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MULTIPLE QUANTUM NMR INVESTIGATIONS OF STRUCTURE-PROPERTY RELATIONSHIPS IN SYNTHETIC AND AGED SILICONE ELASTOMERS

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Abstract

Complex engineering elastomeric materials are often characterized by a complex network structure obtained by crosslinking network chains with multiple chain lengths. Further, these networks are commonly filled with thixotropic reinforcing agents such as SiO₂ or carbon black. Degradation of such materials often occurs via mechanisms that alter the fundamental network structure. In order to understand the effects of modifications of network structure and filler-polymer interaction on component performance, a series of model compounds have been studied by ¹H multiple quantum NMR analysis and traditional mechanical property assessments. The ¹H NMR data provides insight into the distribution of segmental dynamics that reveals insight into the changes in mechanical properties.

Introduction

It is generally accepted that the properties of polymeric materials are controlled by the network structure¹ and the reactions by which they have been constructed. These properties include the bulk moduli at creation, but also the properties as a function of age during use. In order to interpret mechanical properties and predict the time dependent changes in these properties, detailed knowledge of the effect of structural changes must be obtained. The degree and type of crosslinking, the molecular weight between crosslinks, the number of elastically ineffective chains (loops, dangling chain ends, sol-fraction) must be characterized.

A number of theoretical and experimental efforts have been reported in the last few years on model networks prepared by endlinking reactions² and the relationships of those structures with the ultimate mechanical properties.³ A range of experimental methods have been used to investigate structure including rheometric, scattering, infrared, ²⁹Si MAS and CPMAS, ¹H relaxation measurements, and recently ¹H multiple quantum methods.

Characterization of the growth of multiple quantum coherences have recently been shown to provide detailed insight into silicone network structure by the ability to selective probe the individual components of the polymer network, such as the polymer-filler interface or network chains. We have employed recently developed MQ methods to investigate the structure-property relationships in a series of complex, endlinked filled-PDMS blends. Here, a systematic study of the relationship between the molecular formulation, as dictated by the amount and type of

crosslinks present and by the remaining network chains, and the segmental dynamics as observed by MQ NMR was performed.

Experiment

Materials

The silicone-based materials were constructed using a series of varying molecular weight polydimethylsiloxane (PDMS) polymers, which were synthesized using a tin(II) ethylhexanoate catalyst and diatomaceous earth filler. Three different crosslinking agents were used: (1) polymethylhydrosiloxane (PMHS), which contains many (up to 60) crosslinking sites; (2) tetra-*n*-propoxysilane (TPS), containing up to four crosslinking sites; and (3) diphenylmethyl silanol (DPMS), which forms terminating crosslinks. The relative amounts of the various molecular weight PDMS components and the PMHS crosslinking agents were systematically varied, resulting in a series of formulations with different mechanical properties. An example of a final configuration is shown in Figure 1, which demonstrates the different types of crosslinks formed using PMHS vs. TPS.

Samples were cured from Dow Corning 745U silicone fluid cured with Luperox 101, Varox DBPH peroxide curing agent. DC-745U fluid is a proprietary formulation with an unknown network structure. For irradiation studies, samples were sealed in glass ampoules and placed in irradiation chamber for the specified time. The irradiation pit contained a Co-60 source (1.2 MeV). The samples were irradiated at 5 kGray/hr for sufficient time to expose the samples to cumulative doses of 5 kGray to 250 kGray.

To investigate the effects of tensile strain, the strain was applied for a defined time for the non-control samples. Ends of elastomer test samples were pinched between steel plates and the strain was applied by stretching the elastomer samples to the strain $\lambda_1 = L(\text{aging})/L(0)$ using preset pins. Here $L(\text{aging})$ and $L(0)$ are the sample lengths in the strained and initial unstrained state. The entire tensile set was placed within the stainless steel irradiation vessel. The vessel was then evacuated through an attached valve and lowered into the irradiation chamber as described above

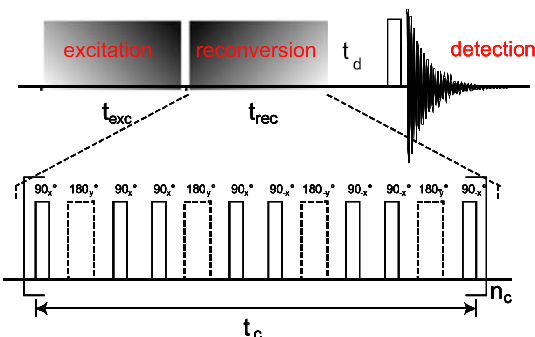


Figure 2. Multiple quantum pulse sequence used to generate MQ buildup curves.

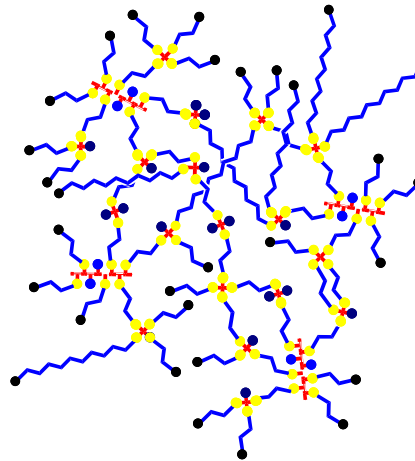


Figure 1. Typical structure of silicone elastomers showing different types of crosslinks and chain lengths.

^1H NMR Methods.

Experiments were performed at 400.13 MHz on a Bruker Avance 400 spectrometer using a Bruker TBI (HCX) 5mm probe. In all cases, small (0.1 cm x 0.1 cm x 0.1cm) squares of elastomer were cut from a larger piece and set in the portion of a 5 mm NMR tube that would be within the coil volume of the probe. Traditional ^1H spin echo experiments were performed using 90° pulse lengths of 5.5 μs and recycle delay times of 6 sec, and echo delays were varied from 0-15 ms. Echo intensity curves were plotted on a logarithmic scale and fit to a bi-exponential decay representing two

separate relaxation processes.

Multiple quantum NMR experiments were performed using the refocused multiple quantum excitation and reconversion pulse sequence shown in Figure 2 and described previously.^{4,5} Pulse lengths of 5.5 μ s were used with delay $\Delta 1$ and $\Delta 2$ equal to 4.83 μ s and 6.16 μ s respectively. Detailed descriptions of the experimental procedure can be found elsewhere.^{5,6}

Results and Discussion

¹H relaxation and multiple quantum NMR experiments were first performed on a series of polymers prepared with varying PMHS concentrations. The MQ-NMR buildup curves, shown in Figure 3, were fit using two different values of the residual dipolar coupling (RDC).^{5,6} The higher RDC values represent regions of lower mobility, here indicating the more highly crosslinked sites, while the lower RDC values result from chains with higher mobility, here the longer network chains. The ratio of RDC(low):RDC(high) can be used to provide information about the molecular partitioning of network vs. interfacial regions in a polymer system. In the case of varying PMHS, the ratio of RDC (low):RDC (high) decreased with increasing PMHS, indicating that higher concentrations of PMHS lead to larger contributions from the stiffer portion of the polymer as the polymer crosslinks. The trends observed in the NMR data follow closely with mechanical testing of load requirements, indicating that the amount of load increases with increasing PMHS concentration.

Comparable studies were performed with samples of varying molecular weights of PMHS crosslinkers. In general, a slight increase in $1/T_2$ was observed at higher molecular weights, as the number of available crosslinking sites increased. Additionally, both the low and high contributions to the RDC's were observed to decrease with higher MW of the PMHS, as did the ratio of RDC(low):RDC(high). Again, these changes are due to the presence of more crosslinking sites with higher MW PMHS chains.

Detailed investigations were also performed on hybrid materials consisting of varying amounts of low-MW, high-MW, or mid-MW) PDMS components. In these studies, the relative amounts of high-MW and low-high-MW PDMS were varied. NMR relaxation experiments revealed that the value of $1/T_2$ decreased with increasing ratios of MMW materials due to a softening of the material. While there were few significant changes in the high or low contributions to the residual dipolar coupling, the ratio of RDC(low):RDC(high) increased with increasing ratios of MMW PDMS. It is speculated that the relative populations of the mobile regions, which contribute to RDC(low) and also ultimately to the T_2 value, generally increase with increasing numbers of long PDMS chains. The presence of the longer chains leads to a softer polymer. Again, this is verified by mechanical load measurements, which indicate that the load decreases with increasing ratio of MMW PDMS.

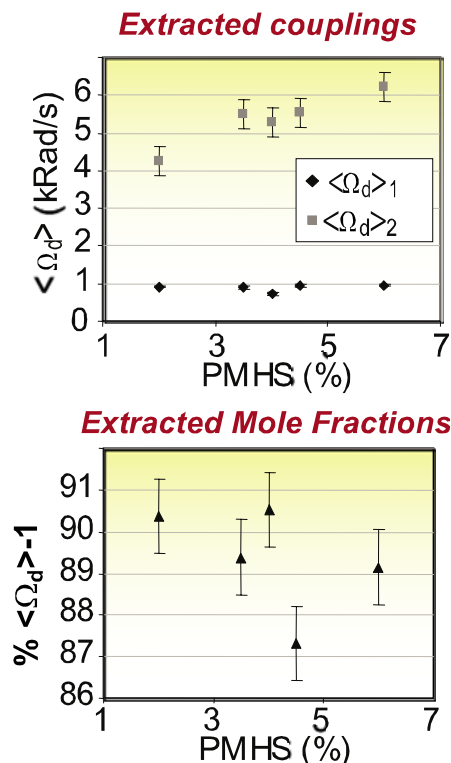


Figure 3. MQ results of variable PMHS study.

Multiple quantum growth curves for the 5, 50, and 250 kGray radiatively aged samples are shown in Figure 4.⁷ The initial growth rate was clearly observed to be dose dependent with higher exposures leading to higher growth rates. As the dose increased, it became increasingly difficult to fit the growth curves with only one site. A fit of the MQ growth curves to a bi-modal superposition of a relatively large coupling and a lower coupling, however, did adequately reproduce the experimental data. This indicates that there are two distinct network domains in this material. The domain with lower residual dipolar couplings (and thus faster segmental dynamics) is likely due to the general network polymer chains. The chains associated with the higher residual dipolar couplings we assign to the polymer chains physically or chemically interacting with the silica filler surface. It has been shown by both NMR and dielectric relaxation studies that surface adsorbed polymers are generally characterized by a slower segmental dynamics time constant.⁸⁻¹¹ Given the lack of any further information regarding the network structure in these composites (DSC thermograms did not show a dose dependence in the thermal properties), it is likely that the high residual dipolar coupling spins reside in chains associated with the silica surface.

MQ NMR has also been used to quantify the amount of tensile set that occurs in these materials when irradiated under strain.⁵ NMR relaxation times indicate an overall reduction in the segmental mobility in samples irradiated with and without tensile strain. The MQ NMR results indicate that the majority of the damage that is occurring in these materials with the addition of tensile strain is a crosslinking of the polymer network (decrease of ~15% in segmental dynamics) rather than a change in the filler-polymer interaction (decrease of ~5% in amount of surface interacting polymer) that is seen with radiation exposure alone. Tensile testing of the damaged and set materials, in contrast, indicates that the materials are softening. This would imply an effect of chain scissioning or a reduction in the filler-polymer interactions. Though radiation exposure does lead to competing rates of chain scissioning and crosslinking in all polymers, the radiation induced degradation in silicone polymers is well known to be dominated by crosslinking reactions.^{12,13} A reduction in the filler-polymer interaction has been observed in the MQ NMR measurements and given the small decrease in tensile stiffness in these materials it is likely that it is this reduction that is responsible for the softening affect.

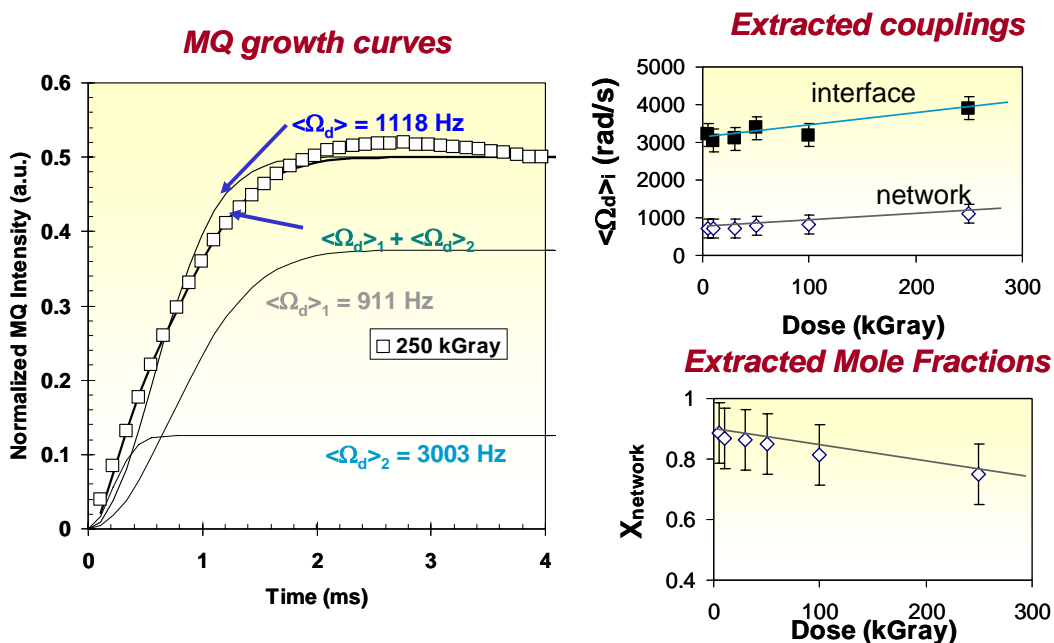


Figure 4. MQ results of DC745 exposed to γ -radiation.

Conclusions

The material properties of silicone materials can be tailored by varying proportions of individual components of the polymer. ^1H relaxation and multiple-quantum NMR can be used to reveal network-specific information and provides valuable information about the segmental dynamics as a function of formulation. In the study of the model compound presented here, increasing amounts of the PMHS crosslinker leads to a stiffer polymer, while larger amounts of the high molecular weight PDMS chains contributes to a softening of the polymer. A detailed focus on chemistry followed by detailed characterization of the material properties of polymer formulations is crucial in achieving a thorough understanding of the structure-property relationships of the materials. The extension of recently reported MQ NMR methods to radiatively damaged filled systems shown in this study further demonstrates the additional insight obtainable from multiple quantum NMR analysis compared to traditional relaxation and lineshape based methods, particularly in systems where detailed characterization of the network structure is unobtainable by other means.

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