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Characterization and Modeling of Segmental Dynamics in Silicone Based Nanocomposites

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CHARACTERIZATION AND MODELING OF SEGMENTAL DYNAMICS IN SILICONE BASED NANOCOMPOSITES

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Introduction

The addition of nano-particles with novel chemical, optical, or barrier properties further opens the door to the development of so-called multifunctional materials (1). Key to developing robust, tailored composites is a detailed understanding of the structural contributions to the engineering properties of the composite and how they may change with time in harsh service conditions. The segmental dynamics and local order underlie much of the fundamental physics that influence the performance of elastomers and can serve as important diagnostics for reinforcement and other fundamental properties (e.g., network topology, cross-link density, the number and distance between chemical and physical (entanglements) cross-links, the type and volume fraction of filler) and thus provide a route to this fundamental understanding.

^{1}H MQ-NMR spectroscopy has shown the ability to provide more reliable and quantitative information regarding the elastomer network structure and heterogeneities (2). ^{1}H MQ-NMR methods allow for the measurement of absolute residual dipolar couplings ($<\Omega_d>$) and thus the segmental/cooperative dynamics Thus, the MQ-NMR method allows for the direct measure of network topology and in many cases, filler-particle interactions. The ability of MD methods to uncover structural motifs and dynamics at the atomistic scale is well known. In polymer systems, however, the relationship to bulk material properties can be somewhat tenuous due to often limited number of atoms and short time durations that can be studied. Extending these MD simulations to large assemblies of atoms and extending them to longer times using state of the art computational resources has allowed us to probe some useful relationships. MD provides static and dynamic properties for a collection of particles that allow atomic scale insights that are difficult to gain otherwise.

We have been exploiting these methods to characterize the effects of network structure and filler content on a number of silicone based nano-composite systems. This data is providing improved insight into the structural contributions to the changes in segmental dynamics. Here we provide an overview of our ongoing work toward understanding the influence of the network structure on the physical and chemical properties of advanced composite elastomers, including material performance in severe environments (high temperature, high strains, high radiation fluxes).

Experimental

Materials and Synthesis. Silane- and vinyl-functionalized POSS molecules (Hybrid Plastics), vinyl-terminated PDMS prepolymer (17.2k, Gelest), tetrakisdimethylsiloxysilane (Gelest), Meta-Carborane (m-CB) (Katchem Limited), and anhydrous tetrahydrofuran (Sigma-Aldrich) were all used as received. The hydrosilylation catalyst, cis dichlorobis(diethylsulfide)platinum (Sigma-Aldrich), was dissolved in dry THF (1 mg/mL) and the catalyst solution was stored under N_2 for use in the polymer syntheses. Poly(dimethylsiloxane) (PDMS) resin materials were made into foamed pads or solid elastomers about 2 inches in diameter using standard silicone cure chemistry using a bimodal distribution of two average PDMS chain lengths. Crosslinking was accomplished with stoichiometric quantities of tetrapropoxysilane (TPOS) in the presence of 5% tin(II) 2-ethyl(hexanoate) catalyst. Typical formulations were 10.333 g high molecular weight (HMW) PDMS (Mn ~ 77000 g mol-1), 4.6663 g low molecular weight (LMW; Mn ~ 550 g mol-1) PDMS, 1.1375 g TPOS, and 0.75 g Sn catalyst. Further details on composite synthesis can be found elsewhere (3, 4, 5).

Instrumentation. All MQ-NMR experiments were performed on a Bruker Avance 400 MHz spectrometer equipped with a 5mm Bruker TBI probe. MQ growth curves were obtained for each sample and normalized as discussed elsewhere (2, 6). Insight was obtained on the network structure from the distributions of the residual dipolar couplings extracted from the MQ growth curves using a fast Thikonov regularization (FTIKREG) algorithm (7) using the following analytical expression as the kernel:

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

Modeling. The MD simulations of PDMS and silica-filled/PDMS composites were carried out on a variety of bulk amorphous ensembles using three-dimensional periodic boundary conditions. In the simulations, the PDMS polymer chains are each composed of repeating silicon-oxygen bonds along the polymer chain backbone, and two methyl (CH_3) moieties (treated here as united-atoms) pendent to the Si atoms along the polymer backbone. The united-atom model representation treats each carbon and its bonded hydrogen atoms as a single united particle, whereas Si and O atoms are each represented as individual particles. The chemical structure of the PDMS molecule is $[\text{-O-Si}(CH_3)_2\text{-}]_n$, where n is the number of repeat units or monomers; where $n = 120$ for all PDMS chains used in this work. Thus, the molecular weight of our PDMS chains is M_w = 8,880 *g/mol*, where the molecular weight between entanglements for PDMS has been determined to be M_e ~ 8,100 *g/mol,* thus, our PDMS melts are weakly entangled, since $M_c < M_w$. Further details of the MD simulations reported here can be found elsewhere (*8*).

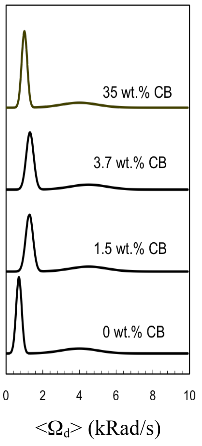

Figure 1. Distribution of residual dipolar couplings derived from MQ NMR for PDMS samples filled with m-CB to the indicated wt.%.

Results and Discussion

Effect of spherical nanoparticle fillers on segmental dynamics. We have been studying the effect of loading of spherical or near spherical nanoparticles, such as meta-carborane (m-CB) or functionalized Polyhedral Oligomeric Sesquioxanes (POSS) and others, on the segmental dynamics of PDMS resins. The distributions of residual dipolar couplings obtained from MQ-NMR are shown in **Figure 1** for samples prepared with m-CB at various filling levels. The data show that addition of these spherical nano-fillers does perturb the amplitude of the segmental dynamics. Upon addition of less than 10% m-CB the segmental dynamics as measured from the MQ-NMR experiments were observed to decrease. At higher loadings the segmental dynamics were increased. Similar results were observed by Broadband Dielectric Spectroscopy (4). We postulate that the primary mechanism of reinforcement at low fill level is one of "space filling", whereby the nanoscale m-CBs are on the correct size scale to effectively occupy free volume within the network without necessitating large scale reordering of the network in order to accommodate the particles. A consequence of the reduction in free-volume will however be that as the network goes through T_g, segmental motion will be inhibited by the presence of the nanoscale particles. At low loadings of m-CB, the free volume for the network is reduced and there is a significant reinforcement effect with an increase in compressive strength. At higher temperatures large-scale multi-segment co-operative motions will be influenced in a similar manner. At higher fill levels agglomeration of the m-

CB begins to dominate and the modulus and residual dipolar couplings begin to decrease as a result.

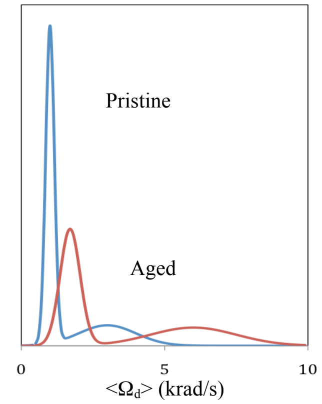

Figure 2. Results of MQ NMR of PDMS networks crosslinked with silane functionalized POSS and subject to thermal degradation at 250 °C.

Effect of thermal aging on POSS-PDMS composites. We have also studied the effects of addition of POSS both in blends and in networks crosslinked via silane functionalized POSS. In both cases, significant decrease in the amplitude of the segmental dynamics was observed by MQ-NMR and BDS. We have recently begun to characterize the time dependence of the segmental dynamics in thermally harsh environments. At above ambient temperatures, untethered POSS molecules tend to phase separate due to relatively high mobilities and low sublimation temperatures. When POSS is covalently linked to the PDMS network however, this mechanism is minimized and standard chain scission and crosslinking mechanisms begin to dominate. For example, MQ-NMR results for thermally aged POSS-PDMS network are shown. The distribution of residual dipolar couplings obtained for a pristine PDMS-POSS composite and after aging at 250 C for 15 hrs are shown in **Figure 2**. The extracted <Ω_d> distributions indicate a decrease in the segmental dynamics for both domains of the network structure. This is likely due to thermally induced crosslinking reactions from two sources: post-curing reactions of residual silane sites and oxidative crosslinking, known to occur in some silicone formulations [9].

MD modeling of effect of network topology in crosslinked PDMS-POSS networks on mechanical properties. The structural motifs that can be exhibited in nano-composites are many and subtle changes in crosslinking placement can, of course, have significant influence on the mechanical and dynamic properties of the composite (10). Changes in network structure and crosslinking sites with time in aging environments will thus have a strong influence on the time dependent changes in properties. We have employed large scale MD simulations to gain insight into the effects of different structural motifs on the mechanical and dynamic behavior of nano-composites. As an example, in **Figure 3** we show the calculated change in stress-strain behavior for PDMS networks crosslinked or blended with functionalized POSS to different levels. Two crosslinking topologies are illustrated. Topology I: Crosslinking from the vertices of the POSS unit only attached to PDMS chain ends; II: Crosslinks from the vertices of the POSS unit are allowed to attach to any methyl group on the PDMS chain at random locations. The consequences to the mechanical properties of the system are predicted, as might be expected, to be completely different. For Topology I: we predict a significant change in modulus as the number of crosslinking sites increase, whereas for Topology II, much less dependence on the number of crosslinks per POSS is predicted.

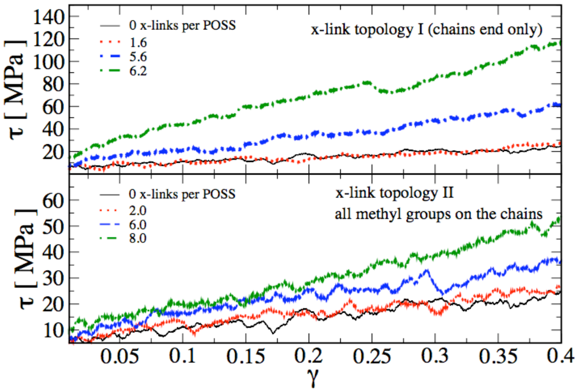

Figure 3. Large scale MD predictions of the stress strain behavior of POSS-PDMS networks created by crosslinking from variable number of vertices of the POSS filler to sites on the PDMS chains (chain ends only (I) or random locations on chain (II)).

Conclusions

Our studies employing MQ-NMR, BDS, and large scale MD simulations are allowing us increased insight into the impact of structural changes on the chemical and engineering properties of PDMS based nanocomposites. These structural changes can occur due to engineered changes via synthesis routes or through aging mechanisms during processing, sterilization, or long term service. The insights gained from this work offer the hope of understanding and predicting composite service life, as well as aiding in the rational creation of designer materials.

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