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PROBING STRUCTURE PROPERTY RELATIONSHIPS IN COMPLEX ENGINEERING SILICONES BY ^{1}H NMR

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Introduction

It is generally accepted that the properties of polymeric materials are controlled by the network structure[1] 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 reactions[2] 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, [29]Si MAS and CPMAS, ^{1}H relaxation measurements, and recently ^{1}H 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.

Experimental

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.
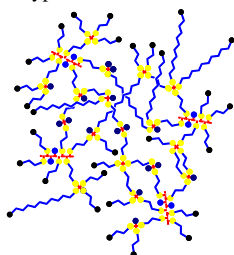

Figure 1. Typical structure of silicone elastomers showing different types of crosslinks and chain lengths.

^{1}H 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 ^{1}H spin echo experiments were performed using 90º 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 described previously.[4,5] Pulse lengths of 5.5 μs were used with delay Δ1 and Δ2 equal to 4.83 μs and 6.16 μs respectively. Detailed descriptions of the experimental procedure can be found elsewhere.[5]

Results and Discussion

[1]H relaxation and multiple quantum NMR experiments were first performed on a series of polymers prepared with varying PMHS concentrations. The spin-echo relaxation data was fit to an exponential decay to determine the T_2 relaxation time. As seen in Figure 2, the value for $1/T_2$, which can be correlated to the relative crosslink density or stiffness of the material,[6] increased with increasing PMHS. MQ-NMR buildup curves were fit using two different values of the residual dipolar coupling (RDC).[5] The higher RDC values represent regions of higher order, such as chains at a polymer-filler interface, while the lower RDC values result from chains with higher mobility, such as 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. 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.
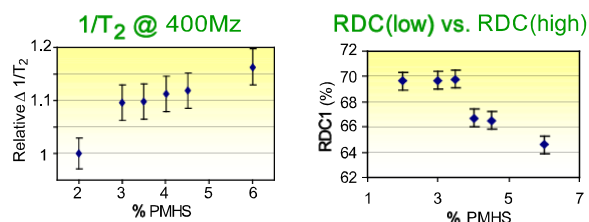

Figure 2. NMR results of variable PMHS study.

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 (termed "low-high" 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 H/LH MW 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 H/LW MW 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 H/LH MW PDMS.

Conclusions

The material properties of silicone materials can be tailored by varying proportions of individual components of the polymer. [1]H 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 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.

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