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EXPERIMENTAL AND MODELING STUDIES OF WATER-SILICA-PDMS INTERACTIONS IN M97-BASED STRESS CUSHIONS

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Abstract

In filled PDMS based composites, such as M97XX stress cushions, significant mechanical reinforcement of the polymer component is obtained from hydrogen bonding between the silica filler surface hydroxyls and the siloxane polymer backbone. It is expected that these interactions are influenced by the amount and structure of interfacial water. We have chosen to investigate in detail the effect of chemisorbed and physisorbed water on the interfacial structure and dynamics in silica-filled PDMS-based composites. Toward this end, we have combined classical molecular dynamics simulations and experimental studies employing nanoindentation, temperature programmed desorption (TPD), Dynamic Mechanical Analysis (DMA), and Nuclear Magnetic Resonance (NMR) analyses. Our TPD results suggest that moisture desorption and adsorption in M9787 can be approximated by the interaction of its silica constituents (Cab-O-Sil-M-7D and Hi-Sil-233) with moisture. Our experimental data also reveal that, in general, as heat-treated silica particles are exposed to moisture, chemisorbed states, then physisorbed states are gradually filled up in that order. Molecular modeling results suggest that the polymer-silica contact distance and the mobility of interfacial polymer chains significantly decreased as the hydration level at the interface was reduced. The reduced mobility of the PDMS chains in the interfacial domain reduced the bulk motional properties of the polymer, thus causing an effective "stiffening" of the polymer matrix. This finding is consistent with both NMR and modal analysis experimental data on desiccated M97XX samples. We show that both the motional dynamics of the polymer and the structure in the interfacial region are indeed controlled by the concentration of water in this region and that by considering the thermodynamic and kinetic parameters derived from TPD experiments, we can begin to approach a predictive capability for the time dependence of water speciation and thus the mechanical properties of the composite material as a function of service environment and age.

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 tailorability is due to, at least in part, the presence of inorganic filler materials which are well know to significantly alter polymer material mechanical properties. Understanding of the interfacial chemistry is important for the ultimate engineering of mechanical, electrical, or chemical properties. The reinforcing mechanisms that control the material property changes in polymer-silica composite materials, for example, are poorly understood and rational control of the mechanical properties is difficult and often based solely on empirical correlations. M97 and S5370 type composites are such materials and have been used for decades in weapon applications and the composite material is generally considered stable over long service lifetimes against numerous stress inducing aging mechanisms: thermal and mechanical loads, and environmental, radiative, and chemical attack. However, little data specific to these materials has been documented changes in these materials when aged in dry environments for long times. In order to begin to assess such changes, we have employed Temperature Programmed Desorption (TPD), Nuclear Magnetic Resonance (NMR), and Molecular Dynamics (MD) calculations. This presentation will present a overview of our experimental and modeling data and present our stratagy for employing this data to make lifetime predictions of material lifetimes.

Experimental

Material description and synthesis methods have been described elsewhere [4, 5]. Molecular modeling methods and TPD methods have been detailed previously [6,7]. Experimental desiccation of M97 materials was performed by sealing a small sample of polymer in a 5mm NMR tube over ~100 mg of chemical desiccant (P_2O_5, LiH, or molecular sieve.)

Results and Discussion

The techniques of TPD and nanoindentation with an atomic force microscope (AFM) in a vacuum environment were employed to investigate the outgassing characteristic of and its effect on the properties of M9787 that had been annealed to 460 K for 24 hours then exposed to different moisture levels. Our experimental results [6,7] establish that moisture desorption and adsorption in M9787 can be approximated by the interaction of its silica contents (Cab-O-Sil-M-7D and Hi-Sil-233) with moisture, as shown in Figure 1A.

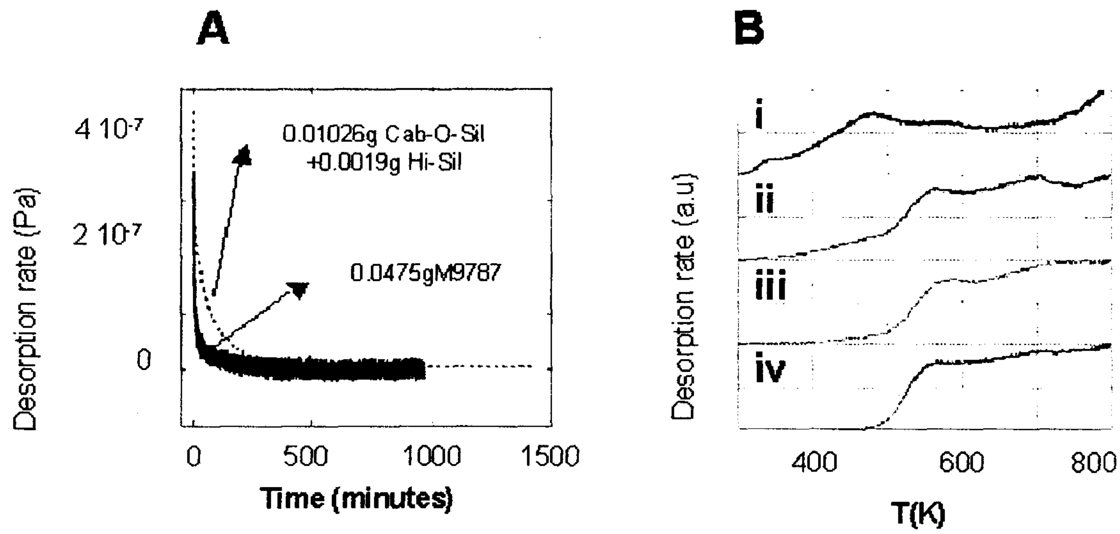

Fig. 1: A) Comparison of water desorption rate for a M9787 composite and a mixture of silicas with equivalent amounts of Cab-O-Sil-M-7D and Hi-Sil-233 as found in the M9787 composite at 460K. B) TPD results as a function of hydration level for Cab-O-Sil-M-7D: i) as received; ii) heat treated then re-exposed to ambient air 50% relative humidity for 15 minutes; iii) heat treated then re-exposed to 2.1 Pa of moisture for 24 hours; iv) heat treated only.

Currently, we performed TPD on silicas to temperature as high as 800-900K. Unfortunately, due to the low decomposition temperature of M9787, only isothermal desorptions at 460-500K have been done. The isothermal desorption curves for M9787 and for a mixture of silicas with equivalent amounts of Cab-O-Sil-M-7D and Hi-Sil-233 behave very similarly. But within the first 200 minutes of heating at 460K, there was less water coming out from the 0.0475g of M9787 than from the sample containing an equivalent amount of silica particles. The wt. % of water removed over 1500 minutes of annealing at 460K are ~ 0.03 to 0.04 and 0.09 to 0.13 for the M9787 and the equivalent silica amounts respectively. This suggests that when silica particles were embedded in the M9787 during production, some portion of the H_2O molecules and/or Si-OH bonds on the surfaces of silicas have been tied up in the bonding with the polymer matrix or effectively removed by processing (likely this is the effect of the Processing aid used in production) resulting in less H_2O outgassing from M9787 than from its constituent silica content. The difference in the two isothermal curves might very well be due to our systematic errors in the calibration of the mass spectrometer and sample to sample variation. Current efforts to improve the precision and accuracy of the calibration procedure for our mass spectrometer and to assess sample to sample variation are under way. Since the H_2O desorption rates for the equivalent silica sample have consistently been higher than those of the corresponding M9787 under different heating and moisture exposure conditions, water outgassing from Cab-O-Sil-M-7D and Hi-Sil-233 can be regarded as the upper limit for water outgassing in M9787. Current efforts in performing and analyzing TPD on M9787 to high temperatures are under way.

The annealing at 460 K for 24 hours is shown to effectively remove ~ 95-100% of all water sources that would otherwise slowly outgas at room temperature over 100 years. Our experimental data also reveal that, in general, as heat-treated silica particles are exposed to moisture, chemisorbed states, then physisorbed states are gradually filled up in that order. There seems to have some rearrangement of SiOH bonds as moisture desorbs or absorbs on the surfaces of the silica particles, however. Figure 1B illustrates this for Cab-O-Sil-M-7D.

Finally, nanoindentation was performed on M9787 silicones that were simultaneously pumped down to a few hundred Pa of residual pressure at room temperature. Our data shows that the removal of physisorbed water in M9787 has none or reversible little effect on the mechanical properties of M9787. A detailed and full-length report can be found in [7].

In hopes of elucidating the influence of the silica filler on the PDMS dynamics we next turn our attention to the local dynamics of the polymer both as a function of hydration level of the silica surface as well as the distance from its surface. Among the various types of local motion found in polymer liquids, the change in the orientation of individual bonds with time is one that can be readily evaluated from the MD simulations. The bond reorientation motions are also amenable to experimental measurements such as NMR or modal analysis. Here we investigate the PDMS motional dynamics using the following time autocorrelation function (ACF),

$$P_1(t) = \langle \mu(0) \bullet \mu(t) \rangle \qquad (1)$$

where $\mu(t)$ is a unit vector and ⟨ ⟩ denotes an ensemble average over all such vectors. In particular, we have investigated the bond vector ACF between the methyl and backbone

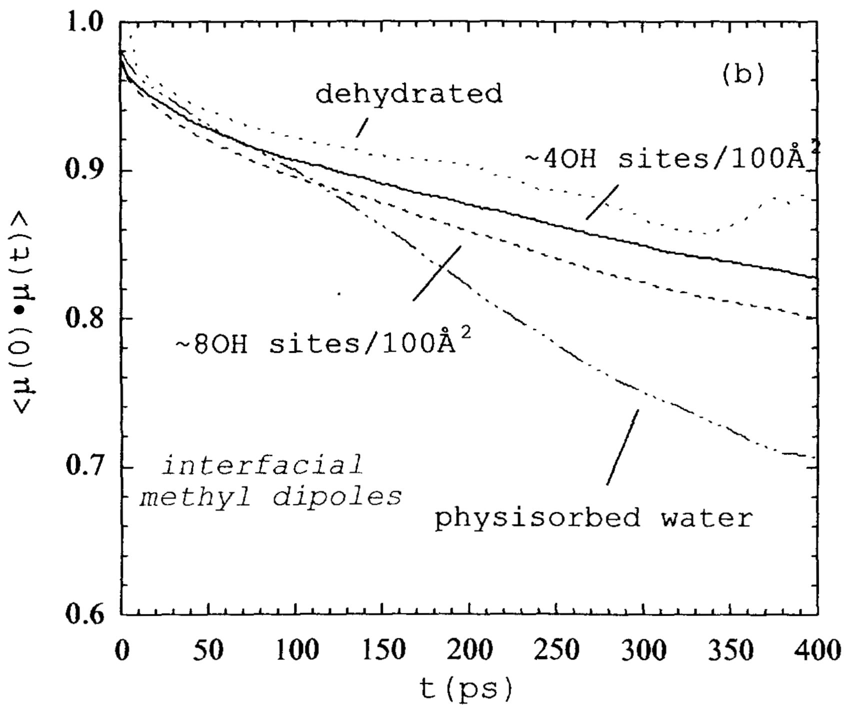

Figure 2. The decay of $P_1(t)$ at 550 K. Panel a shows decay for those PDMS *C-CH$_3$* bonds closest to the silica surface as a function of surface hydration, where panel b shows decay as a function of contact distance at a hydration level of ~8 OH/100 Å^2.. Lines are labeled in the figure.

carbon atoms (*C-CH$_3$*). Figure 2 shows $P_1(t)$ for PDMS at 550 K as a function of both the distance from the silica surface at a surface hydration level of ~8 OH/100 Å^2 and hydration level of the surface for those bonds near the surface. The PDMS dynamics are also found to be effected by the hydration levels of the silica surface. The general trend is that the relaxation times tend to increase as the hydration level decreases, thus effectively "stiffening" the polymer matrix. This may be in part due to screening of the long-ranged electrostatic charge by the hydroxyl groups or free physisorbed water in the interfacial region. To test this assumption, relaxation dynamics of *non*-charged analogues were studied. The results show that the PDMS relaxation dynamics are slow by roughly an order of magnitude at 550 K in the presents of the long-ranged electrostatic interactions.

Conclusions

We show that both the motional dynamics of the polymer and the structure in the interfacial region are indeed controlled by the concentration of water in this region and that by considering the thermodynamic and kinetic parameters derived from TPD experiments, we can begin to approach a predictive capability for the time dependence of water speciation and thus the mechanical properties of the composite material as a function of service environment and age.

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