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Additively Manufactured Silicone Polymer Composite with High Hydrogen Getter Content and Hydrogen Absorption Capacity

Santosh Adhikari,* Douglas J. Safarik, John R. Stockdale, Xavier M. Torres, Adam Pacheco, Shelbie A. Legett, and Andrea Labouriau*
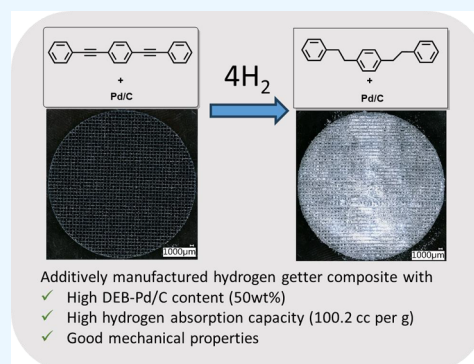
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ABSTRACT: Hydrogen getters consisting of 1,4-bis[phenylethynyl] benzene (DEB) and a carbon-supported palladium catalyst (Pd/C) have been used to mitigate the accumulation of unwanted hydrogen gas in a sealed system. Here, we report the formulation of a composite resin consisting of silicone polymer plus DEB-Pd/C as an active getter material and the additive manufacturing of silicone getter composites with a high getter content (up to 50 wt %). NMR and DSC studies suggest no reaction between the silicone polymer resin and DEB even at elevated curing temperatures (75 °C). Getter composites with varying amounts of getter and filler were formulated, and their rheological properties were studied. The two composite resins with good printability parameters and different getter contents were chosen to make 3D-printed samples. The hydrogen absorption capacity of these samples was studied at a low hydrogen pressure of 750 mTorr of pure hydrogen. The getter composite with 50 wt% of getter showed normalized DEB conversion of 83%, with the hydrogen adsorption capacity of 100.2 mL of H_2 per gram of polymer getter composite.

Additively manufactured hydrogen getter composite with
- ✓ High DEB-Pd/C content (50wt%)
- ✓ High hydrogen absorption capacity (100.2 cc per g)
- ✓ Good mechanical properties

1. INTRODUCTION

Generation of hydrogen in a sealed container, whether in small electronic packages or in transuranic waste transportation packages, is of concern due to potential performance and safety issues associated with hydrogen accumulation.[1−3] For example, in electronics and semiconductor industries, where ultrahigh-purity environments are often required to prevent contamination and ensure the reliability of electronic components, trace amounts of hydrogen gas can cause defects and affect the performance of sensitive electronic devices.[3] Similarly, in the transportation of transuranic waste packages, or in spacecraft and satellites, the built up hydrogen pressure poses a safety concern as it may lead to the degradation of optical and electronic components and also the risk of explosion.[1,2] This unwanted hydrogen gas is generally produced by radiolytic and/or thermal decomposition of hydrogen-containing materials, degradation of organic molecules, and so on.[1−5]

Hydrogen getter or scavenger materials have been used to aid in the removal of hydrogen gas and mitigate the issues related to hydrogen gas accumulation. Over the past few decades, research has been conducted on both inorganic[6−11] (metal alloy or metal oxides) and organic (unsaturated molecules)[12−16] materials as hydrogen getters. In particular, organic-based getters formed by mixing acetylenic compounds with a noble metal catalyst have been widely investigated. This is mainly due to the strong thermodynamic driving force (ΔG = −500 kJ/mol) for hydrogenation of the alkyne linkages,

which leads to a complete and essentially irreversible transformation to the analogous alkane structure in the presence of a hydrogenation catalyst.[13] One of the most studied organic getter compositions consists of 1,4-bis-(phenylethynyl)benzene (DEB) mixed with palladium (Pd) catalyst dispersed on activated carbon.[2,16−19] The high adsorption capacity of DEB (1 mol of DEB consumes 4 mol of hydrogen gas, Figure 1) together with its high melting point (∼179 °C) makes this getter suitable for a wide range of applications. The standard getter composite formulation consists of 75 wt % of DEB and 25 wt % of catalyst (the catalyst has 5 wt % palladium dispersed on activated carbon) and has a capacity of 241 mL hydrogen per gram of getter.[2]
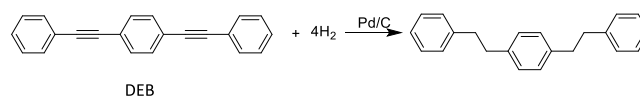
Figure 1. Reaction scheme of DEB with hydrogen gas in the presence of a Pd/C catalyst.

After its development in the late 1970s at Sandia National Laboratories,[2] it has been widely utilized in powdered or pressed pellet forms.

The use of a getter in a powder or pressed pellet form can limit its potential applications because of difficulties in handling powdered getter and the brittle nature of pressed pellets. In addition, due to the large exothermic heat of hydrogenation of DEB (~ -578 kJ/mol), powder or pellets may sinter if the reaction occurs quickly or if the density of reaction centers is large.[2] Therefore, DEB-Pd/C composites created by blending with other materials such as polymer substrates or carbon materials help to avoid the sintering of the getter by reducing the heat release per unit volume and unit time. This also provides an opportunity to tune the shape and properties of the getter for the desired application. However, when blended with other materials, the accessibility of hydrogen gas to the active materials plays an important role in the hydrogen getter capacity and reaction rate as well. Thus, getter composites with a large surface area and high hydrogen gas permeability are desirable. One of the techniques to enhance surface area and gas permeability is to develop a highly porous getter composite using a polymer substrate having high hydrogen gas permeability. Dong et al.[20] showed excellent hydrogen getter activities of a porous polymer getter composite containing 30 wt % of DEB-Pd/C. The porous polymer framework was developed by hot press mixing of low-density polyethylene, polyethylene glycol (PEG), and DEB-Pd/C and then removing PEG as a sacrificial material. Similarly, Sangalang et al.[21] reported a getter composite formed by DEB-rubberized coating on a silicone foam substrate and demonstrated a good hydrogen capacity and excellent performance, with the hydrogen uptake exceeding 80% of theoretical values. Most recently, Zhao et al.[22] reported a method for preparing a formable graphene aerogel hydrogen getter. This was developed by integrating DEB into the palladium-loaded three-dimensional layered porous aerogel, and such a getter composite showed a high hydrogen absorption capacity of 215.4 mL/g.

Additive manufacturing techniques such as direct ink write (DIW) have also been used to create 3D-printed polymer getter composites. These 3D-printed materials showed improved hydrogen getter performance due to the enhanced surface area of the polymer getter composite.[5] Such techniques provide an opportunity for the fabrication of unique 3D-printed getter materials with customized shapes and properties for various applications. However, previously reported 3D-printed silicone polymer getter composites have several drawbacks such as (1) low hydrogen absorption capacity due to the low hydrogen getter content (5.3 wt % of DEB-Pd/C) and low normalized DEB conversion (0.50), (2) unwanted reaction between the silicone polymer resin and DEB at elevated temperatures, and (3) poor printability properties (rheological properties) of the polymer getter composite resin for DIW.

In this paper, we report 3D-printed silicone polymer getter composites with a high hydrogen absorption capacity. To facilitate these materials, we developed a new silicone polymer getter composite resin having a high DEB-Pd/C content (up to 50 wt %), improved rheology for DIW, and minimal side reactions between the silicone polymer resin and DEB. In addition to the high hydrogen absorption capacity, these materials have good mechanical properties (good flexibility) even with a high getter content (50 wt %) unlike the previous

reported literature[20] where the composite became brittle above 30 wt % of the getter. To our knowledge, this is the first report of 3D-printed hydrogen getter polymer composites with high DEB-Pd/C getter content (up to 50 wt %) and high hydrogen absorption capacity (100.2 mL of hydrogen per gram of the getter composite) with good mechanical flexibility.

2. EXPERIMENTAL SECTION

2.1. Materials. Vinyl-terminated (4−6% dipheynylsiloxane) dimethylsiloxane copolymer (Gelest PDV-541) and trimethylsiloxy-terminated methylhydrosiloxane-dimethylsiloxane copolymer (Gelest HMS-301), used as base polymers in the formulation of the composite resin, were purchased from Gelest Inc. Similarly, a mid-temperature platinum catalyst (Gelest SIP 6832.2; platinum-cyclovinylmethylsiloxane complex; 2% Pt in cylcomehtylvinylsiloxanes), also known as Ashby-Karstedt (AK) catalyst, was used to induce cross-linking. Fillers used for the optimization of rheology included a hydrophilic fumed silica AEROSIL 300 (A300) and a PDMS-functionalized hydrophobic fumed silica CAB-O-SIL TS720 which were purchased from Evonik Industries and Cabot Corporation, respectively. 1-Ethynyl-1-cyclohexanol (ETCH) which was used to prevent premature curing of the resin was purchased from Sigma-Aldrich. 1,4-Bis(phenylethynyl)benzene (DEB) and palladium on carbon, 5 wt % loading (dry basis), were purchased from Ambeed Inc. and Sigma-Aldrich, respectively. All of these chemicals were used as received. The DEB−Pd/C catalyst blend (the active material for hydrogen getter) was prepared by mixing DEB and Pd/C in a ratio of 3:1 by weight and hand-mixing and shaking for 5 min. The particle size distribution of the DEB−Pd/C blend was determined by laser diffraction using an Anton Parr PSA 1090 Model D instrument. The DEB−Pd/C blend showed volume-weighted size distribution of D10, D50, and D90, and mean size of 2.26, 25.6, 84.2, and 39.8 μm, respectively. The bare pellets were prepared by milling 75 wt % DEB powder with 25 wt % carbon-supported Pd catalyst (which is itself 5 wt % Pd), followed by pressing into pellets.

2.2. Sample Preparation for the Investigation of Hydrosilylation Reaction between DEB and Silicone Polymer Resin (HMS-301). To investigate the possibility of hydrosilylation reaction between DEB and silicone polymer resin in a silicone polymer getter composite, DEB−Pd/C and HMS-301 were taken in 1:1 ratio by weight in a Thinky mixture cup and mixed for 2 min at 2000 rpm in a Thinky planetary mixer. AK catalyst (0.2 wt %) was then added and mixed again at 2000 rpm for 2 min. The resulting mixture was cured at three different temperatures (25, 50, and 75 °C) for 3 h. After cooling down to room temperature, about 20 mg of each sample was dissolved in CDCl$_3$ and filtered through a 45 μm Teflon filter and analyzed by ^{1}H NMR spectroscopy. ^{1}H NMR spectra were collected from a Bruker 400 NMR spectrometer at room temperature, and chemical shifts were referenced to the solvent residue peaks of CDCl$_3$ at 7.26 ppm.

2.3. Sample Preparation for Cast Sheets and Direct Ink Write. The base of all polymer getter composite resins consisted of a 9:1 ratio of PDV-541 to HMS-301 and approximately 0.1 wt % of ETCH. Silica fillers (such as A300 or CAB-O-SIL TS 720) at differing amounts were added to the polymer to enhance the shear-thinning characteristics and to optimize the rheological properties for 3D printing. 0.1 wt % of Ashby-Karstedt (AK) catalyst was added to the resin to induce cross-linking and curing of the base polymers. The general

procedure for the preparation of polymer getter composites is explained below in detail.

PDV-541 was taken in a Thinky cup, followed by the addition of A300, DEB-Pd/C, HMS-301, and ETCH, respectively. The mixture was then mixed in a Thinky planetary mixer at 2000 rpm for 2 min, two times with hand-mixing in between. AK catalyst (0.1 wt %) was then added to the ink and mixed again in a Thinky planetary mixer at 2000 rpm for 2 min.

For cast sheet samples, the blended resin was cast onto a Teflon sheet using a metal ring as a mold to provide a disk-shaped sample, approximately 6 mm in thickness. For 3D-printed samples, the blended resin was loaded into a 25 mL stainless steel syringe and centrifuged at 2000 rpm for 1 min to remove air bubbles. The filled syringe was attached to a Hyrel EMO-XT print head and then connected to a Hyrel System 30 3D printer. The resin was extruded onto a clean Teflon-covered glass slide, which was fixed to the *xy* stage at room temperature using 600 μm diameter plastic luer-lock nozzles (Nordson EFD Precision Tips, Nordson Corporation). The printer was controlled using Repetrel software (Hyrel 3D) and custom G-code with the face-centered tetragonal (FCT) lattice geometry, having 1000 μm of center-to-center spacing between struts. Both the cast sheet samples and printed samples were cured for 5 h at 75 °C in a preheated oven unless otherwise noted.

2.4. Material Characterization. The rheological properties of the inks created for this study were determined using a TA Discovery Series Hybrid Rheometer DHR-30. All experiments were conducted using a 25 mm cross-hatched parallel plate fixture geometry with a working gap of 1000 μm and strain sweeps conducted from 0.001% to 10% strain at an angular frequency of 10 rad/s and stress sweeps conducted from 10 to 10,000 Pa (or until the yield stress was reached). The yield stress (σ_y) and equilibrium storage modulus (G'_{eq}) were determined as the onset point where G' starts to decrease and obtained using TA Instruments' Trios software.

Hardness tests of cast sheet samples were performed using a benchtop Zwick Roell Shore hardness tester with a Shore A durometer. Shore A hardness tests were performed following the ASTM D-2240 procedure, in which the samples have a minimum thickness of 6 mm. Samples were tested in five locations, and an average value was reported.

An INSTRON 3343 Low-Force Testing System with BlueHill Universal software was used to perform a uniaxial compression test on all cast sheets and printed samples. Each sample was subjected to four cycles of compression to a maximum stress of 0.6 MPa at a rate of 0.05 mm/s. The stress−strain curve for each print was determined by the final cycle. As the displacement recorded by the BlueHill software was determined by the separation distance of the compression plates rather than the height of the sample, the displacement of each pad was corrected based on when the instrument first recorded force applied by the sample on the plates.

Thermogravimetric analysis (TGA) was performed using a TA Discovery Series TGA550 within the temperature range 25−900 °C at a heating rate of 10 °C/min under a flow of 40 mL/min of ultrahigh-purity nitrogen gas.

DSC experiments were performed using a TA Instruments DSC Q20 series. Samples (printed) were heated from −180 to 200 °C at a rate of 10 °C/min under a 40 mL/min flow of ultrahigh-purity nitrogen. The thermal transitions in the

polymer getter composite were reported using the first heating cycle.

The FT-IR spectra of the membranes were recorded in attenuated total reflectance (ATR) using a Nicolet iS50 FTIR spectrophotometer in the range of 500−4000 cm^{-1} with an accumulation of 32 scans in the absorbance mode.

A confocal microscope (Keyence VHX-6000; Keyence Corporation) was used to obtain optical microscope images, as well as the thicknesses of each printed pad. Overview and cross-section images were taken at 20✗ and 50✗ magnification, respectively, and thicknesses were determined using Keyence analysis software.

2.5. Hydrogen Absorption Experiment. Hydrogen absorption experiments were performed at low H_2 partial pressures, more representative of the working environments using the home-built reactor systems following the same procedure reported in the literature.[5,23] These reactors were constructed entirely from ultrahigh-vacuum-compatible components that were electroplated with gold to minimize the exchange of H_2 between stainless steel and the process gas. Each reactor system was contained within a FrioCell environmental chamber (BMT USA, Monroe, WA), which enabled temperature control to within ±0.05 °C in the range 0−100 °C. Polymer getter composites with a dry mass of 2.7 ± 0.1 g were used for hydrogen absorption study. After sealing the getter composite inside the reactor, the system was vacuum-baked at 75 °C for 24−36 h to remove the residual moisture from the reactor walls and the getter material. Bake-out was carried out at 75 °C, consistent with the curing temperature. To measure the uptake kinetics, an initial charge of 765 mTorr of pure H_2 gas was injected into the reactor. The decay in H_2 pressure as a function of time, owing to uptake by the getter composite, was then recorded by using a high-accuracy, high-precision pressure manometer (Baratron Model 120A, MKS Instruments, Andover, MA). When the pressure had decreased by 4% to 735 mTorr, additional H_2 gas was quickly injected to restore the pressure to its initial value. The pressure decay was then recorded again. This cycle was repeated hundreds or thousands of times until the getter was consumed or until the uptake rate became impracticably slow. The slope of each pressure versus time decay curve gave a direct measurement of the instantaneous reaction rate, once the H_2 pressure was converted to H_2 moles using the known reactor temperature and volume. It should be noted that because of the relatively small pressure window around the nominal set point, 750 ± 15 mTorr for experiments discussed here, these uptake measurements were quasi-isobaric.

3. RESULTS AND DISCUSSION

3.1. Investigation on the Reaction between DEB-Pd/C and Silicone Resin and Determination of Curing Conditions. It has been reported that DEB undergoes a thermally induced hydrosilylation reaction with silicone resin (Sylgard 184), which results in a decrease in the hydrogen absorption capacity of the silicone getter composite.[5] To investigate the thermally induced reaction between DEB and silicone resin used in this study, DEB-Pd/C and HMS 301 were mixed in the presence of AK catalyst and cured at different temperatures for 3 h and analyzed by ^{1}H NMR spectroscopy. HMS-301 silicone resin was chosen for the investigation because HMS-301 is the only base polymer that contains silane (Si−H) functional groups, which are expected to undergo hydrosilylation reaction with DEB. The use of mid-

temperature Pt catalyst (AK catalyst) allows for fast and complete curing even at relatively low temperatures. Therefore, the thermally induced reaction between DEB and HMS-301 was investigated up to 75 °C. The reaction between DEB and HMS-310 would have shifted the aromatic peaks of DEB and also resulted in the appearance of new peaks in the ^1H NMR spectra. However, the ^1H NMR spectra (Figure 2) of the resin
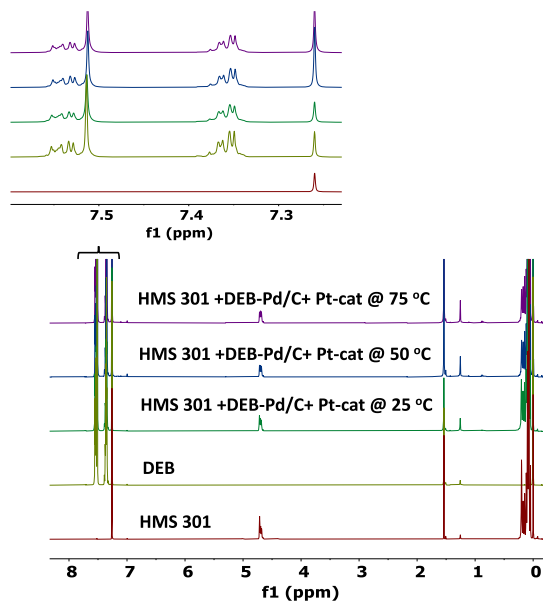

Figure 2. ^1H NMR spectra of HMS-301, DEB, and HMS-301+DEB-Pd/C−Pt-cat blends after curing at 25, 50, and 75 °C for 3 h.

indicated no noticeable changes in the chemical structure of DEB even after heating at 25, 50, and 75 °C. This suggests that no significant reactions occurred between the silicone polymer resin (HMS-301) and DEB in the presence of the AK catalyst, even at elevated temperature (75 °C).

Next, the curing conditions of the resin were evaluated by monitoring the Shore A hardness of the polymer getter composites prepared by curing at different temperatures. For this, cast samples of the polymer getter composites containing the same amount of getter (20 wt % of DEB-Pd/C) were prepared by curing in air at 25, 50, or 75 °C. The curing temperature, curing time, and the measured Shore A hardness of these cast samples are listed in Table S1. As expected, the Shore A hardness of the polymer getter composite increases

with an increase in temperature. The polymer getter composite sample cured at 75 °C showed the high Shore A hardness of 35 ± 2 at 5 h and did not significantly change with curing time. Since we did not observe any reaction between DEB and the polymer resin at 75 °C, and the polymer getter composite cured at 75 °C for 5 h showed a high Shore A hardness, all the 3D-printed samples studied in this work were cured at 75 °C for 5 h.

3.2. Rheology of Different Polymer−Getter Composite Resins and 3D Printing. Rheological properties such as equilibrium storage modulus, G'_{eq} (the stress at which a material behaves like a viscoelastic solid) and yield stress, σ_y (the stress at which a material flows) are important parameters that dictate the printability of polymer resin for DIW. For DIW applications, the printing resin must exhibit a shear thinning yield stress behavior. Such behavior allows the resin to flow out of the printing nozzle when the applied stress exceeds the yield stress. Once the resin is extruded and deposited, the stress is removed, and the resin regains its original viscoelastic properties, which allows the resin to retain its printed shape. For DIW applications, the printing resin should have G'_{eq} and σ_y in a certain range for the resin to flow through the nozzle and retain its printed shape after deposition.[24] While resins with low G'_{eq} and σ_y have difficulties retaining their printed shapes, resins with high G'_{eq} have difficulties flowing out of the nozzle, regardless of the nozzle size or flow rate. In this study, a series of polymer getter composite resins were formulated by adding different amounts of getter and filler, and their rheological properties were studied by measuring the oscillatory amplitude at an angular frequency of 10 rad/s from 10 to 10,000 Pa. It should be noted that addition of a filler is necessary to optimize the rheological properties of the polymer getter composite resin for DIW applications, and the amount of filler may vary with respect to the amount of getter used because the getter can act as a thixotropoic agent in addition to providing hydrogen absorption capability to the composite. Table S2 and Figures 3 and S1 provide the rheological results for different polymer getter composite resins and their composition. As shown in Figure 3, all of the polymer getter composite resins formulated in this study exhibited a shear thinning yield stress and a rubbery plateau region. In general, the printing resin for DIW application should have G'_{eq} and σ_y in the range of 43,000−2,800,000 Pa and 2,000−11,500 Pa respectively, for the resin to flow through the nozzle and retain its printed shape after deposition.[25] The polymer getter composite resin, 10 wt %
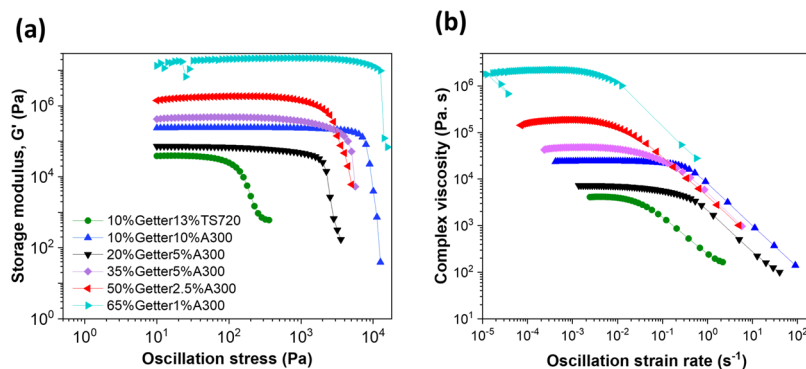
Figure 3. Rheology of different polymer getter composite resins; (a) storage modulus as a function of oscillation stress and (b) complex viscosity as a function of oscillation strain rate.
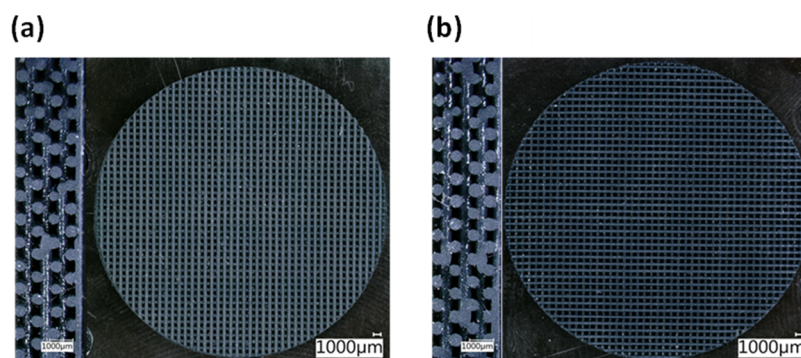
Figure 4. Cross-sectional view (left) and top view (right) of FCT pads printed with 600 μm nozzle: (a) 20 wt % getter + 5 wt % A300 and (b) 50 wt % getter + 2.5 wt % A300.
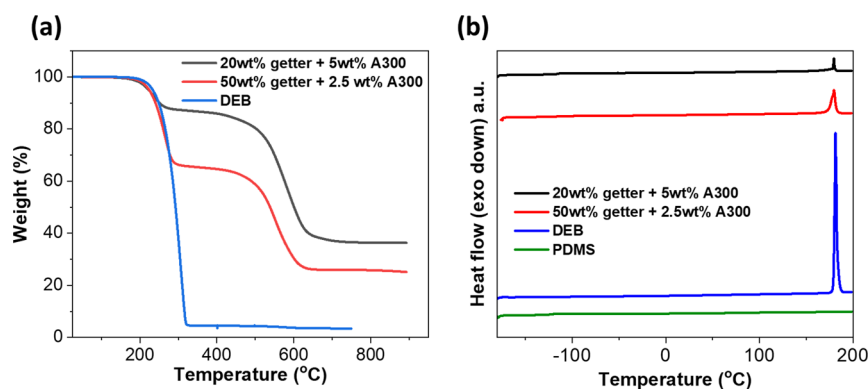
Figure 5. (a) TGA curves and (b) DSC thermograms for 20 wt % getter + 5 wt % A300, 35 wt % + getter 5 wt % + A300, and 50 wt % + getter and 2.5 wt % + A300.

getter + 13 wt % TS720, has very low G'_{eq} and σ_y (<129 Pa and <36,720 Pa, respectively), and the polymer getter composite resin, 65 wt % getter + 1 wt % A300, has very high G'_{eq} (>18,583,800 Pa), suggesting that these resins are not suitable for DIW feedstock. All other polymer getter composite resins investigated in this work have desirable rheological properties for DIW application. The very low G'_{eq} and σ_y values of the polymer getter composite resin with TS720 silica filler, despite the high filler content (13 wt %), are attributed to the weaker interaction of hydrophobic TS720 silica filler with the silicone polymer. On the other hand, due to the presence of a large number of silanol groups (free, vicinal, and germinal silanols), A300 silica filler has a stronger interaction with the silicone polymer resin via hydrogen bonding, resulting in increased viscosity and cohesiveness even with a small amount of A300 silica filler.[26]

All four polymer getter composite resins that showed good rheological properties for DIW application were successfully used for 3D printing. Among them, one with a very high getter content (50 wt % getter + 2.5 wt % A300) and the one with a medium getter content (20 wt % getter + 5 wt % A300) were chosen to study the hydrogen absorption capacity and are discussed here in detail. Figure 4 shows the cross-sectional and top views of FCT pads printed with these composite resins. These FCT pads were printed using a 600 μm nozzle and had a 1000 μm center-to-center spacing between struts and a layer height of 385 μm.

3.3. Thermal and Mechanical Properties of Polymer Getter Composites. The thermal properties of polymer getter composites were investigated using TGA and DSC. The TGA curves are shown in Figure 5a, which clearly indicate similar trends of degradation for all polymer getter composites, as expected. As shown in Figure 5a, the thermal degradation of DEB begins at ~220 °C and ends at ~325 °C. Thus, the first degradation temperature ($T_d \approx 220$ °C) of the polymer getter composites corresponds to the degradation of DEB, and hence the percentage of weight loss at 325 °C corresponds to the amount of DEB contained in each polymer getter composite, confirming the composition of the polymer getter composites (note that the getter contains 75 wt % of DEB and 25 wt % of Pd/C catalyst). DSC scans of the first cycle (heating cycle) for the polymer getter composites, DEB, and silicone polymer (PDMS) without getter and silica are shown in Figure 5b, and data are listed in Table S3. In DSC thermograms, no additional peaks other than that for the melting point of DEB molecules were observed, confirming that DEB molecules did not react with the silicone polymer resin during the curing process at 75 °C. However, the melting point of DEB in the composite (~179 °C) was less than that of pristine DEB (~181 °C) (see Table S3), which could be attributed to the melting point depression due to the presence of impurities in the polymer getter composite. The glass-transition temperature (T_g) of all polymer getter composites was similar (approximately −116 °C), which is higher than T_g of the pristine PDMS polymer (−125 °C). This is due to the reduced molecular mobility and flexibility of the polymer chains due to the interactions between the filler and polymer matrix.[27]

The mechanical properties of printed and the cast polymer getter composites were evaluated via Shore A hardness and compression stress−strain tests. The Shore A hardness and compressive strain data for the printed and cast polymer getter composite are listed in Table S4 and are shown in Figure 6. As
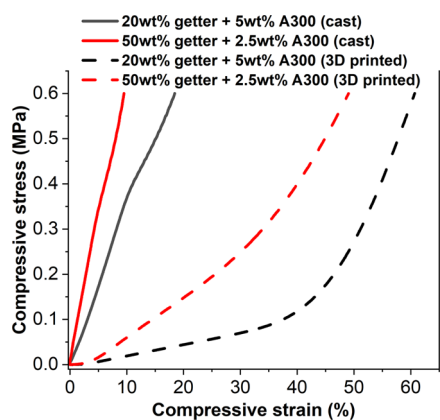
Figure 6. Compressive stress strain curves of polymer getter composites. Solid lines for cast samples and dashed lines for 3D-printed samples.

expected, the 50 wt % getter + 2.5 wt % A300 cast sample showed high hardness (52) and less compressive strain (9.5%) among the cast and printed samples. Similarly, all cast samples have less compressive strain compared to their corresponding 3D-printed samples. All the 3D-printed samples, even the one with a very high getter content (50 wt %), showed good compressibility (compressive strain of ~50% at 0.6 MPa compressive stress), indicating good mechanical flexibility of these printed samples. Note that the porous polymer getter composites were reported to become brittle above 30 wt % getter content.[20]

3.4. Hydrogen Absorption Study. The hydrogen getter performance of the samples; 20 wt % getter + 5 wt % A300 (cast and 3D-printed) and 50 wt % getter + 2.5 wt % A300 (3D-printed), was evaluated at 25 °C and 750 mTorr hydrogen partial pressure. The hydrogen absorption experiment was run for almost 50 days until the reaction rate for each sample became significantly slow (around 30 mL of H_2/g sample/year). Note that the hydrogen absorption study is done at a very low hydrogen pressure of 750 mTorr, which is more relevant to working conditions. The plot of reaction rate versus fractional conversion of DEB is shown in Figure 7, while the plot of fraction conversion of DEB versus time is shown in Figure S2, and the data are listed in Table 1.

As expected, the final DEB conversion (when the hydrogen uptake rate becomes significantly slow) and initial hydrogenation reaction rate were higher for the 3D-printed sample when compared to its cast sample (Figure 7a and Table 1). We speculate that this is mainly due to the high surface area resulting from the 3D-printed structure and, hence, easy hydrogen gas access to the catalyst surface. Among the 3D-printed samples, the sample with a higher getter content showed a higher reaction rate as well as a higher DEB conversion (Figure 7b). For example, the initial reaction rate and normalized DEB conversion for the 50 wt % getter + 2.5 wt % A300 sample were 3.75×10^3 mL/g sample/year and 0.83, respectively, while for 20 wt % getter + 5 wt % A300, the values were 1.65×10^3 mL/g sample/year and 0.71, respectively. This observation is consistent with the previously reported results, as a higher getter content is more likely to have more hydrogen gas contact with the catalyst, resulting in a higher rate and DEB conversion.[20] When compared to the hydrogenation rate of bare pellets, these composites have a lower reaction rate of almost 2 orders of magnitude. We assume that this could be due to the presence of impurities (polymers and fillers) in the getter composite, which may slow down the rate of hydrogenation by slowing down the diffusion of hydrogen to the surface of the catalyst. However, a detailed study on the kinetics of hydrogen absorption could provide more insights to explain this observation. The plateau of reaction rate over the fraction of DEB conversion (Figure 7b) indicates that the getter has been homogeneously distributed in the composite, and hydrogen has good access to the catalyst surface due to the high surface area of the printed pad.

The hydrogen getter performance of the composite (50 wt % getter + 2.5 wt % A300 3D-printed) developed in this work is compared to the other reported porous polymer getter composites (Table 2).[5,20,21] Our 3D-printed 50 wt % getter + 2.5 wt % A300 getter composite has the highest getter content and hydrogen absorption capacity and also shows a high fraction of DEB conversion even at a relatively low hydrogen gas pressure (750 mTorr). Additionally, it has good mechanical properties (flexibility) and has the advantage of 3D printing technology for the fast and relatively low-cost production of custom polymer getter composites for several applications.
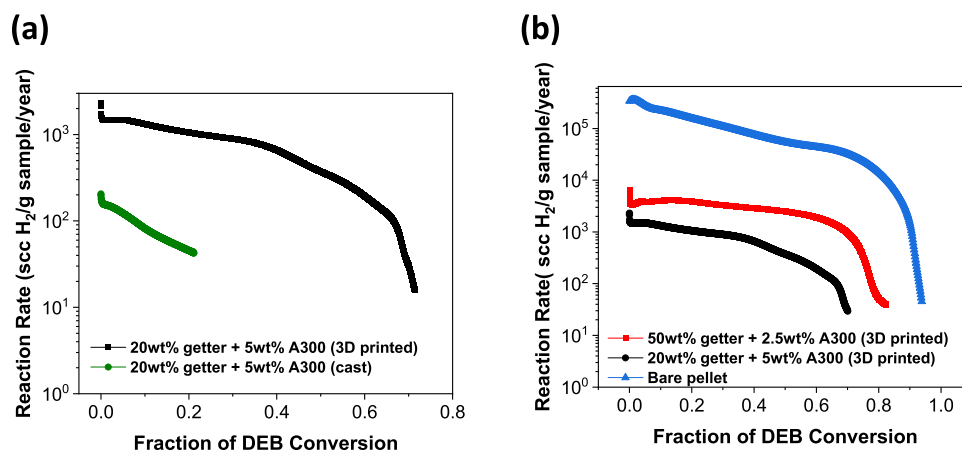
Figure 7. Reaction rate vs fraction of DEB conversion comparison between (a) 20 wt % getter + 5 wt % A300 cast and 3D-printed samples and (b) 20 wt % getter + 5 wt % A300 and 50 wt % getter + 2.5 wt % A300 3D-printed samples and bare pellets.

Table 1. Initial Reaction Rate, Normalized DEB Conversion, and Hydrogen Absorption Capacity of the Silicone Getter Composite[a]

sample	wt % of DEB-Pd/C	initial reaction rate (× 10³ mL H₂/g sample/year)	normalized conversion of DEB	hydrogen absorption capacity (mL/g) theore.[a]	hydrogen absorption capacity (mL/g) exp.
20 wt % getter + 5 wt % A300 (cast)	20	0.17	0.22	48.3	10.6
20 wt % getter + 5 wt % A300 (3D-printed)	20	1.56	0.71	48.3	34.3
50 wt % getter + 2.5 wt % A300 (3D-printed)	50	3.75	0.83	120.7	100.2
bare pellets	100	340	0.93	241.4	224.5

[a]Calculated considering complete DEB conversion.

Table 2. Comparison of Hydrogen Getter Content and Hydrogen Absorption Capacity of Different Polymer Getter Composites Containing DEB-Pd/C as the Active Getter Material

polymer getter composite	polymer substrate	wt % of DEB-Pd/C	normalized conversion of DEB	hydrogen absorption capacity (mL/g) theore.[a]	hydrogen absorption capacity (mL/g) exp.
ref[20]	low-density polyethylene	30	0.80[b]	72.4	57.9[b]
ref[21]	silicone foam	40	0.85[c]	96.5	82.0[c]
ref[5]	silicone (3D-printed)	5.3	0.50[d]	12.8	6.4[d]
this work	silicone (3D-printed)	50	0.83[e]	120.7	100.2[e]

[a]Calculated considering complete DEB conversion. [b]Measured at 2 bar (~1,500,000 mTorr) hydrogen pressure. [c]Measured at 6666 pa (~50,000 mTorr) of hydrogen pressure. [d]Measured at 750 mTorr of hydrogen pressure. [e]Measured at 750 mTorr of hydrogen pressure.
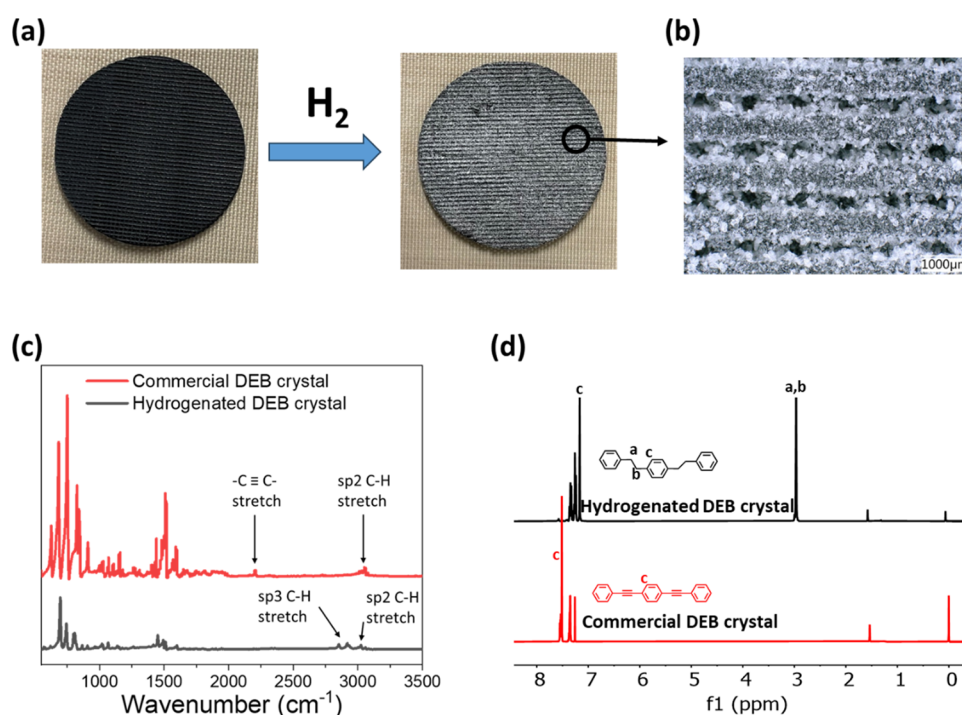
Figure 8. (a) Optical pictures of the 3D-printed samples before and after exposure to hydrogen, (b) optical microscope picture of the small portion of the 3D-printed pad after exposure to hydrogen, (c) FT-IR spectra, and (d) ¹H NMR spectra of commercial DEB crystals and hydrogenated DEB crystals.

The uptake of hydrogen gas by the polymer getter composite likely occurs in three main steps: diffusion of hydrogen gas into the polymer matrix, dissociative chemisorption of hydrogen gas on the catalyst surface, and then a surface hydrogenation reaction between the adsorbed H atoms and adsorbed DEB molecules.[16,20] In addition to the abovementioned three main steps, the migration of the hydrogenated DEB molecules away from the catalyst, providing space for the pristine (unreacted) DEB molecules to react, is also a very important step for the efficient uptake of hydrogen gas. The high vapor pressure of saturated DEB molecules compared to unreacted DEB molecules,[28] plus the heat generated during the hydrogenation reaction due to the exothermic nature of hydrogenation of DEB (heat of

hydrogenation reaction is ~ −578 kJ/mol), might have enhanced the migration of fully hydrogenated DEB molecules away from the catalyst surface, thus providing space for unreacted DEB molecules.[21] The hydrogenated DEB molecules appear to segregate the macroscopic surface of the 3D-printed strands, as evident in Figure 8a,b. The white crystals deposited on the surface of the sample were collected and analyzed by FT-IR and NMR spectroscopies and compared with commercial DEB crystals (Figure 8c,d). The complete disappearance of the C−C triple-bond stretch around 2210 cm^{-1} and the appearance of sp2 C−H stretch around 2800−2900 cm^{-1} in the FT-IR spectra (Figure 8c) of the crystal collected from hydrogenated samples provides evidence of hydrogenation of DEB molecules. Similarly, the appearance of peaks at 2.97 ppm corresponding to benzylic hydrogens ($-CH_2-CH_2-$) and shifting of aromatic peaks (for example, central phenyl hydrogens from 7.51 ppm in commercial DEB to 7.17 ppm) in hydrogenated DEB crystals in the ^1H NMR spectra (Figure 8d) confirms that the deposited white crystals are hydrogenated DEB molecules. Thus, in addition to the removal of unwanted hydrogen gas, these 3D-printed silicone getter composites can also serve as an indicator for the presence of hydrogen gas, as indicated by the change in their appearance from black to white (Figure 8a).

4. CONCLUSIONS

In summary, we have formulated a new silicone composite resin with a high hydrogen getter content (up to 50 wt % of DEB-Pd/C) and used it as a DIW feedstock to develop 3D-printed silicone polymer getter composites. NMR and DSC studies on this formulation confirmed no noticeable reaction between DEB and the silicone resin. All the 3D-printed samples showed good mechanical flexibility, and when evaluated for hydrogen getter performance, the 3D-printed sample with a high getter content (50 wt % getter) showed a high initial reaction rate as well as a high fraction of DEB conversion (0.83) and total hydrogen absorption capacity (100.2 mL/g sample). To the best of our knowledge, this is the first reported 3D-printed polymer getter composite with high DEB-Pd/C content and high hydrogen absorption capacity. Future work will be focused on studying the kinetics of hydrogen absorption and the aging of this polymer getter composite.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c00386.

> Rheological, thermal, and mechanical data of the polymer getter composite (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Santosh Adhikari − C-CDE: Chemical Diagnostics and Engineering Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States; ⬤ orcid.org/0000-0001-6063-5903; Email: san_adh@lanl.gov

Andrea Labouriau − C-CDE: Chemical Diagnostics and Engineering Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States; ⬤ orcid.org/0000-0001-8033-9132; Email: andrea@lanl.gov

Authors

Douglas J. Safarik − Sigma-1: Fabrication Manufacturing Science Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

John R. Stockdale − C-CDE: Chemical Diagnostics and Engineering Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

Xavier M. Torres − C-CDE: Chemical Diagnostics and Engineering Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

Adam Pacheco − C-CDE: Chemical Diagnostics and Engineering Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

Shelbie A. Legett − C-CDE: Chemical Diagnostics and Engineering Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.4c00386

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. The authors declare no competing financial interest.

Notes

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