langle\Omega_d\rangle_{static}} = \frac{3r^2}{5N}$$

{1}

Thus, the MQ-NMR method allows for the direct measure of network topology and in many cases, filler-particle interactions. In the case of time dependent changes in structure due to aging, origins of degradation in material performance can be detected. A number of examples are shown here.

EXPERIMENTAL

Experiments were performed on crosslinked, filled, silicone networks, described elsewhere [15-17, 29]. The gum stocks for all formulations were either co-block polymers of dimethylsiloxane, diphenylsiloxane, methylphenylsiloxane, and/or methylvinyl siloxane [29] or endlinked networks of PDMS chains of variable length [15, 17]. The gum stocks were reinforced with silica filler and crosslinked with either peroxide or organometallic curing agents. These materials were tested in both new as well as laboratory aged conditions.
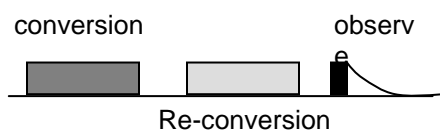

Figure 1. Multiple Quantum NMR pulse. Growth curves are obtained by incrementing either the interpulse delays or the number of multiple pulse excitation trains in the conversion and reconversion sequences [13].

All MQ-NMR experiments were performed on a Bruker Avance 400 MHz spectrometer equipped with a 5mm Bruker TBI probe. The pulse sequence used is illustrated in Figure 1. MQ growth curves, as illustrated in Figure 2A, were obtained generally by incrementing the loop counter, n. Alternately, the delay between pulses could be incremented instead. Further details are described elsewhere [13-18]. Insight was obtained on the network structure from the distributions of
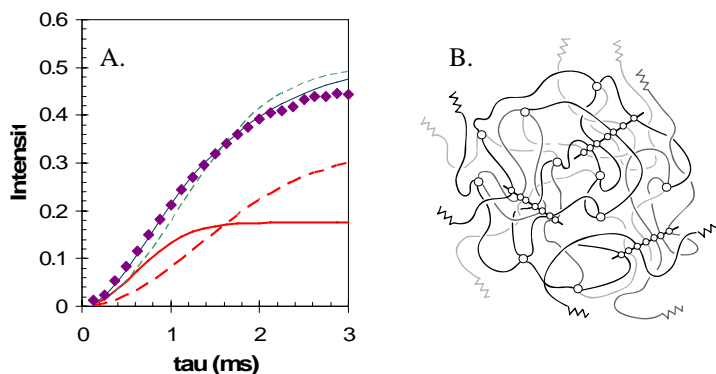

Figure 2. (A) Growth curve for pristine sample showing results of one site fit (dotted line) and two site fit (solid line – components are shown underneath curve in red); (B) Schematic of network structure of typical engineering silicone with both short and long chain constituents and standard four site crosslinking species and highly functional crosslinking sites.

the residual dipolar couplings extracted from the MQ growth curves using a fast Thikonov regularization (FTIKREG) algorithm [22] using the following analytical expression as the kernel:

$$I_{nDQ}(\langle \Omega_d \rangle; \tau_{DQ}) = 0.5 * (1 - e^{-\frac{2}{5}\langle \Omega_d \rangle^2 \tau_{DQ}^2})$$

{2}

Illustrative fits to equation 2 or a two site modification [16] are shown in Figure 2A. Results of FTIKREG regularization is shown in Figure 3.

RESULTS AND DISCUSSION

Characterization of thermally degraded materials:

Silicone materials are known to be fairly resistant to thermal degradation under relatively harsh conditions (less than a few hundred degrees centigrade). However, they are known to be subject to post-curing reaction, oxidative chain scissioning and crosslinking reactions, hydrolysis and unzipping reactions [23-25]. These reactions are typically observed indirectly by measurement of offgassing signatures by mass spectrometry based methods, though interesting results have been obtained by ^{17}O NMR [26, 27]. The effects of these reactions on the remaining, insoluble network structure are unfortunately more difficult to characterize.

The MQ growth curve for a typical pristine material is shown in Figure 2A. The pristine material in this case was constructed from PDMS chains of three different MW using primarily two different types of crosslinking sites: a typical 4 site junction and a highly functional multi-site crosslinking species with 60 crosslinking sites [17], as illustrated in Figure 2B. The
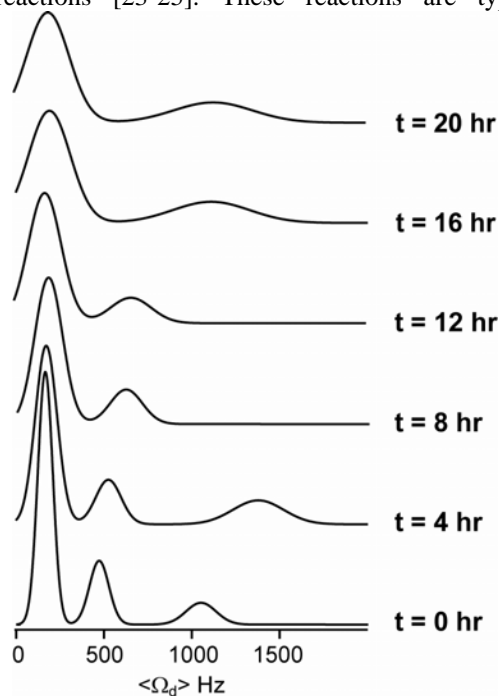

Figure 3. Distributions of residual dipolar couplings obtained from MQ-NMR analysis of thermally degraded (250 °C for indicated times, in air) PDMS composites.

growth curve could not be fit to one single residual dipolar coupling with equation 2 and required at least two sites to provide a reasonable fit. These two sites are assigned in this case to chains with high molecular weight between crosslinks and those chains with much shorter chain lengths. Estimates of the MW between crosslinks can be extracted Equation 1 and yield averages of 7500 g/mol and 1600 g/mol, in agreement with the expected MW between entanglements in the first case and the MW from the starting material [17]. Extraction of the distribution of the residual dipolar couplings from FTIKREG regularization is shown in Figure 3A and show surprisingly narrow distributions. Similar results have been obtained for the other pristine networks studied and can be found elsewhere [14-18].

We subjected the pristine material to thermal degradation at 250° C for times ranging from 0 to 20 hrs. TGA analysis indicated ~3% weight loss for 20 hrs of aging and standard Hanh-echo based experiments showed no change in the network T_2 with aging time, but did show a steady, but small increase in the sol-fraction component [17]. Despite these small changes, the material became markedly more brittle after 20 hours of aging. We applied MQ-NMR to these samples and the results obtained from FTIKREG regularization using equation 2 as a Kernel are the results are shown in Figure 3. Changes in both the low ($<\Omega_d>$ ~ 200 Hz) and high ($<\Omega_d>$ ~ 500 Hz) frequency peak width were observed. A third distribution at ~ 1000 Hz was also observed for zero and four hours of aging. This site has been assigned to a systematic fitting artifact due to the small sampling frequency at early MQ growth times. The small sampling frequency was limited by the smallest tau resolvable by the specific pulse
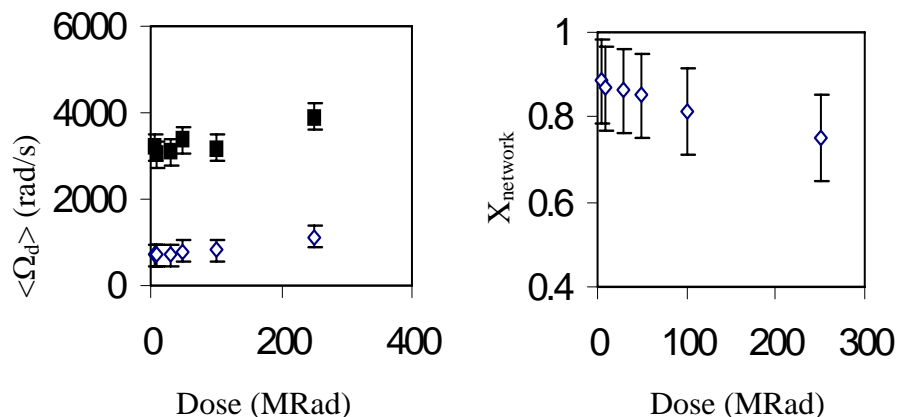

Figure 4. Results of MQ-NMR analysis of radiatively degraded silica highly filled PDMS networks. (A) Change in residual dipolar coupling ($<\Omega_d>$) with dose, (B) change in amount of polymer chains not interacting with the filler surface.

sequence used here [18]. The low frequency site was observed to broaden with time, while the high frequency site was observed to broaden and move to higher average residual dipolar coupling.

The MQ NMR data is consistent with simultaneous crosslinking (increased residual dipolar couplings) and chain scissioning (reduction in residual dipolar couplings). Observation of scissioning reactions is consistent with degradation products observed by GC/MS and NMR analysis of volatile and soluable degradation products [23-25]. Crosslinking during thermal aging at similar temperatures was previously observed for unfilled PDMS samples by Grassie et al. [30]. Continued post-curing re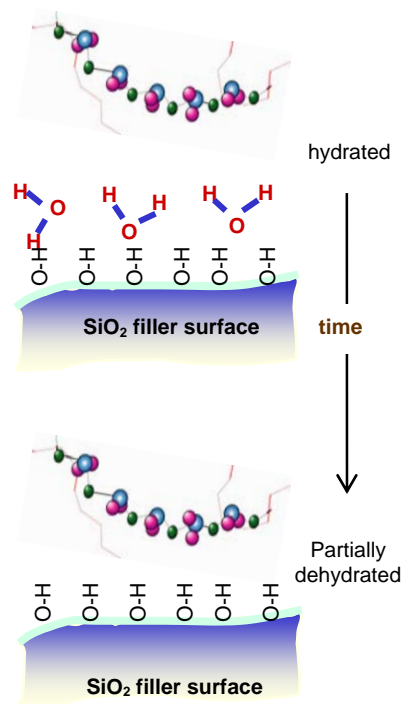actions of the residual silane species present from unreacted sites on the crosslinking moieties would lead to increased crosslink density for all chains. ^{1}H MAS NMR of the pristine and aged samples showed no difference within experimental error. This, however, is not surprising, given the small amount of material present. The MQ NMR, however, provides detailed insight into the result of these degradation mechanisms on the network structure of the polymer composite.

Characterization of radiation degraded materials:

Exposure of silicone polymers to ionizing radiation is generally understood to cause random crosslinking as the primary degradation mechanism [31]. Previously, this insight has been obtained via observing relative changes in T_2 relaxation times via spin-echo analysis [28, 33]. The direct quantitative correlation of T_2 relaxation times with network structural parameters such as crosslink density has proven difficult due to a number of limitations of the method, as described elsewhere [19-21]. We have applied MQ NMR to the characterization of a highly filled, PDMS composite material [15, 16]. Due to the high surface area of the filler used in these experiments and the network

Figure 5. Illustration of speciation changes at polymer-filler interface that would be expected to alter the interaction strength and effect reinforcement.

structure of the bulk polymer (roughly monomodal), the observed two site distribution obtained from deconvolution of the MQ growth curves were assigned to bulk polymer chains far from the surface ($<\Omega_d>$ ~ 3000 rad/s) and polymer chains in close proximity to the polymer surface ($<\Omega_d>$ ~ 1000 rad/s). As shown in Figure 4, upon exposure to γ-radiation at 1.2 MeV, 500kRad/hr, the residual dipolar couplings in both domains were observed to increase due to the effects of random crosslinking. In addition, we observed a steady increase in the amount of the chains associated with the filler surface, presumably due to formation of crosslinks to the filler surface or between chains already motionally constrained crosslinking to bulk polymer chains. These results have been described in more detail elsewhere [15, 16]. Again, the MQ NMR investigation provided insights into the composite structure unobtainable previously.

Characterization of desiccatively aged materials:

It has been postulated that hydrogen bonding between filler surface hydroxyls, water, and the oxygen atoms on the backbone of the polymer is a significant mechanisms of reinforcement [1, 32]. Aging of filled silicone materials in highly dry environments has the potential to alter the water speciation at the filler-polymer interface, as illustrated in Figure 5. In an effort to understand how altering water speciation affects the segmental dynamics, we applied MQ methods to highly filled samples aged in a sealed environment in the presence of a strong desiccating agent (including molecular sieve, P_2O_5, and LiH). Results of MQ NMR analysis of the pristine material and a sample aged for 4 years are shown in Figure 6 and clearly indicate that desiccation causes reduced the segmental dynamics both in the bulk polymer and in the polymer chains associated with the polymer interface. These data are consistent with recent MD simulations of modulus changes in filled composites where the interface interaction parameters are changed [34].
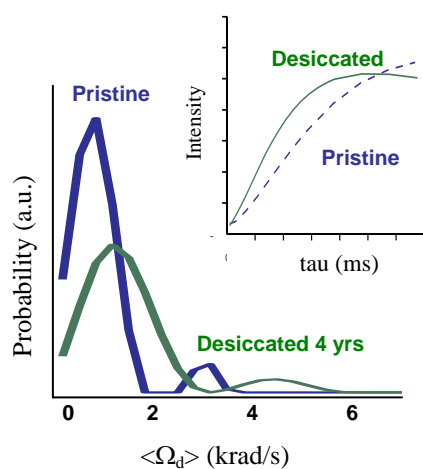

Figure 6. Results of MQ-NMR analysis of highly filled PDMS sample exposed to highly desiccating environment for 4 years. Inset: MQ growth curves.

CONCLUSIONS

Multiple Quantum NMR methods have been used to characterize the results of multiple degradation mechanisms on complex silicone polymer composites. The MQ NMR analysis provides direct, quantitative insight into the changes in the network structure and at the filler-polymer interface in these materials that has proven difficult to obtain via other characterization methods. For samples exposed to elevated temperatures, the MQ NMR indicated that degradation occurred via simultaneous chain scissioning and crosslinking reactions. For samples exposed to ionizing radiation, the MQ NMR indicated the dominance of random crosslinking. The MQ NMR analysis also indicated an increase in the amount of chains associated with the filler surface. For samples aged in a dry environment, MQ NMR measured a decrease in the segmental dynamics with aging time. This decrease occurred for chains in the bulk polymer network and associated with the filler surface. Many of these observations have not been observed prior to these analyses.

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