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Dynamic Moisture Sorption and Desorption in Fumed Silica-filled Silicone Foam

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ABSTRACT: Characterizing dynamic moisture sorption and desorption in fumed silica-filled silicone foam is necessary for determining material compatibilities and life predictions, particularly in sealed environments that may be exposed to a range of environmental conditions. Thermogravimetric analysis (TGA) and near infrared spectroscopy (NIR) were performed on S5470 fumed silica-filled silicone foam to determine the weight percent of moisture at saturation. Additionally, TGA was used to determine the time, temperature, and relative humidity levels required for sorption and desorption of physisorbed moisture in S5470.

INTRODUCTION

Silicone foams are relatively inert, nontoxic, and thermally stable cellular elastomeric materials. They are used in a broad range of applications, from medical dressings to fire protection systems.[1] The versatility of silicone foams is also largely due to the addition of particulate fillers such as fumed silica. Adding fumed silica to silicone foam can increase modulus and improve maximum extensibility and stress at rupture.[2] Silica is sold commercially as a desiccant and is therefore very hydrophilic. The addition of such a hydrophilic filler to silicone foam results in the increased total water content of the material. This is due to an absorbed layer of water at the interface between the polymer matrix and the fumed silica particles, shown in Figure 1.[3,4]

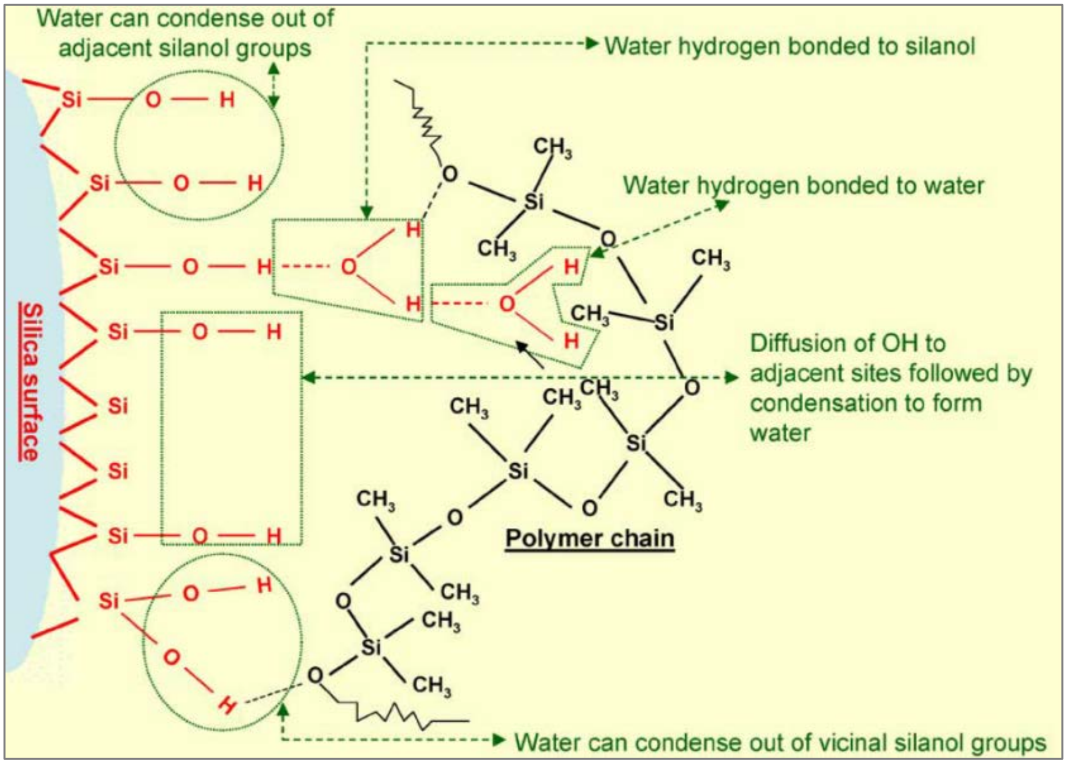

Figure 1. Depiction by Dinh et al. of the different ways that water can be desorbed from silicone. 4

Figure 1 by Dinh et al. depicts both physisorbed and chemisorbed water at the interface between the silica surface and polymer chains. Physisorbed water is more readily removed from the interface by simply hydrogen bonded to nearby silanol groups or water molecules. Chemisorbed water is chemically bonding to the fumed silica particles, and must be removed via condensation reaction of adjacent or vicinal silanol groups.[4] Desorption of physisorbed water occurs between 30°C - 230°C, while chemisorbed water has a greater bond energy and is gradually desorbed between 230°C - 600°C.[5] This study focused on physisorbed water because it is more likely to be desorbed under ambient conditions.

Not only does water desorption present compatibility issues, but Patel et al. determined that reducing water content at the interface between the polymer matrix and the fumed silica filler also influences the mechanical properties of the material by reducing segmental mobility.[3] Reduced mobility of the silicone chains leads to embrittlement of the elastomer. Furthermore, diminished elastic recovery properties caused by prolonged periods in a desiccating environment will reduce the reliability of the material.

The goal of this research was trifold. First to determine the total weight percent of moisture contained in S5470 fumed silica-filled silicone foam at saturation. Then, the conditions of sorption and desorption were studied. Those conditions included respective temperature and relative humidity (RH) levels, as well as the time required for complete sorption or desorption of S5470 to occur. Finally, ongoing research aims to predict the long term moisture dynamics and compatibility of S5470 in a sealed system.

METHODS

The research focused on S5470, a flexible silicone foam filled with Cab-O-Sil fumed silica. S5470 filled silicone foam samples were prepared prior to the study. The general process of polymerizing S5470 first involved combining silicone and Cab-O-Sil filler with urea pellets. The mixture was polymerized with heat and then the urea was washed out with water, leaving behind a filled silicone foam. The foam was then dried in desiccant before use.

Four chambers were developed using either a desiccant or saturated salt solutions in order to achieve desired relative humidity levels ranging from approximately 0% RH – 90% RH at 23°C. The sealed chamber with 0% RH contained Drierite desiccant. Ambient humidity, or about 20% RH, was achieved with an open chamber. The remaining sealed chambers with 50% RH and 90% RH were prepared using respective saturated magnesium nitrate and potassium sulfate solutions. S5470 samples were stored in the chambers for 24 hours before analysis.

Thermogravimetric analysis (TGA) was the first method employed in order to analyze the thermal stability of S5470 fumed silica-filled silicone foam stored at different humidity levels. TGA experiments were performed on TA Instruments Q500 Thermogravimetric Analyzer. The two TGA methods utilized were scanning mode and isothermal mode. Scanning mode measured changes in weight as a function of temperature, while isothermal mode measured changes in weight as a function of time. All TGA experiments were carried out under a nitrogen atmosphere to avoid oxidation reactions.

Infrared spectroscopy was performed on S5470 samples stored at 0% RH and 90% RH in order to qualitatively compare the water absorbance of each sample with that of pure water. Near infrared spectroscopy (NIR) was chosen because high infrared energy levels and low molar absorptivity were required to penetrate the fumed silica-filled silicone foam samples. Each experiment was performed on the Thermo Scientific Nicolet iS50 FT-IR at 4.000 resolution with 32 sample scans and 15798.3 cm^{-1} laser frequency.

RESULTS & DISCUSSION

The total moisture content in S5470 fumed silica-filled silicone foam stored at 20% RH and 23°C, was determined via scanning mode TGA. Figure 2 shows the thermal ramp of S5470 from 40°C to 570°C at a rate of 5°C/min. The thermal decomposition curve in Figure 2 revealed that S5470 contained approximately 1% moisture by weight (wt%) when stored under ambient conditions. Furthermore, the loss of 1 wt% moisture occurred gradually from 100°C - 350°C. When the sample temperature reached 400°C, the silicone began to degrade in nitrogen. If the experiment were performed in an air atmosphere, oxygen would serve as a catalyst for the depolymerization reaction of silicone. In the presence of oxygen, silicone degradation begins at 290°C.[8] Therefore sealed systems containing S5470 at temperatures above 100°C risk 1 wt% moisture desorption, and eventual silicone degradation if temperatures exceed 290°C in air or 400°C in nitrogen.

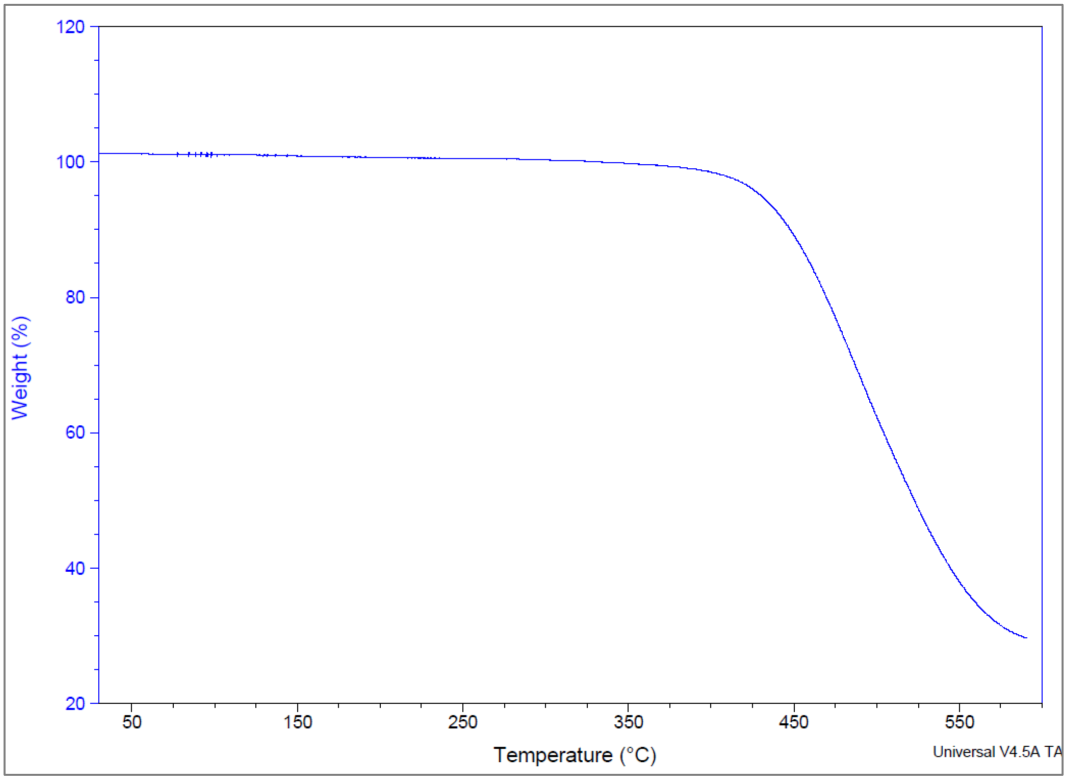

Figure 2. TGA ramp of S5470 from 30°C to 600°C at 5°C/min, sample stored at 20% RH and 23°C.

The desorption characteristics of physisorbed moisture in S5470 were then determined as a function of time. Four isothermal TGA runs were performed at temperatures ranging from 100°C to 200°C. In each isotherm, the temperature was increased from room temperature to 100°C, 150°C, 175°C, or 200°C at a ramp rate of 50°C/min. The isotherms were held at the desired temperature for 20 minutes. In Figure 3, the overlaid isothermal TGA curves revealed an initial weight increase inconsistent with Figure 2. The increased weight at the beginning of each isotherm in Figure 3 was the result of convection. Rapidly heating the nitrogen atmosphere at 50°C/min first heated the gas present at the furnace walls. This caused a downdraft in the center of the cylindrical furnace, where the sample pan was positioned.[9]

Figure 3 revealed that only 0.5 wt% moisture was desorbed during 20 minutes at 100°C. Moisture loss increased with increasing isotherm temperatures. The greatest desorption of 0.9 wt% moisture occurred after 20 min at 200°C. Therefore the moisture present in S5470 stored at 20% RH was almost completely desorbed after 20 minutes at 200°C. An isotherm of 200°C was subsequently used for the remaining TGA experiments in order study the effect of humidity on physisorbed moisture desorption of S5470.

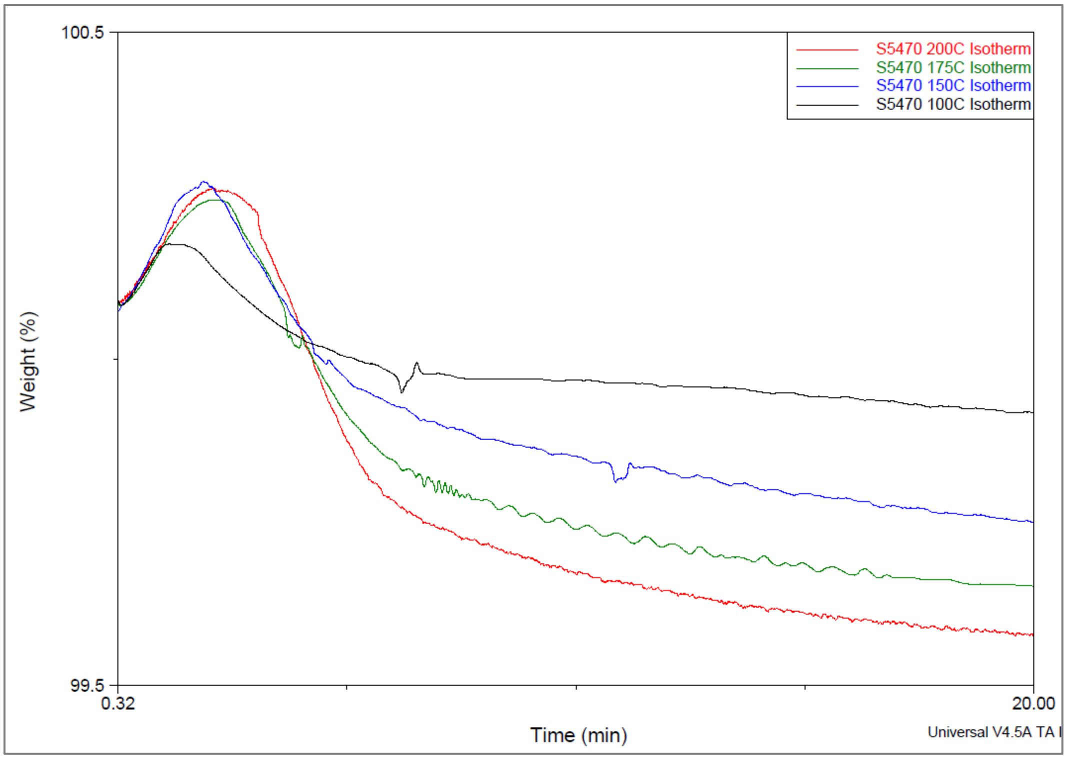

Figure 3. Isothermal TGA of S5470 at 100, 150, 175, and 200°C, all samples stored at 20% RH and 23°C.

The following 200°C isothermal TGA experiments were performed in order to determine the moisture content of S5470 after storing samples at elevated relative humidity levels, 50% RH and 90% RH. Figure 4 displays the data for such isotherms sustained for over 250 minutes. There was not a significant difference in the desorption of S5470 stored at higher humidity levels when compared to the 0.9 wt% moisture loss of S5470 stored at 20% RH. S5470 samples stored at 50% RH and 90% RH each exhibited 0.8 wt% - 0.9 wt% moisture loss. The results indicated that S5470 reached equilibrium saturation of physisorbed moisture in as little as 20% RH. Furthermore, the isothermal TGA revealed that the majority of moisture desorption occurred within the first 20 minutes, but gradual desorption continued to take place for the full duration of the isotherm. This may have been due to the complex cellular structure of the fumed silica-filled silicone foam, resulting in restricted movement of water within the material.

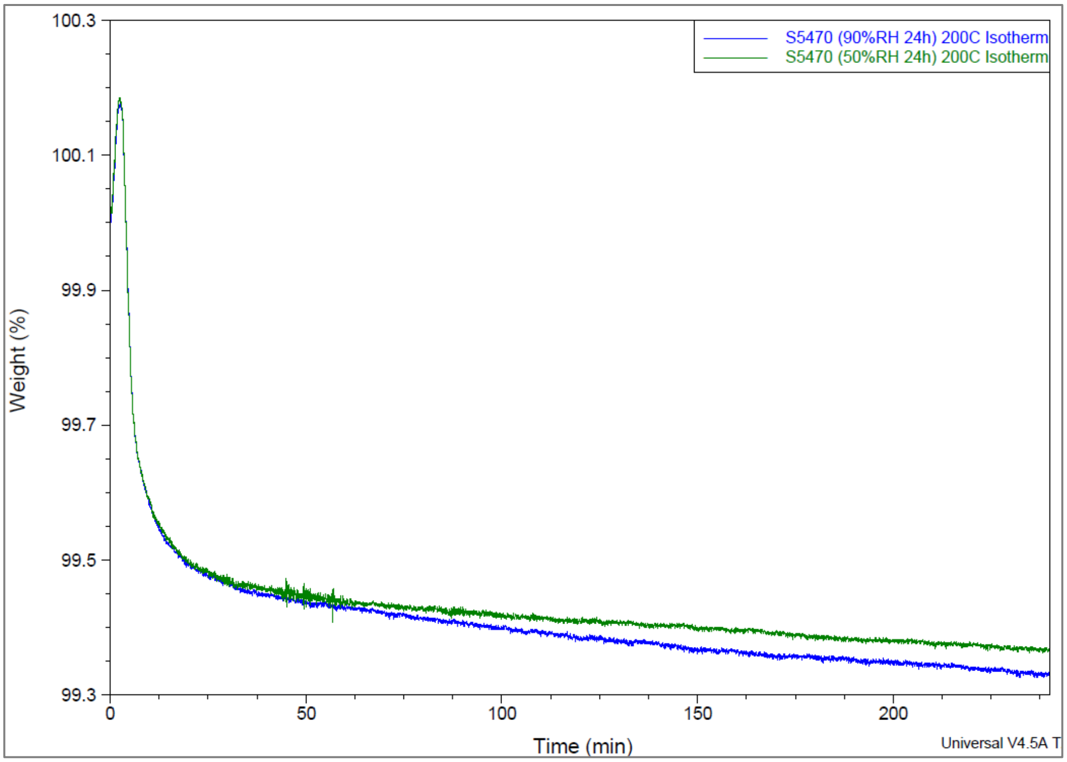

Figure 4. 200°C Isothermal TGA of S5470 stored at 90% RH and 50% RH for 24h.

The 200°C isothermal TGA experiments in Figure 5 were performed to study how rapidly moisture resorption occurs in S5470. The initial isotherms performed in triplicate (blue curves in Figure 5) indicated that each sample of S5470 lost 0.9 ± 0.1 wt% moisture after storage at 90% RH and 23°C for 24 hours. After the first TGA isotherm, the three samples were exposed to ambient conditions, 20% RH and 23°C, for 15 minutes. Immediately following the 15 minute period at ambient conditions, the samples underwent the same 200°C TGA isotherm. During the second isotherm, S5470 lost 0.2 ± 0.1 wt% moisture. The curves in Figure 5 revealed that after 15 minutes at ambient conditions, dry S5470 samples resorbed about 22% of their equilibrium moisture content.

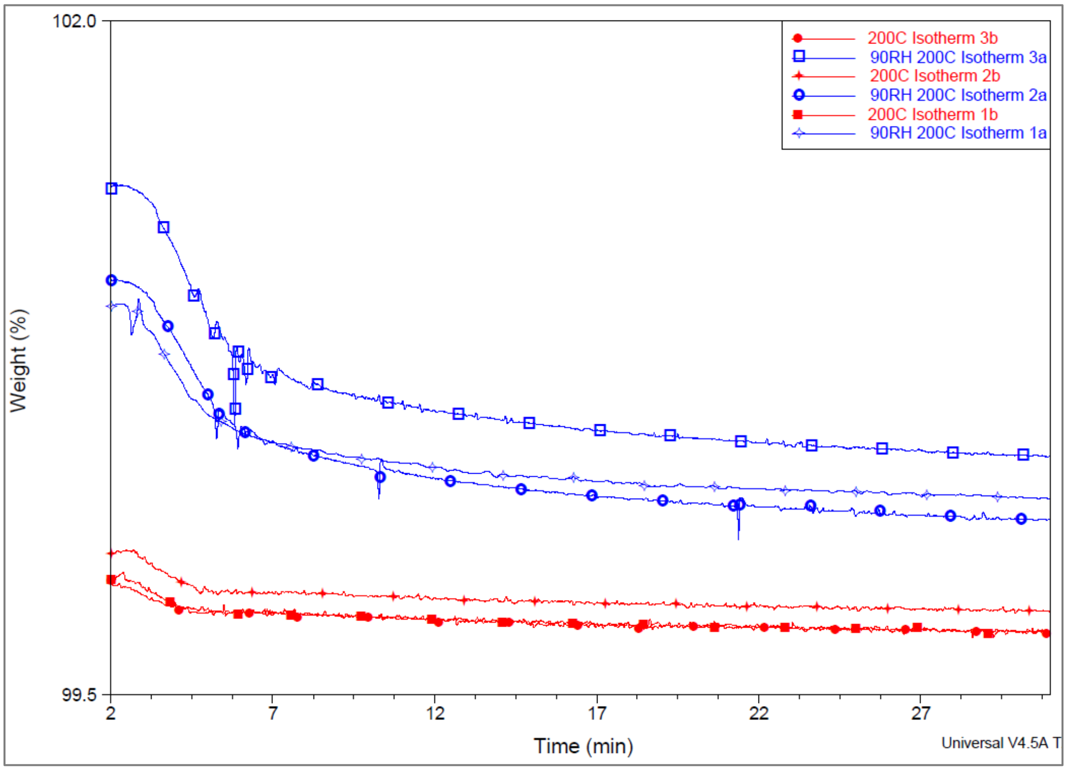

Figure 5. 200°C Isothermal TGA comparing three S5470 samples stored at 90% RH for 24 h to the same samples stored at ambient (20% RH) for 15 min after initial isotherm.

The NIR spectra in Figure 6 further indicated that there was only a small amount of moisture present in S5470 fumed silica-filled silicone foam. The regions of interest in Figure 6 were the water combination bands and first overtone which occurred at 5100 cm^{-1} and 6900 cm^{-1} respectively.[6,7] The two samples of S5470 chosen for this experiment were a sample stored at 90% RH and a sample stored in desiccant. There was minimal absorbance in these regions for either sample of S5470 when compared to the pure water sample. Additionally, there was not a significant difference in the moisture absorbance bands between the moist and dry sample. Due to the rapid resorption of S5470 revealed in Figure 5, the dry sample may have been exposed to ambient conditions long enough to resorb moisture in the time required to move the sample from the desiccating chamber into the Thermo Scientific Nicolet iS50 FT-IR.

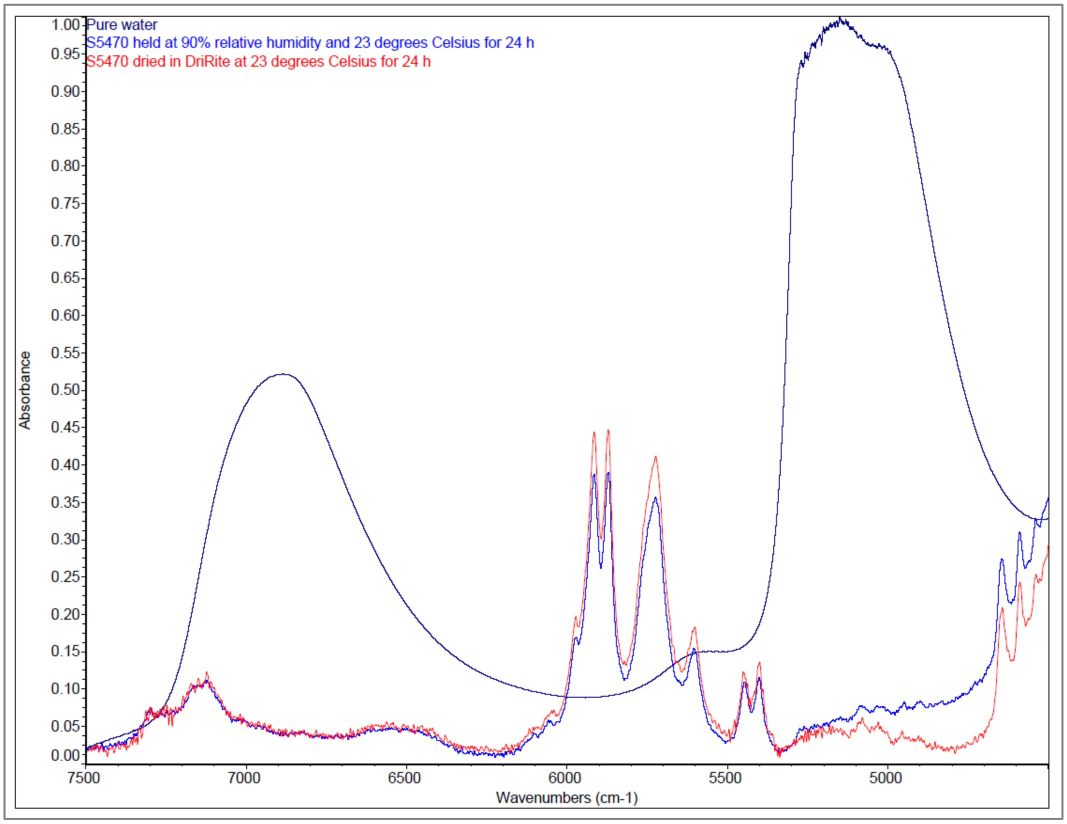

Figure 6. NIR spectroscopy of pure water, S5470 stored at 90% RH and 23°C, and S5470 stored in Dririte at 23°C.

CONCLUSIONS & FUTURE DIRECTIONS

S5470 fumed silica-filled silicone foam contained a small amount of moisture, only about 1 wt% at saturation. However, even a small amount of moisture may affect the surrounding materials in a sealed system. Moisture desorption occurred between 100°C - 350°C, followed by silicone degradation at 400°C under nitrogen. These values vary in an atmosphere that contains oxygen, namely by lowering the temperature required for silicone degradation. At 200°C, the majority of physisorbed moisture loss took place within the first 20 minutes of an isotherm, but gradual desorption continued for over 250 minutes. After desorption, 22% of the equilibrium moisture content of S5470 was resorbed within 15 minutes at 20% RH and 23°C. In addition to affecting material compatibility, repeated sorption and desorption of S5470 may eventually reduce segmental mobility of the foam. Therefore, it is important to control moisture levels in storage and service applications involving S5470 and other silica-filled silicone foams.

The next steps for this research involve determining the kinetics of moisture sorption and desorption in S5470. The moisture kinetics of S5470 can be determined via heated cell infrared spectroscopy and dynamic mixed gas moisture sorption analysis (Hiden IGA-003). Heated cell infrared spectroscopy will reveal how the NIR spectra changes as the sample is heated. Whereas dynamic mixed gas moisture sorption analysis will measure the sample weight as a function of humidity and temperature. Unlike TGA, the Hiden IGA-003 has the ability to control humidity within the sample chamber. Kinetic information determined from these two instruments will be useful for predicting the length of time required for complete moisture desorption to occur at a specific temperature. This information will then enable predictions of the long-term moisture dynamics and compatibility of S5470 in a sealed system.

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