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Microporous Structure in Silicone Polymers with Polylactic Acid and Polyethylene Glycol Microspheres – Synthesis and Characterization

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Abstract:

Porosity in polymer parts could improve mechanical properties while reducing weight and density. Individual pores must be small enough that bulk mechanical properties are retained but significant enough to reduce the density of the material. Filler materials can be incorporated into polymer matrices and removed to create voids. This paper focuses on creating spherical pores in silicone matrices by inserting and removing core materials or fillers during post-cure. A method was developed to incorporate pore formers into an uncured polymer resin and remove the pore former materials from the matrix.

Polyethylene Glycol (PEG) and Polylactic Acid (PLA) microspheres were created and incorporated into silicone matrices as pore formers. Microspheres with controllable size distributions were formed via an emulsion formation. Microspheres are removed from the matrix by solvent extraction and calcination. Thermogravimetric Analysis (TGA), Dynamic Mechanical Analysis (DMA), and optical imaging characterize and determine the successful creation of micropores in the polymer matrices.

Keywords: Microspheres; PLA; PEG; emulsion; planetary mixing; silicone; TGA; DMA; matrix; solvent extraction.

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4 **1. Introduction**
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6 Polymeric foam materials are prevalent in several applications and serve various
7 functions, notably in machine systems, including the distribution and relieving of stress,
8 mitigating effects of shock and vibration, accommodating dimensional changes caused by
9 thermal variations, and maintaining the position of surrounding parts by applying the
10 appropriate spring force [1-4]. Foams made from polysiloxanes are particularly
11 interesting due to their relatively high thermal stability and chemical resistivity.
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14 Traditionally, siloxane pads and cushion materials have been molded similarly to many
15 other materials [5, 6]. However, there has recently been a shift to consider additive
16 manufacturing to control mechanical properties. Even with the varied options for direct
17 ink write lattice structures, the desired density and stiffness are not always achievable by
18 changing the print structure alone. Feedstock polymers incorporating the porous region
19 during processing pose a viable solution. With the shift to additive manufacturing
20 processes where 3-D structures are built layer by layer, with each layer being 200
21 microns or less [7], there is a need for pore formers with average sizes in the range of 5-
22 100 microns. This size range is consistent with the strand size and small enough not to
23 contribute to clogging issues during printing. Polymeric spheres on the micron scale
24 (microspheres) are potential candidates. Another requirement is suitable matrix materials
25 compatible with the pore formers. Several polymer matrix materials are being considered
26 to embed the pore formers in a compatible polymer matrix and remove the pore formers
27 during processing, thus resulting in porous structures. A fundamental material and
28 process understanding of the pore former and polymeric matrix materials is needed and is
29 focused on the present work. A polymer matrix of interest is polydimethylsiloxane
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4 (PDMS). PDMS is a commonly used polymer in several applications. Its unique
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6 properties, such as thermal stability, low glass transition temperature, high chemical
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8 resistance [8], and transparency, make it a choice material for direct ink-write
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10 applications.
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14 Pore former materials can be embedded in polymer matrices and removed during
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16 post-processing, forming porous structures. Pores in polymeric foams control the physical
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18 and mechanical properties, such as the density and yield stress. Chemical blowing agents
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20 are typically used for creating irregularly shaped cellular structures. Some applications,
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22 however, require well-defined pore structures, so pore formation via chemical blowing
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24 agents may not be ideal. Removable polymeric microspheres as pore formers, unlike
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26 chemical blowing agents, provide reasonably better control over the size, shape, and
27
28 porosity of polymer parts, with the added benefit of repeatability in pore formation.
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31 However, polymeric microspheres are not readily available, and methods to prepare them
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33 are not always intuitive. A repeatable method for making microspheres within the desired
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35 size range is desired to ensure that the process of synthesizing microspheres can be scaled
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37 successfully. Developing a process for making polymeric microspheres that act as pore
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39 formers in a polymer matrix would allow for porous structures that are more controllable
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41 in the porosity distribution. The density reduction of materials from void creation can be
42
43 predicted more quantitatively by identifying the mass fraction of pore formers to
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45 incorporate into the polymer matrix before curing. Pores created in this manner can be
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47 more evenly distributed, each with similar morphology. The pore former microspheres
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49 can also be loaded into a direct ink-write polymer ink for 3-D printing applications, given
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51 that the microsphere sizes will be smaller than the thickness of each printed layer.
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4 Poly(lactic acid) (PLA) and poly(ethylene glycol) (PEG) emerge as forerunners among
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6 polymers that can be used to form microspheres. Poly(lactic acid) and poly(ethylene glycol)
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8 are biocompatible and used in various biologically related applications, notably drug
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10 delivery and encapsulation. Such characteristics make PLA and PEG biologically inert.
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12 PLA is also biodegradable, and PEG is chemically inert. PLA and PEG can be dissolved
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14 easily in organic solvents, and bulk PLA and PEG can be converted into particles with
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16 varying morphologies (microspheres, nanoparticles, etc.).
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21 This paper discusses porosity creation in PDMS matrices with PLA and PEG
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23 microspheres. Our previous work focused on synthesizing PEG and PLA microspheres
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25 for pore former applications [9]
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31 **2. Materials and Methods**

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33 Silicone (polysiloxane) is chosen due to its prevalence in additive manufacturing
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35 applications and elastomeric properties. Sylgard 184, an RTV silicone, is the PDMS
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37 formulation used. The solid PLA microspheres previously synthesized [9] are blended
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39 into PDMS matrices at 10%, 25%, and 35% by weight loading rates prior to the curing of
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41 PDMS. PEG 200 (liquid) obtained from Sigma Aldrich[®] is used to create liquid PEG
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43 microdroplets in the PDMS matrices by mixing vigorously in a planetary mixer. These
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45 are then cured simultaneously with the PDMS to form solid PEG microspheres evenly
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47 distributed in the silicone matrix, forming the PEG microspheres simultaneously as the
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49 matrix material is cured. In the case of PLA microspheres, they were prepared separately
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51 and blended into the silicone polymer matrix. PEG is blended into PDMS at the same
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53 loading rates as the PLA microspheres. A planetary (Thinky) mixer is used to evenly
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4 blend the solid PLA microspheres and create evenly distributed liquid PEG microdroplets
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6 within the silicone matrix under vacuum conditions. Two PDMS matrix composites
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8 blended with only PLA or PEG microspheres were formed. The rheological properties of
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10 the uncured polymer blends are studied. The matrices are then cured in an oven set at 100
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12 °C for 35 minutes. The cure time and temperature indicated are based on the DOW®
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14 recommended parameters for PDMS (Sylgard 184). The cured polymer blends are
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16 characterized. The blended microspheres are then removed from the polymer matrix by
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18 solvent extraction and calcination. The solvents used are water at 69°C and
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20 dichloromethane (DCM) at room temperature. One extraction cycle is carried out using
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22 both DCM and water, and the extraction in each case is carried out overnight.
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31 Before and after microsphere removal, the polymer material is studied and
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33 characterized by optical imaging, thermogravimetric analysis (TGA), and dynamic
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35 mechanical analysis (DMA). The changes in the density and porosity of each polymer
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37 blend and each polymer are also investigated.
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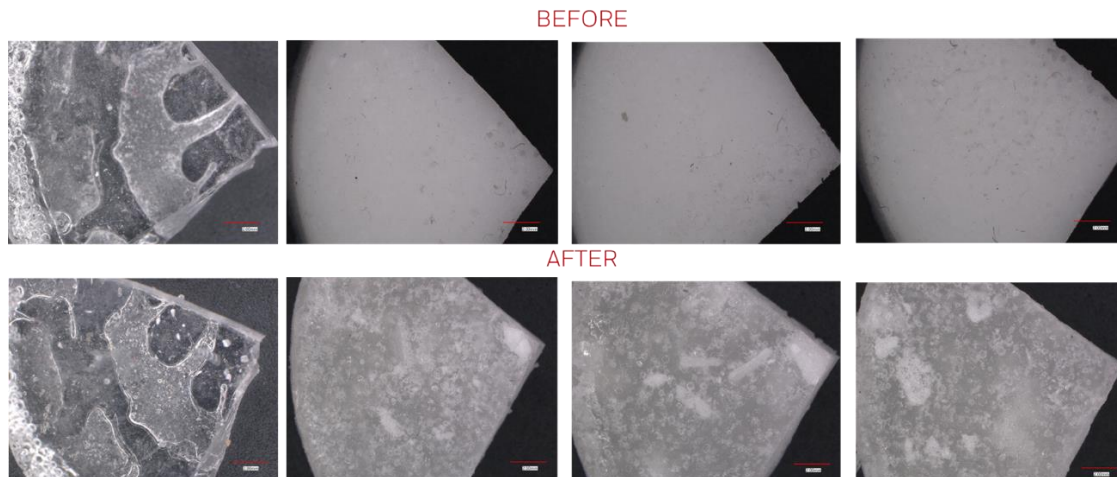
43 **3. Results and Discussions**

44 **3.1. Optical Imaging Results**

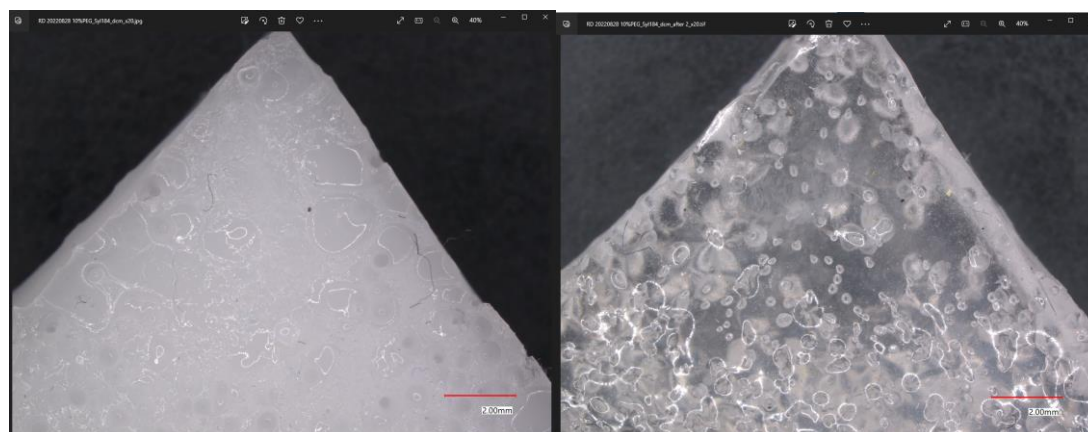
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46 Figure 1 (a) shows the PDMS-PLA composite material system images before and
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48 after removing PLA microspheres from the matrix by organic solvent leaching for 25 wt.
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50 % PLA. Figure 1 (b) shows the images of PEG-loaded polymer matrices before and after
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52 removing PEG microspheres at 10wt. % loading of PEG, with the removal via organic
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54 solvent etching. Figure S-1 (Supplementary Information) shows the images of the PEG-
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4 loaded polymer matrices after removing PEG microspheres at 25wt. % and 35wt. %
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7 loading. In each case, three sets of material samples were used, in addition to a neat
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9 sample containing no microspheres, to determine the repeatability of our data. The
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11 presence of dissolved microspheres can be seen visually in all the samples. The surfaces
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13 of PEG composite samples were not visually transparent after calcination, but the
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15 presence of leached microspheres can be seen. Optical imaging is employed to see the
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17 distribution of the dissolved PLA and PEG microspheres over a larger sample area. The
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19 figures show that DCM sufficiently leached the microspheres from the polymer blend, as
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21 evidenced by the translucence of the polymer blends observed after solvent extraction. It
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23 appears, however, that some of the microsphere trapped in the matrix are not removed.
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26 DCM swells PDMS and, as such, leaches the PLA and PEG microspheres from the
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28 matrix by dissolving them. After extraction, matrices expand due to swelling but return to
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30 their normal size after all the solvent has evaporated. Matrices are placed in a vacuum
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32 oven overnight at 60°C to remove any remaining DCM. Figure 1 and experimental
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34 observations show no changes in the volume of the matrices. Therefore, any change in
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36 the mass of each matrix material can be proportionally attributed to a change in density.
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(a)



(b)

Figure 1. (a) Optical microscope images of matrices before and after DCM extraction and removal of PLA microspheres – 25 wt% PLA loading. (b) Images of 10wt% PEG-loaded PDMS matrices before (left) and after (right) the removal of PEG microspheres.

3.2 Thermogravimetric Analysis

Figures S-2, S-3, and S-4 (Supplementary Information) TGA analysis data for PDMS, PDG, and PLA at various temperatures. Figure 2 is the TGA data comparing the degradation rate of PLA-loaded PDMS matrices loaded at 0, 25, and 35 wt. % after

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4 solvent (DCM) extraction. Complete removal of PLA microspheres from the PDMS
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6 matrix should result in similar TGA profiles for all three samples and concur with the
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8 neat PDMS.
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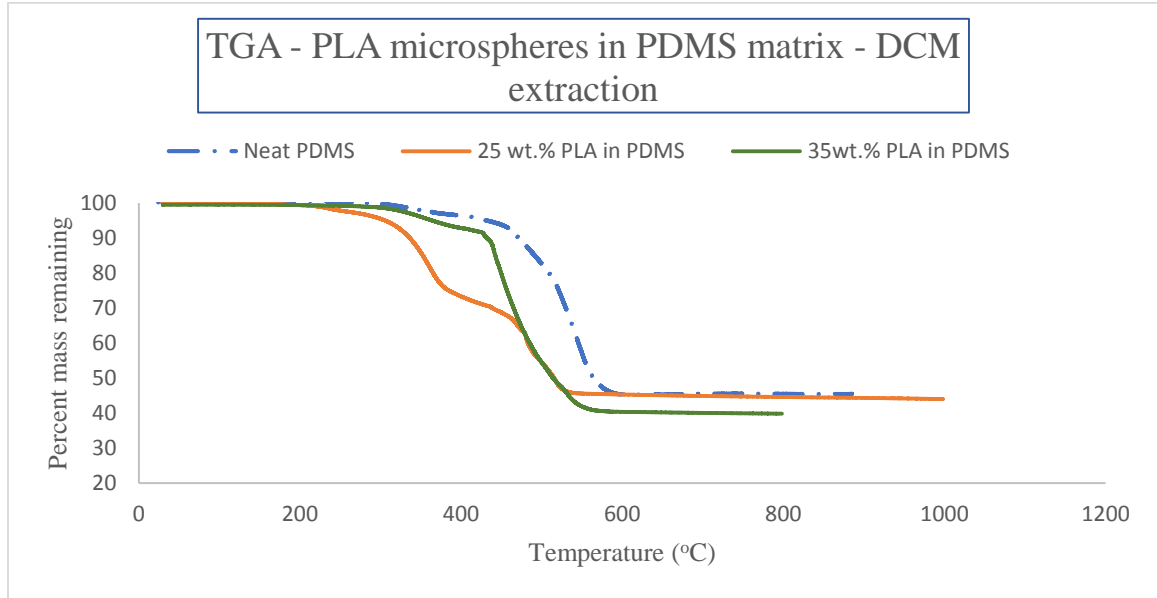


Figure 2. TGA characterization of PLA microspheres in PDMS loaded at 0 (neat), 25, and 35wt. % with PLA microspheres after the solvent DCM extraction.

Figure 1, however, shows that all the microspheres are not removed from the polymer matrix during extraction. The relative amount of PLA microspheres remaining in the matrix can be determined from the TGA data, provided the only change in the matrix is the removal of PLA microspheres. It was determined that about 71% of the PLA microspheres were removed from the matrix loaded with 35% PLA microspheres ($(100-90) * 100/35$). The TGA profile of the DCM extracted matrix with the 25 wt.% PLA loading indicates that the non-PDMS portion of the matrix amounts to about 65% of the entire matrix, which is much higher than 25%. It was concluded that a portion of the

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4 PDMS matrix remained uncured. Such presence of uncured PDMS would explain the two
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6 degradations in the TGA profiles observed for 25% wt% composite system below 450°C.
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8 The degradation between about 350°C and 450°C can be attributed to the decomposition
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10 of the PLA microspheres remaining in the matrix. The uncured PDMS accounts for about
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12 10% of the whole sample, corresponding to about 40% $((75-65) * 100/25)$ of
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14 microspheres remaining in the matrix after microsphere removal, implying that we could
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16 remove only about 60% of the microspheres.
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22 PEG microspheres loaded at ten wt.% were removed using three removal
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24 pathways: water extraction, solvent (DCM) extraction, and calcination. The calcination
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26 was performed by placing the PDMS-PEG composite in an oven at 150°C to remove the
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28 PEG microspheres formed. The temperature and duration of the calcination process were
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30 obtained from a temperature study performed on a higher molecular weight PEG material
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32 and on PDMS to determine an ideal temperature that would completely remove PEG
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34 without compromising the thermomechanical integrity of the PDMS matrix.
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40 Figure 3 shows TGA characterization after the microsphere removal of PDMS
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42 matrices loaded with 10wt.% PEG microspheres. Each removal method shown appears to
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44 remove PEG from the matrix only to a certain degree. The water extraction profile shows
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46 two degradation profiles. The first profile appears to occur between ~200-350°C,
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48 consistent with the degradation seen in Figure 1(b). A similar degradation profile is also
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50 observed for the other two profiles in Figure 3 for the other removal methods at about the
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52 same temperature range. TGA characteristics indicate the presence of uncured Sylgard
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54 184 in the matrix.
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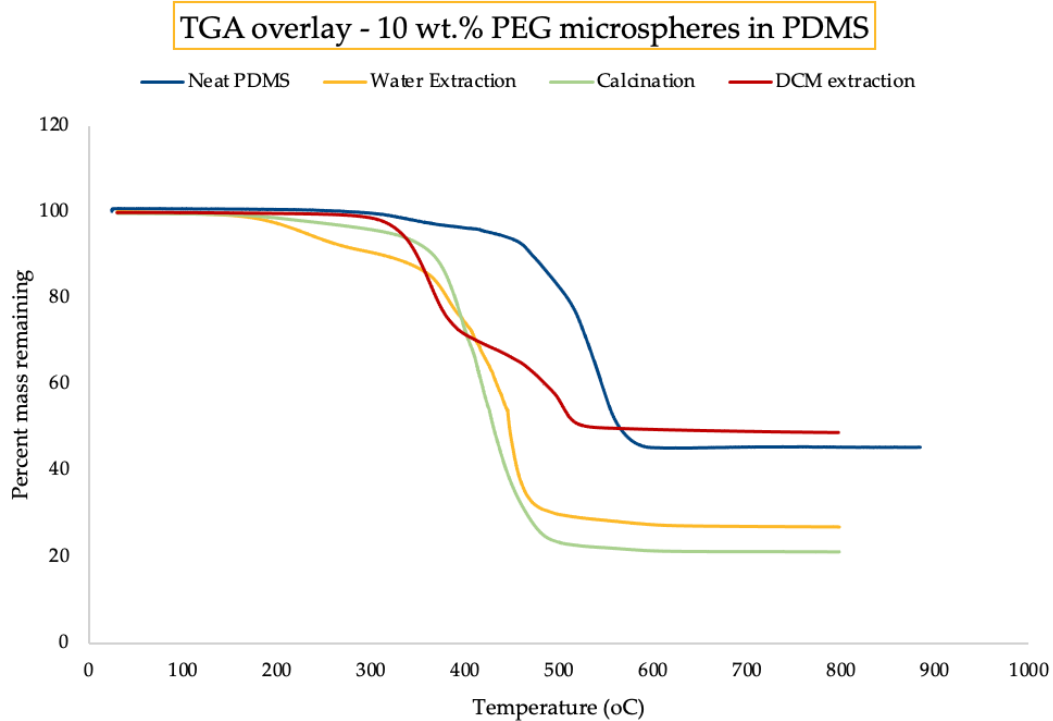


Figure 3. TGA characterization of microsphere removal methods for 10wt. % PEG in PDMS.

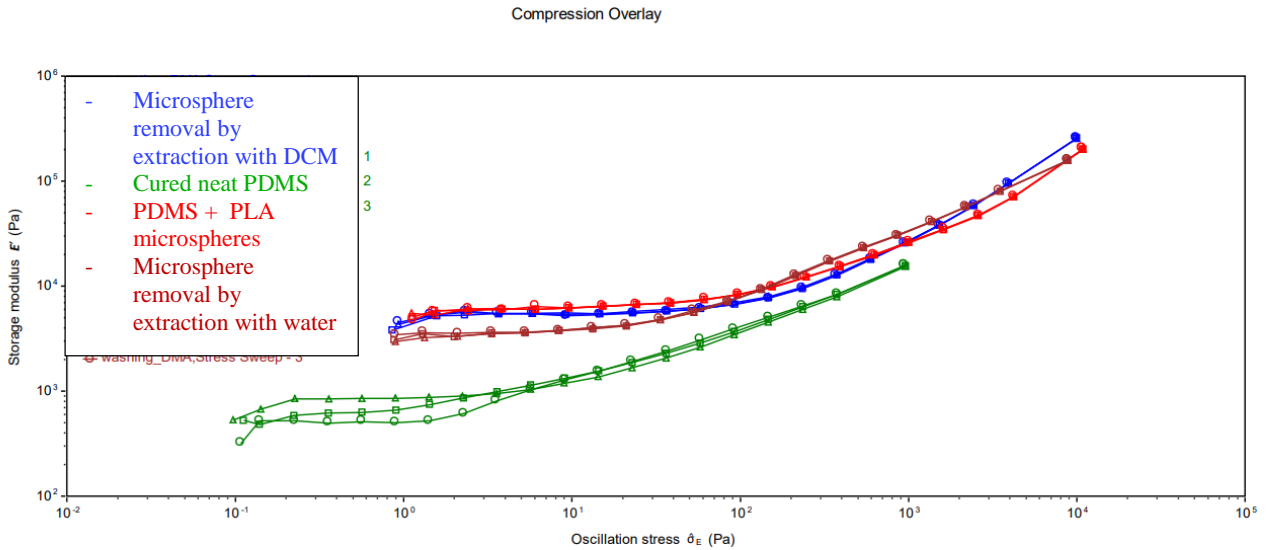
However, removal by calcination is shown to be the most efficient way to remove PEG from a PDMS matrix. Nearly 100% of all the PEG microspheres are removed this way. We infer that we can optimally remove PEG from a PDMS matrix without altering the matrix material's physical, thermal, and mechanical properties. Similar results are observed for higher loading rates.

3.2 Characterization of Sylgard 184 matrix before and after microsphere removal

- Dynamic Mechanical Analysis

Figure 4 shows a compression DMA analysis of the PDMS-PLA blends loaded at ten wt. % for the various pore former removal processes. The storage modulus was measured as oscillatory stress was applied to each sample. Three porous samples representing two of

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4 the three removal methods were used for each test. The graph shows that the mechanical
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6 behavior of each material remains unchanged from one sample to another. A lower
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8 storage modulus is recorded for the neat PDMS compared to samples loaded with
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10 microspheres.
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33 **Figure 4.** DMA Compression Analysis - Storage Modulus vs. Oscillation Stress for the
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35 10% PLA-in-PDMS microsphere-matrix blend
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37 Figure S-5 (Supplementary Information) shows the changes in strain rate with
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39 respect to temperature under a constant stress condition. This characterization aimed to
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41 identify whether the resulting porosity changed the elasticity of the matrix material at
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43 varying temperatures. In Figure 4, we infer that the result of both solvent extraction
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45 techniques (DCM and Water) does not significantly change the internal structure and
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47 properties of the polymer matrix. The glass transition temperatures reported for each test
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49 under the same strain are identical. In the case of the calcinated sample, however, it is
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51 apparent that the polymer matrix is destroyed by removing the pore materials. Figure S-6
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53 (Supplementary Information) shows the dynamic viscosity changes of the PLA
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4 microsphere-loaded PDMS Sylgard 184 matrix, indicating an increase in the viscosity in
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7 the composite system with the microspheres.
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10 Tables S-1 and S-2 (Supplementary Information) present the density changes in
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12 PDMS composites before and after removing PEG and PLA microspheres. The density
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14 reduction does not lead to a reduction in the storage modulus of the polymer matrix,
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16 indicating that we could change the polymer matrix's density without changing the
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18 polymer's other physical and mechanical characteristics.
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22 23 **4. Concluding Remarks** 24

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26 The synthesis and characterization of PDMS porous composites formed with the
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28 removed PLA and PEG pore formers were presented. The curing period for a given
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30 temperature of PDMS should be extended beyond the time recommended for the
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32 commercial Sylgard 184® to ensure that cross-linking is complete. Future studies can
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34 consider microsphere-matrix prepared at different cure times to study the impact of cure
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36 times on cross-linking, particularly on PEG removal. Future studies should also consider
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38 effective methods for a higher percentage of PEG formulations and microdroplet
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40 formulations with higher PEG weight percentages. The evasiveness of DCM, combined
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42 with its likelihood to dissolve uncured polymers and difficulty removing all traces of it
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44 from the polymer matrix, calls for exploring other solvent systems that are safer to work
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46 with and have the same efficacy as chlorinated organic solvents. Removing PEG
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48 microspheres from a polymer matrix presents fewer challenges than removing PLA
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50 microspheres from the same matrix. Calcination is the most efficient method for
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52 microsphere removal for PEG microspheres in a PDMS matrix. Calcination was
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54 ineffective for PLA because, at temperatures greater than 200°C, it was found that PLA
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4 undergoes charring and does not sublime out of the matrix. An in-depth solvent study
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6 based on the protocol described by Vandenburg et al. [10] is required, which would be
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8 considered in the future to identify a more effective approach for removing PLA
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10 microspheres from a silicone matrix.
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15 Removable microsphere-modified matrix polymer should not significantly alter
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17 the viscosity characteristics for effective processing and use as a feedstock material in
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19 additive manufacturing applications. A preliminary experimental study indicated that the
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21 viscosity of the PLA microsphere-modified PDMS (Sylgard 184) showed acceptable
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23 viscosity with relatively minimal changes compared to the neat PDMS, as shown in
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25 Figure S-6 (Supplementary Information).
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29 30 **5. Acknowledgment** 31

32
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46 Administration (NNSA)
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50 51 **DATA AVAILABILITY STATEMENT** 52

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54 Data will be made available on reasonable request and upon clearance for availability by KCNSC.
55

56 57 **CONFLICT OF INTEREST** 58

59 On behalf of all authors, the corresponding author states that there is no conflict of interest.
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Author Contributions

The authors confirm contributions to the paper as follows: study conception and Design: S. Torres, R. Dampney, L. Cummings, and R. Mohan; Experiments and Data Collection: R. Dampney; Analysis and Interpretation of Results: R. Dampney, L. Cummings, S. Torres, and R. Mohan; Draft Manuscript Preparation: R. Dampney, R. Mohan, S. Torres, and L. Cummings; Review and Revisions: R. Mohan and R. Dampney. All authors reviewed and approved the final manuscript.

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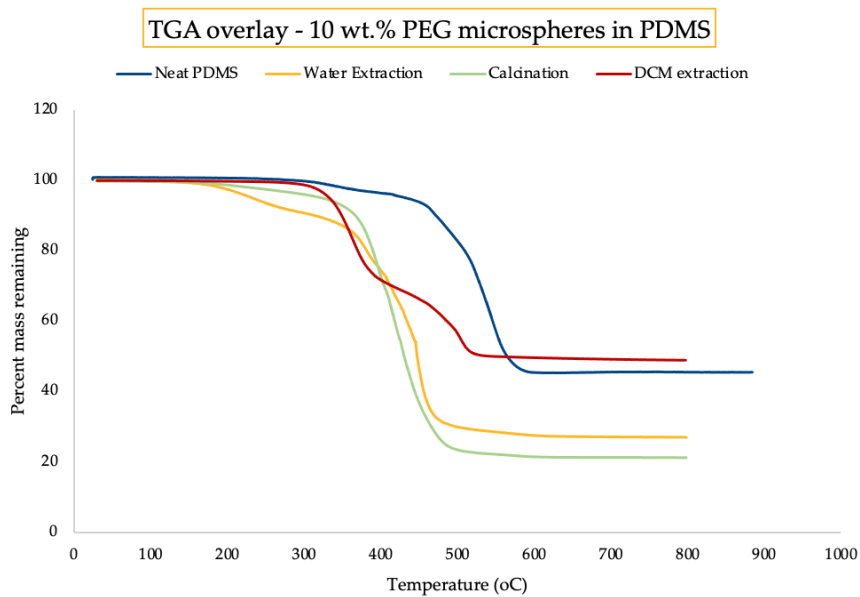
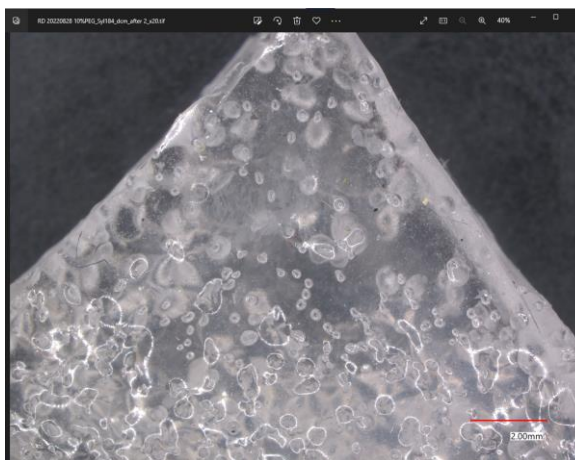
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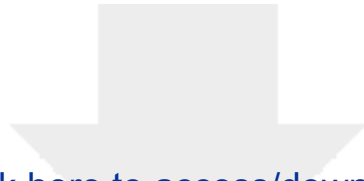
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PEG-PDMS Composite Pore Structure after PEG Removal and TGA Analysis Quantification



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Supplementary Material

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