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NMR AND THERMAL ANALYTICAL INVESTIGATIONS OF STRUCTURE PROPERTY RELATIONSHIPS IN END-LINKED MODEL PDMS NETWORKS

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Introduction

Crosslinked Poly(dimethylsiloxane) (PDMS), elastomeric networks are an academically and technologically relevant sub-group of polysiloxane based materials, having wide-spread application in a large number of diverse technological, commercial and research areas[1]. Simple end-linked, unfilled, condensation, addition or peroxy cured PDMS networks typically exhibit poor mechanical properties and are of limited use as engineering elastomers. It is understood that in order to obtain the desired combinations of mechanical, physical and chemical properties for a specific real world application, such commercial 'silicones' must be formulated as complex multi-component systems - incorporating multi-modal distributions of chain lengths, varied crosslink topologies/densities, chemically modified free chain ends, non-stoichiometric excesses of reactive moieties, and often large volume fractions of a variety of reactive and/or passive filler materials.[2] The end result of this formulation effort is often a material with empirically tuned physical properties and a complex, yet often poorly defined network structure (see Figure 1).
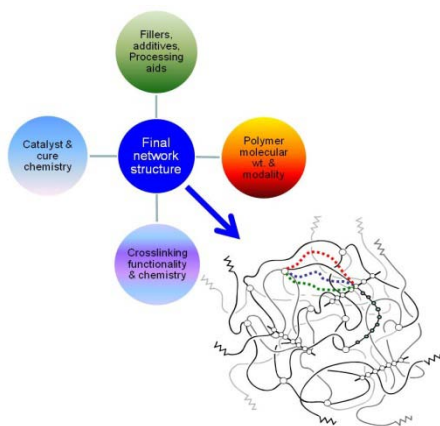

Figure 1. Illustration of the main contributory factors that define the complex structural architecture of an engineering silicone elastomer.

The physical, chemical properties and hence the performance of a siloxane elastomer are governed by this underlying network structure. Therefore, in order to make accurate assessments and predictions of a materials performance and lifetime over a broad range of environmental conditions, we must gain a better understanding of the relationship between network architecture and macroscale physical properties.

In this paper a combined, multilevel experimental approach towards understanding structure property relationships in silicone networks is discussed. Model, end linked PDMS networks have been formulated which incorporate individually and in combination, key structural elements: Mono- and bimodality, ranges of crosslink density, inter-chain molar mass and percentage of free chain ends. By utilizing a combination of solid state NMR and analytical degradative thermal analysis, the influence of each basic structural component the global properties of the system(s) as a whole have been investigated. With this methodology, we aim to build a compartmental phenomenological model which progressively and realistically describes the effects of network architecture on the physical behavior of PDMS elastomers.

Experimental

Materials. All PDMS polymers, tetraethoxysilane (TEOS) crosslinker and Tin(II)2-ethylhexanoate catalyst used in this study were obtained from Sigma Aldrich Chemical Co. Silanol terminated, linear PDMS polymers were obtained with number average molar masses (M_n) of 8.0, 9.6, 32.3, 54.4, 68.4 and 132.6 KDa (as determined by GPC) for the formulation of free chain end systems, a linear mono-silanol terminated PDMS (M_n = 14.1 KDa) was obtained, also from Sigma Aldrich.

Instrumentation. Solid-state NMR studies were performed on a low field Bruker Minispec spectrometer at 37±0.1°C under *static* conditions. Ninety degree pulse lengths of τ_p = 2.25 μs and recycle delays of 15 seconds were used. Carr–Purcell–Meiboom–Gill (CPMG) measurements were used to obtain Free Induction Decay's (FID's) free from the effects of magnetic field inhomogeneities. A spin preprocessing magic sandwich pulse sequence was used to refocus any spins with relaxation times faster than the ring down time of the probe, no so such fast relaxing domains were observed. The FID was then submitted to a fast Tikhonov regularization routine, FTIKREG, to obtain T_2 distributions.

All pyrolysis studies were carried out using a CDS Analytical 5150 Pyro-probe coupled to an Agilent 7890 GC using an Agilent 5973N quadrupole MSD for detection of analytes. Samples (~0.05 mg) of each model elastomer were pyrolysed at a ballistic heating rate from 60 to 1000 °C under a purge flow of helium. A 1:20 split flow from the pyrolysis chamber was injected continually into the GC HP-5 analytical column under constant flow conditions of 1 ml/min Helium as the carrier. The GC oven was set to ramp from 40 to 300 °C at a rate of 10 °C /min with a 30 minute hold for each injection. Total ion chromatograms of the pyrolysis products were collected for each run and normalized for sample mass in each case. Up to five repeats runs were carried out for each sample.

Synthesis of model networks. Model networks were formulated using organo-tin catalyzed condensation cure chemistry: For each formulation a stoichiometric level of the tetra-functional blocked silane crosslinker, tetraethoxysilane (TEOS) was mixed into 5 g of the appropriate PDMS base polymer. The averaged M_n values for each PDMS polymer (as determined by GPC) were used in calculating the stoichiometry required in each formulation. In this way, networks were synthesized which were as close as ideal as possible. Importantly – by carefully controlling stoichiometry, the formation of branched TEOS residues or unwanted silica (via the condensation of excess TEOS) was minimized in the networks. To this formulation, 0.5 to 0.05% (level dependant on the number of OH sites present) tin(II)2-ethyl hexanoate catalyst was added and stirred thoroughly. The resin was de-gassed under vacuum for twenty minutes and allowed to cure for 15h at 60 °C to form an elastomeric mat. This mat was then post-cured for a further 15h at 80 °C under vacuum, swollen overnight in toluene to remove small molecule impurities/reaction residues and finally oven dried under vacuum for 24h at 80 °C.

Principal component analysis (PCA). The raw TIC data was normalized based on the D_3 (trimer; hexamethylcyclotrisiloxane) peak (the most abundant) thus that all responses were a ratio of the D_3 peak. PCA of the collected data was carried out using Solo PLS Toolbox v. 6.3 (Eigenvector Research, Manson, WA). The software assembled the py-GCMS TIC data into a matrix comprised of the normalized responses vs. retention time for each group of samples to be analyzed. Preprocessing of the data consisted of this normalization followed by mean-centering, after which a PCA model was calculated consisting of significant principal components that described about 85 - 90% of the total variance. Scores and loadings plots were subsequently generated for each sample set of interest from the PCA model in order to examine significant groupings and variances in the sample sets.

Results and Discussion

NMR analysis of selected model networks. In a recent publication by the authors[3] it was demonstrated that solid state NMR methodologies could be employed in order to determine and predict effective molecular weight distributions between crosslinks in model end-linked PDMS networks. While highly informative and successful, the double quantum methodology employed[4] is a time intensive and experimentally complex technique. For the analysis presented here, we demonstrate the use of a rapid to implement and experimentally robust method of assessing shifts in the motional dynamics of siloxane elastomers (as a function of network architecture) that can be carried out on a low field instrument such as the Bruker Minispec. T_2 distributions were obtained for three end-linked model networks, based on a 68 KDa PDMS precursor: 68 KDa monomodal, 68 & 8 KDa bimodal and a 68 KDa base network with 20 mol. % free chain ends (see Figure 2).
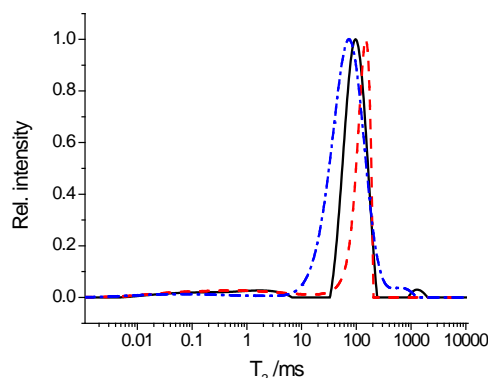
Figure 2. Normalized T_2 distributions for three end-linked model networks, based on a 68 KDa PDMS precursor. The Solid line represents a monomodal 68 KDa system, the dashed line a bimodal end-linked network of 68 and 8 KDa chains and the dash-dot line a 68 KDa network with ~20% free chain ends.

From distributions shown in Figure 2 it can clearly be observed that the observed T_2 response varies as a function of network structure – In the bimodal system a narrowing of the T_2 distribution function and a shift towards longer relaxation times is observed, when compared to the monomodal network. The sharpening of the distribution and shift in relaxation time can be attributed to a relative stiffening of the network (as a consequence of the inclusion of short 8 KDa segments), resulting in a more rigid (ordered) proton environment. Conversely, in the free chain end containing system, a shift towards shorter relaxation times is observed when compared to the base monomodal network – This can be directly attributed to a relative increase in the population of mobile chain segments in the 20 mol % free chain end system. From this NMR analysis it is clear that rapid assessments of structure-property relationships can be obtained for end-linked silicone elastomers, using comparatively simple, low field NMR techniques.

Degradative thermal analysis of selected model networks. In stark contrast to the *non-destructive* NMR methodologies discussed above, degradative thermal analysis (specifically, pyrolysis gas chromatography mass spectrometry, Py-GCMS) has been employed as a tool to probe the effect(s) of network architecture on thermal stability and the degradation mechanisms of polysiloxane elastomers. In a recent publication[5], the authors demonstrated that speciation of cyclic, oligomeric siloxane degradation products, formed during the non-diffusion limited thermal degradation of PDMS networks varied as a function of network structure. Shown in Figure 3 is a total ion chromatogram (TIC) obtained from the pyrolysis of a 68 KDa monomodal PDMS network, showing the distribution of cyclic oligomeric degradation products.
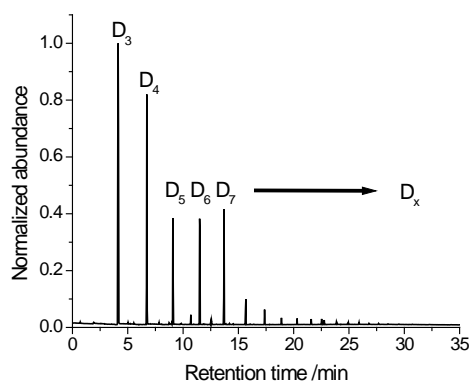

Figure 3. TIC of the pyrolysis products from a 0.04 mg sample of the 68 KDa KDa monomodal PDMS elastomer. The products of pyrolytic degradation are labeled D_3 to D_x (cyclic siloxanes).

The profile of degradation products from the 68 KDa model system, is typical of polysiloxanes - which are known to degrade in the most part via a series inter- and intra-molecular chain backbiting reactions, yielding ~60-80% of the 'D_3' cyclic triamer and progressively decreasing quantities of higher MW cyclics.[6] However, if the speciation of higher cyclic degradation products *relative* to the major (and somewhat invariant) D_3 triamer are examined, small yet significant differences can be observed. Shown in Figure 4 are the statistical scores from the PCA analysis of the degradation products of the linear precursors, a range of monomodal, bimodal and free chain end networks.
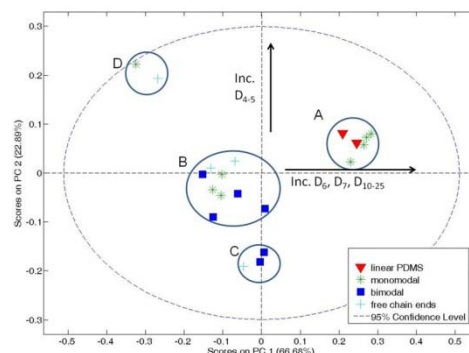

Figure 4. Samples-scores (PC's 1&2), complete synthesized matrix of materials. There are four classes of data, corresponding to the linear PDMS, the monomodal, bimodal and free chain end subsets respectively. Statistical groupings of samples are circled and labeled A-D. *Positive scores on PC1 (x-axis) have been correlated with increased relative yields of D_6, D_7 & D_{10-25} cyclics. Positive scores on PC2 have been correlated with increased relative yields of D_4 & D_5 cyclics.*

An analysis of the relative changes in the distributions of degradation products from a range of model systems using PCA (Figure 4) reveals several significant groupings. Group 'A' (linear PDMS prepolymers and monomodal networks up to 54.4 KDa) yield increased levels of larger cyclic siloxanes relative the rest of the matrix. Groups 'B & C' (bimodal networks and the 1-10% free chain end systems) are representative of the mean degradation behavior of the model matrix. Group 'D' (132 KDa monomodal and the 20% free chain end systems) samples evolve significantly reduced quantities of larger cyclics and increased levels of smaller D_{4-5} cyclic siloxanes. From these data it appears that crosslink density and the levels of available free chain ends influence the relative yields of small to larger cyclic oligomers on degradation. And while an in-depth discussion of the origins of these differing degradation profiles is beyond the scope of this paper and is discussed elsewhere,[5] it is clear that statistically significant differences in siloxane degradation can be observed as a function of network structure.

Conclusions. The underlying architecture of end-linked siloxane networks can be understood and investigated using a physical model and applied analysis approach. This work and others cited here, have demonstrated that ssNMR and degradative thermal analysis methodologies be applied to detect and quantify changes in the properties of silicone elastomers as a function of network structure.

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