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ABSTRACT

Predictions of component performance versus lifetime are often risky for complex materials in which there may be many underlying aging or degradation mechanisms. In order to develop more accurate predictive models for silica-filled siloxane components, we are studying damage mechanisms over a broad range of size domains, linked together through several modeling efforts. Atomistic and molecular dynamic modeling has elucidated the chemistry of the silica filler to polymer interaction, as this interaction plays a key role in this material's aging behavior. This modeling work has been supported by experimental data on the removal of water from the silica surface, the effect of the surrounding polymer on this desiccation, and on the subsequent change in the mechanical properties of the system. Solid State NMR efforts have characterized the evolution of the polymer and filler dynamics as the material is damaged through irradiation or desiccation. These damage signatures have been confirmed by direct measurements of changes in polymer crosslink density and filler interaction as measured by solvent swelling, and by mechanical property tests. Data from the changes at these molecular levels are simultaneously feeding the development of age-aware constitutive models for polymer behavior. In addition, the microstructure of the foam, including under load, has been determined by Computed Tomography, and this data is being introduced into Finite Element Analysis codes to allow component level models. All of these techniques are directed towards the incorporation of molecular and microstructural aging signatures into predictive models for overall component performance.

INTRODUCTION

Silica-filled polydimethylsiloxane (PDMS) composite systems are of broad appeal due to their chemical and environmental resilience and the availability of a wide range of tailorable chemical and mechanical properties [1-3]. This composite material is stable for decades against numerous stress inducing aging mechanisms: thermal and mechanical loads, and environmental, radiative, and chemical attack. These materials are, however, subject to chemical and physical degradation over long service lifetimes. In addition, synergistic effects of degradation mechanisms occurring simultaneously may occur over many length and timescales (see Figure 1). The result is that the mechanical property changes associated with multi-mechanism aging may be subtle and may not necessarily change linearly as a function of time in service.

Further, it is impractical to performance-test existing materials and/or components for their design lifetimes, and this is clearly impossible for new materials that have only been available for a fraction of a component's design lifetime; thus, predictive models are needed. Current models are typically an extrapolation of historical data with the prayer that the process is linear on a log-log plot. The aging process may be accelerated by

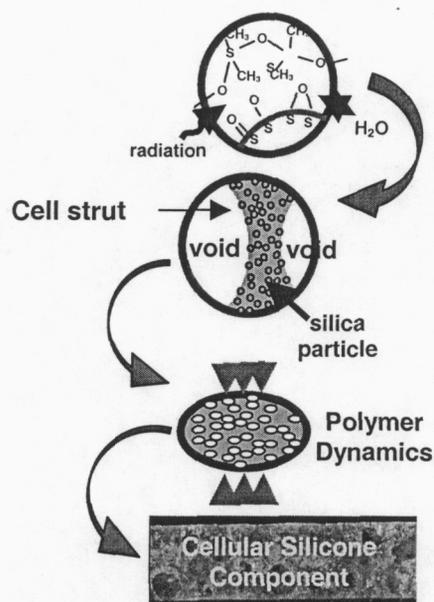


Figure 1. Diagram of the impact multiscale damage mechanisms will have on ultimate material performance issues.

increased temperature/humidity/etc, but this doesn't address the quantitative relationship of aging under the aggressive test conditions to the response at much longer times under more realistic service conditions. Rational predictive models for long term aging that acknowledge the underlying chemical and physical processes are needed. The need for these rational predictive models is particularly important for materials with significant microstructure, e.g., foams, highly filled polymers, polymer blends, and polymer composites. Because of the highly heterogeneous nature of these materials, small changes in one feature of the microstructure can often effect large overall changes in the macroscopic behavior.

Table 1. Overview of length scales and the experimental and modeling approaches applied to cellular silicon aging.

Domain	Experimental	Modeling
Atoms/Molecules	NMR & TPD	Mol. Dynamics
Polymer Viscoelasticity	Crystallization&DMA	Constitutive equations
Microstructure	CT	n.a.
Component	CT to Mesh	FEA

Since such linear relationships are often used in service lifetime predictions, there is a fundamental need to employ sensitive methods to investigate the structural and motional changes that occur in these materials as a result of aging in chemically, thermally, or radioactively harsh environments. Ideally, these methods would allow a complete assessment of aging mechanisms in order to yield predictive capabilities. We have developed and are testing a generalized experimental plan to address multiscale contributions to complex polymer degradation processes. These methods span from the

atomistic to the component scale and some of the experimental approaches are listed in Table 1. This paper highlights some of our recent results.

EXPERIMENTAL

The materials studied were a copolymer of polydimethylsiloxane and polydiphenylsiloxane, crosslinked by a vinyl monomer/vinyl-specific catalyst system. The percentages of each monomer unit in the base rubber were 90.7 wt.% PDMS, 9.0 wt.% PDPS, and 0.31 wt.% polymethylvinylsiloxane. The resultant rubber was then milled with a mixture of fumed (Cab-o-sil M7-D: 21.6wt.%) and precipitated filler (Hi-sil 233: 4.0 wt.%), and 6.8 wt% of an ethoxy endblocked siloxane as a processing aid. The processing aid averaged about 12 monomer units long and was added to block a percentage of the surface reactive sites on the filler and to reduce the filler-polymer interaction to meet mechanical and processability property specifications. A foam composite material was then made by processing the filled polymer with prilled urea (solid spheres of urea obtained from Coastal Chem, Inc [Cheyenne, WY] with particle sizes between 0.4 and 0.7 mm). The urea was subsequently washed out after curing providing a foamed composite with mm size pores. The investigated foams exhibited 60 percent porosity..

Details of experimental procedures for SPME, crystallization studies, NMR, solvent swelling, and molecular modeling can be found elsewhere [4,5].

RESULTS AND DISCUSSION

Laboratory aged samples subjected to γ -radiation degradation and exposure to desiccation atmospheres have been studied by NMR and molecular modeling for atomistic scale structural changes and for changes in polymer dynamics. We have previously established for M97 cellular silicones that NMR relaxation times are correlated to both polymer chain dynamics and to viscoelastic properties [5]. As such, NMR can be used to measure polymer degradation in situ. Figure 2 shows results of our NMR studies on degraded polymers. In general increased stiffening has been observed

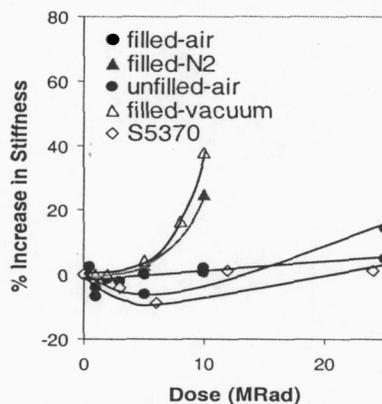


Figure 2. Increase in stiffness measured by NMR as a function of γ -radiation dose for M97.

for all exposures, though some differences due to atmospheric conditions are detectible. Similar results have been obtained for M97 polymers aged in desiccative environments, where a significant stiffening of the polymer matrix was observed with increasing exposure time (data not shown). This has been assigned to changes in the interfacial interactions between the PDMS polymer and the inorganic filler [4]. We have modeled both degradation mechanisms with Molecular Dynamics simulations. Using this approach we have been able to validate and predict the degradation effects of ionizing radiation and changes in water speciation on the mechanical properties, as measured by the polymer dynamics, in M97 type cellular silicons.

To measure bulk changes in viscoelastic properties due to degradation mechanisms, we have also used both solvent swelling and DMA methods. Results from these studies have supported our atomistic modeling and our NMR results [6]. The results have also allowed us to span the gap between the atomistic scale and the polymer microstructure. Results from these measurements are being fed into constitutive equations to provide detailed understanding and predictive capability for the aging of these complex polymeric foams.

In order to observe structural changes occurring on a larger scale as a function of both physical and chemical aging, we have employed computed tomography (CT) to image pore structure collapse as a function of compression. Results from one such measurement are shown in Figure 3 and clearly image the fracture and collapse of cell walls with moderate compressions.

Predictive lifetime predictions maybe possible if data from our atomistic scale studies can be combined with our viscoelastic understanding reflected in the constitutive equations being developed with the CT data. Towards this end we have fed the CT data into Finite Element Analysis input files in combination with simple constitutive equations for the polymer viscoelastic properties [7]. The imaged polymer was then subject to simulated compression. The FEA calculation then predicted the relative strains throughout the polymer component and is shown in Figure 4. As can be seen, significant strain develops at cell wall struts. This localized strain may explain the strut collapse seen in the CT data shown in Figure 3.

CONCLUSIONS

The work reported here represents our initial efforts towards attaining a detailed understanding of the multiscale aging phenomena in cellular silicone materials aged in

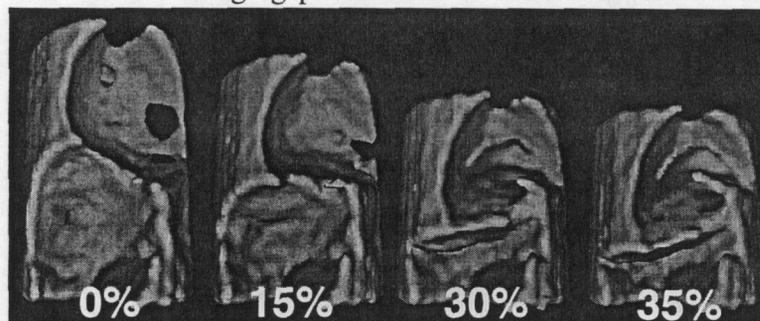


Figure 3. CT scans of pores structure deformation during compression.

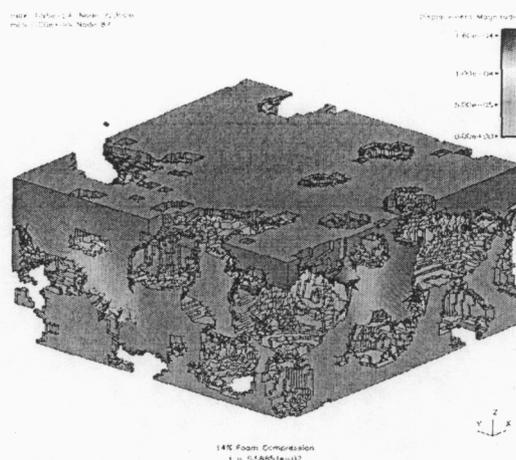


Figure 4. Results of FEA simulations of a component undergoing compression lighter areas are regions of higher strain.

radiation rich and water poor environments. We have combined experimental methods to assess aging signatures at both the atomistic and the microstructural scale with multiscale modeling approaches. Work is continuing to incorporate the chemical aging kinetics obtained from NMR, TPD, and MD calculations into constitutive equations of polymer viscoelastic response that will eventually be used in the FEA simulations.

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