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Aging of Silica-Filled PDMS/PDPS Copolymers in Desiccating Environments: A DSC and NMR Study

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Summary: The involvement of water in the reinforcing mechanism in silica-filled polydimethylsiloxane (PDMS) based composite systems, potentially leaves the polymer composite susceptible to mechanical property changes when exposed to desiccating environments. We have studied the effects of thermal and chemical desiccation on a silica filled PDMS/PDPS copolymer system by DSC and NMR analysis. Our results show that as the polymer was desiccated, segmental dynamics in the polymer network were reduced significantly and changes in melt heats of fusion and stress relaxation were observed. NMR ^{1}H relaxation measurements have measured a change in ^{1}H T_{2e} of 30% after storage in desiccating environments longer than 1 year. The experimental data presented argue that the reduced mobility of the PDMS chains in the interfacial domain after desiccation reduced the overall, bulk, motional properties of the polymer, thus causing an effective "stiffening" of the polymer matrix.

Keywords: desiccation; DSC; filler; NMR; siloxane

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 versatility is due, at least in part, to the presence of inorganic filler materials which are well known to significantly alter polymer material mechanical properties, but which may be characterized by complex water speciation and chemistry.[4] This interfacial water, in fact, is thought to be, in part, the reinforcing mechanism of the silica via hydrogen bonding interactions with the siloxane bridging oxygen atoms in the PDMS polymer backbone.

In an effort to gain further insight into the reinforcing mechanisms of inorganic fillers on PDMS based composites, we have initiated experimental and computational studies of the

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effects of changes in interfacial hydroxyl content on the chain dynamics of adsorbed PDMS chains. Results of computational studies of segmental dynamics at various hydration levels have predicted that removal of water from the silica surface should cause a reduction in the segmental dynamics of the adsorbed polymer chains.[5] These simulations revealed that the polymer-silica contact distance decreased as the level of "water" in the interfacial region decreased. It was also reported that the "water" in the interfacial region seemed to effectively "screen" the long-ranged interactions and mediated the polymer relaxation and reduced polymer "stiffening". A slight diminished contact distance due to the long-ranged electrostatic interactions between hydroxyl surface groups and the oxygen polymer backbone atoms were also revealed upon water removal in these simulations.

In this paper, we report the changes in thermal behavior, as studied by Differential Scanning Calorimetry (DSC), and segmental dynamics, as studied by Nuclear Magnetic Resonance (NMR), as a function of time stored in a desiccating environment. The data obtained in this study show that silica-filled PDMS/PDPS (polydiphenylsiloxane) copolymers undergo time dependent hardening in desiccating environments.

Experimental

The polymer gum used in this study was a random copolymer of dimethyl (DMS), diphenyl (DPS), and methyl vinyl (MVS) siloxanes. The percentages of each monomer unit in the base rubber were 90.7 wt.% PDMS, 9.0 wt.% PDPS, and 0.31 wt.% PVMS (NuSil Corp., Carpenteria, CA). This elastomer was compounded into a reinforced gum by milling with a mixture of 21.6 wt.% fumed silica (Cab-o-Sil M7D, Cabot Corporation, Tuscola, Il), 4.0 wt.% precipitated silica (Hi-Sil 233, PPG Industries Inc., Pittsburgh, Pa), and 6.8 wt.% ethoxy-endblocked siloxane processing aid (Y1587, Union Carbide Corp, Danbury, CT). After bin aging, this reinforced gum was formulated with the addition of a peroxide curing agent. The resulting filled-polymer system was studied in two forms: a fully dense form, and a 50% porous open cell material. The porous samples were formed by milling the reinforced gum with 50 weight percent of 25-40 mesh prilled urea spheres (Sheritt-Gordon Mines Ltd., Canada), which were subsequently rinsed out with water after curing of the polymer.[6,7]

For DSC analysis, samples were subject to a 8 hr, 70 °C bake out and subsequent storage in a nitrogen-purged, desiccated box for 6 months. The samples were then placed in hermetically sealed DSC pans, which were coated with Parylene™ to further protect against moisture ingress and analysis was performed with a TA instruments Model Q1000 DSC under a 50 ml/min He purge and a 3 °C/min ramp rate. DSC analysis of hydrated samples with and without the Parylene™ coating were indistinguishable, suggesting that the contribution to the DSC results was negligible. A container with "Drierite™" was used for storage except when the samples were being analyzed.

For NMR analysis, a small sample of polymer was sealed in a 5 mm NMR tube with a small amount of desiccant [Lithium Hydride (LiH), Phosphorous Pentoxide (P_2O_5), and Molecular Seive (MS)] positioned so that only the polymer was within the reciever coil volume and aged for up to 1 year. Transverse relaxation times were measured periodically with standard spin-echo methods.[6-8] 7μs π/2 pulse lengths, 7-second relaxation delays, and a standard Bruker 5mm TBI probe were used on a Bruker DRX-500 NMR spectrometer [Bruker Biospin, Bilerica, MA]. The echo decay curves were analyzed by measuring the time to reach 1/e of the initial intensity, T_{2e}, after removing the effects of the contribution to the decay of the sol fraction of the polymer (~10% of the echo decay curve).

Dynamic mechanical analysis testing was performed (TA Instruments AR2000 Rheometer, New Castle, Delaware) in parallel plate geometry. Specimens were disks approximately 2 mm in thickness and 8 mm in diameter. The sample was sheared at a frequency of f=6.3 rad/sec. For room temperature shear storage modulus (G') measurements, samples were sheared up to 1% strain level with a static compression force of 1 N.

Results and Discussion

DSC thermograms for the virgin filled polymer and the filled polymer aged for 6 months over Drierite™ are shown in Figure 1. For both samples, T_g was observed at -117 °C, while for desiccated samples, T_g was accompanied by a simultaneous stress relaxation of 0.75 J/g in the non-reversible heat flow measurement. In addition, a double melt peak was observed for both samples. The first melt peak was invariant with desiccation (T_{m1} = -78.5 °C) while the second melt peak shifted slightly to a lower temperature upon desiccation (ΔT_{m2} = - 3.3 °C). The heat of fusion also decreased slightly upon desiccation ($\Delta H_f = 9.4$ J/g hydrated and $\Delta H_f = 8.8$ J/g desiccated). Further, the melt as a whole feature shifted from predominantly reversible heat flow for hydrated samples to predominantly non-reversible heat flow for desiccated samples. A small amount of recrystallization heat flow was observed for hydrated samples immediately following the second melt peak. This feature was absent in the desiccated sample. After 24 hours, the DSC pan for the desiccated sample was punctured, exposed to air, and rerun. The DSC thermogram was consistent with a fully hydrated sample, suggesting that the changes observed upon desiccation were reversible, thus due to the action of the desiccant rather than an irreversible chemical reaction.

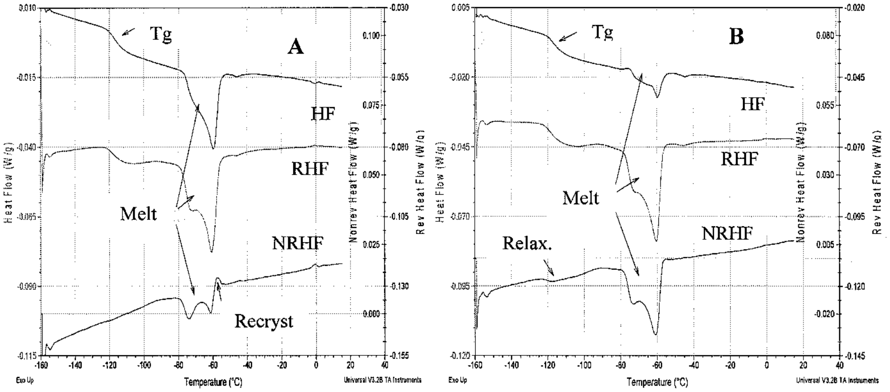

Fig. 1. DSC thermograms of (A) the copolymer at ambient conditions, and (B) the copolymer after 6 months desiccation.

In order to indirectly measure changes in mechanical properties associated with desiccation, NMR relaxation measurements were applied to assess the segmental dynamics changes that might have occurred. ^1H NMR relaxation measurements of transverse relaxation times in this polymer system have been directly correlated to the segmental dynamics of the polymer chains and thus the polymer mechanical properties ($1/T_2 \propto$ dynamics $\propto$ crosslink density $\propto G'$).[6-8] This relationship is documented in Figure 2.

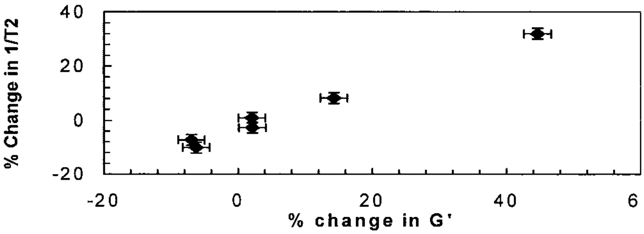

Fig. 2. Relative change in the inverse transverse relaxation time ($1/T_2$) as a function of the relative change in equilibrium storage modulus for various crosslink density copolymers. The crosslinks were modified by exposure to ionizing radiation.

The results of the spin-echo relaxation time experiments on desiccated samples are shown in Figure 3. As can be seen, as the polymer material was aged in the presence of desiccating agents with various relative affinities for water (LiH > P_2O_5 > MS), the polymer segmental dynamics were seen to slow down over the course of one year. Based on the correlation established in Figure 2, this change corresponds to a change in G' after 1 year of ~ 30%. Additionally, the relative stiffening ability of the various desiccating agents was observed to be roughly consistent with their affinities for water.

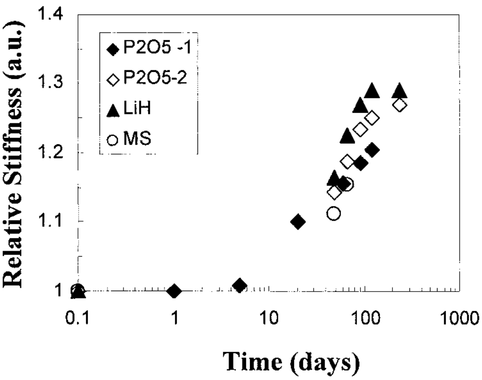

Fig. 3. Relative change in the inverse transverse relaxation time ($1/T_2$) as a function of time the filled PDMS/PDPS copolymer was stored under the desiccating agents indicated.

Conclusions

The DSC and NMR results reported here offer compelling evidence that desiccation of silica-filled PDMS based polymers can lead to dramatic changes in the mechanical properties of the material. Combined with insight from recent molecular modeling results[5] and the sensitivity of NMR to segmental dynamics,[6-8] we believe that this is due to the removal of physisorbed water at the surface. We therefore suggest here the closer polymer-silica contact and the loss of electrostatic "screening" upon dehydration of the silica filler particles as a possible mechanism for polymer "stiffening" seen experimentally in such systems. Once this "screen" has been removed, the polymer directly interacts with the filler and increases the reinforcing mechanism and stiffens the polymer matrix. It is hoped that, with the aid of advance Temperature Programmed Desorption[4] experiments to guide controlled desiccation experiments, improved insight into the aging of these polymers in arid environments might be obtained.

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