STRUCTURE-PROPERTY RELATIONSHIPS IN END-LINKED MODEL PDMS NETWORKS – LINKING NETWORK ARCHITECTURE TO DEGRADATION BEHAVIOR AND MATERIALS PERFORMANCE

James P. Lewicki[a], Rebecca L. F. Albo, Stephen J. Harley, Michael J. Ashmore, Jasmine Finnie, Cynthia T. Alviso, and Robert S. Maxwell

[a]*Lawrence Livermore National Laboratory, 7000 East Ave. Livermore CA, 94550*

(*lewicki1@llnl.gov,* www.llnl.gov*)*

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.

If we are to make accurate assessments and predictions of materials performance and lifetime over a broad range of environmental conditions (information that is of critical importance in many areas, including the electronics, biomedical implant and aerospace industries), there must be an understanding of this underlying network architecture and how it influences, physical properties, materials performance, stability and lifetime.

In this work, a combined, multilevel experimental approach towards understanding structure property relationships in silicone networks is discussed. Well defined, 'clean' 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, conventional silica and nano-scale filler materials (polyhedral oligomeric silsesquioxanes). By utilizing a combination of solid state NMR, analytical degradative thermal analysis and Multivariate data analysis, the influence of each basic structural component on the global properties of the system(s) as a whole have been investigated. Shown in Figure 1 is a 'statistical map' of the relation between sample network architectures and their components of thermal degradation.
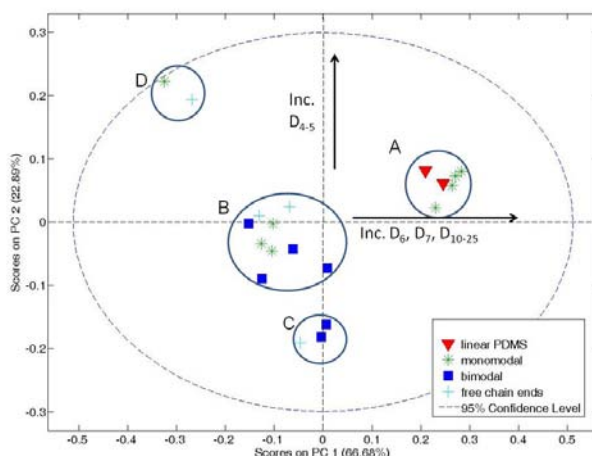
Figure 1. Multivariate statistical analysis of a matrix of model silicones. Statistical groupings of samples are circled and labeled A-D. Positive scores on PC1 (x-axis) have been correlated with increased relative yields of D_6, D_7 & D_{10-25} cyclics. Positive scores on PC2 have been correlated with increased relative yields of D_4 & D_5 cyclics.

This work represents a step towards the construction of a valid a compartmental phenomenological model which progressively and realistically describes the effects of network architecture on the physical behavior of PDMS elastomers.

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1. Arkles B., Chemtech. 13:542-555, 1983

2. Mark J.E., Allcock H.R., West R., Inorganic Polymers Oxford University Press, New York, 2005,159-160.