Investigation of porous polydimethylsiloxane structures with tunable properties induced by the phase separation technique

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Abstract
This article reports the fabrication and characterization of porous polydimethylsiloxane (PDMS) structures developed by the solvent evaporation−induced phase separation technique. Ternary systems containing water/tetrahydrofuran (THF)/PDMS with various concentrations are produced to form a stable solution. The porous PDMS structures are formed by removing the solvent (THF) and nonsolvent (water) phases during the steppping heat treatment procedure. The analytical ternary phase diagram is constructed based on the thermodynamic equilibrium state in the polymer solution to explain the stable/unstable formulations and the possible composition change path. The results show that the isolated pores with the adjustable pore size ranging from 330 to 1900 μm are obtained by tuning the water to the THF ratio. The mechanical properties of the porous PDMS structures are determined by conducting the tensile tests on the prepared dog bone-shaped specimens. A wide range of elastic modulus ranging between 0.49 and 1.05 MPa was achieved without affecting the density of the porous sample by adjusting the solvent and non-solvent content in the solution. It is shown that the flexibility of the porous structures can be improved by reducing the ratio of water to THF and decreasing the PDMS content. The porosity measurements reveal that the PDMS concentration is the major phase controlling the porosity of the structure, while the effect of water/THF is negligible.

KEYWORDS
emulsion polymerization, mechanical properties, microscopy, phase behavior, porous materials

1 | INTRODUCTION

Porous polymers have attracted significant attention due to their excellent properties, such as large surface area, high flexibility, and high-adsorption capacity. The demands for porous polymers in novel applications have been increased recently, including applications for energy storage, oil/water or gas separation, biomedical devices, and wearable electronics.1−5 It is reported that different fabrication techniques can result in distinct porous properties.6 For example, highly interconnected porous structures can be fabricated using the direct templating
technique, while phase separation can result in the porous, cellular framework. Conventional methods for synthesizing the porous polymers include phase separation,\textsuperscript{7} direct templating,\textsuperscript{3} emulsion templating,\textsuperscript{8} and breath figure.\textsuperscript{9} The appropriate fabrication process should be selected based on the desired properties.

Phase separation is one of the most reliable techniques for the manufacturing of porous polymers.\textsuperscript{10} Compared to other methods, the main advantage of this technique is that the pore size is not limited to the template size. Removing the templates after curing the polymer is also not required, making the approach simple and straightforward. Moreover, phase separation is a surfactant-free technique. Hence, there is no adverse impact of the surfactant on the polymer's mechanical properties, and the effort to remove the surfactant after curing is not necessary here. This method can be classified into four groups based on the mechanism of inducing phase separation: solvent evaporation-induced phase separation (EIPS), thermally induced phase separation, nonsolvent-induced phase separation, and vapor-induced phase separation. EIPS is known as a promising approach for developing both three-dimensional structures and membranes.\textsuperscript{6} In this method, polymer and non-solvent phases with different solubility in a solvent are mixed to create a homogeneous single-phase solution. Then, by solvent evaporation, the stable system is changed into two phases of polymer-rich and polymer-lean.\textsuperscript{11} The nonsolvent enriched droplets are formed and grow in the polymer-rich area with the nucleation and growth (NG) mechanism. The isolated cellular pores are developed by removing the large nonsolvent droplets and subsequent solidification of the continuous polymer domain.

Polydimethylsiloxane (PDMS) is an organic and nontoxic silicon-based elastomer, recognized for its outstanding properties, such as mechanical performance, chemical, thermal stability, and biocompatibility. This material has been widely used in various fields, including flexible strain sensors,\textsuperscript{12,13} optical applications,\textsuperscript{14} and biomedical applications.\textsuperscript{15} Recently, the fabrication of the porous PDMS-based structures has received increasing considerations because of two primary purposes. In the first category, the porous PDMS is beneficial for specific applications, such as oil/water separation\textsuperscript{3} or storage.\textsuperscript{16} In the second group, by fabrication of the porous structure, the performance of the PDMS-based materials are improved compared to the solid PDMS structures. For example, it has been reported that the porous PDMS has higher flexibility compared to the bulk, nonporous material.\textsuperscript{17} Besides, it has been established that the porous PDMS-based nanocomposites used as strain sensors have higher sensitivity compared to the solid one.\textsuperscript{18} Based on the desired features, structures with different bulk porosity, pore size, and pore morphology can be produced using PDMS as a primary polymer phase.

It is reported in the literature that the pore size distribution and pore morphology of porous polymers are dependent on the manufacturing method and the material used in the fabrication procedure. For example, the concentration and the type of the solvent, nonsolvent, and polymer used in the EIPS can change the pore morphology of the composition.\textsuperscript{19} It has been shown that the ambient condition during phase separation, such as air circulation\textsuperscript{20} and the rate of solvent removal,\textsuperscript{21} can also affect the pore morphology. Besides, the mechanical properties of the porous structures are different according to the porosity and the porous network. It is reported that different mechanical performances are desirable for specific applications. For example, more flexibility is required for wearable electronics, while higher stiffness is critical for biomedical engineering. Accordingly, a simple method for creating a porous structure with adjustable features required for different applications is of great importance. It is essential to develop a formulation for designing porous structures with the desired properties, such as pore size and mechanical behavior.

This article reports a simple method for the synthesis of porous PDMS structures with tunable properties. Polymer solutions with various PDMS, water, and THF concentrations were prepared, and the porous media was developed by removing solvent and nonsolvent during the stepwise heat treatment. The ternary phase diagram of the three-phase system was also constructed, and the possible mass transfer paths were obtained. The effect of PDMS concentrations and water/THF content on the pore size distribution, mechanical behavior, and porosity of the samples were investigated. Porous PDMS with a wide range of pore size distribution and mechanical properties were fabricated by adjusting the nonsolvent/solvent ratio in the developed approach. The optimal manufacturing parameters to achieve the desired properties of the porous structures were evaluated.

2 EXPERIMENTAL

2.1 Materials

All the materials were used in this study as they received. As the polymer phase, SYLGARD 184 PDMS (base elastomer and hardener) was purchased from Dow Corning and was considered the polymer phase. Tetrahydrofuran (THF) purchased from Sigma-Aldrich was chosen as the solvent phase. Deionized water (DI-water) was used as the nonsolvent phase.
2.2 | Polymer solution preparation and molding

The PDMS polymer solution was prepared by mixing the polymer, solvent, and nonsolvent phases with different concentrations. The whole process of the solution preparation and molding is depicted in Figure 1. First, water was mixed with the PDMS base elastomer at 1000 RPM using a hot plate and magnetic stirrer bar. THF was added to the system in the next step. The solution was blended until a stable viscous mixture is reached, which can remain stable for several weeks without any phase separation. Before molding, the PDMS curing agent (part B) with the ratio of part A to B (10:1) was added and blended for 20 min using a mechanical shear mixer at 2000 RPM.

The prepared polymer solution was poured into a customized mold. The mold was prepared in the form of a window frame ($170 \times 120$ mm$^2$) using a 1.5 mm thick metal shim. The metal frame was secured on a flat metal surface, and the viscous mixture was then poured inside the mold. The poured material was flattened smoothly using a baking scraper tool. The tool was moved in one direction to minimize entrapped air. Next, the mold was covered using a metal plate and placed inside the oven for solvent evaporation and polymer curing using a stepped heating procedure. During the first step, the oven was heated to $50^\circ$C for 90 min. During this step, the viscosity of the polymer solution was increased, and THF started to evaporate slowly. During the second step, the temperature was raised to $65^\circ$C (close to THF boiling point of $67^\circ$C$^{22}$), and all the solvent was evaporated. The phase separation was induced in this step. The sample was kept at $97^\circ$C for 180 min (close to the boiling point of water) to remove the nonsolvent phase (water). Then, the sample was kept at $120^\circ$C to reach a constant weight to ensure that all the THF/water were evaporated and the PDMS was completely cured.

Several formulations were developed in three different categories to explore the effect of different phases in the ternary system on the properties of the porous structure. In the first group, a constant PDMS concentration of 40 wt% was chosen, and the ratio of water to THF ($\alpha$) was varied from 1 to 8. The same $\alpha$ with the 60 wt% PDMS was considered for the second category. In the third group, multiple PDMS concentrations ranging from 20 to 80 wt% and the constant $\alpha = 2$ were prepared. All the formulations developed for further analysis are listed in Table 1.

2.3 | Characterization

The porous PDMS sheets were examined to evaluate the effect of the proposed formulation on the porous structure, including pore size distribution, mechanical properties, and porosity measurement.

2.3.1 | Pore size distribution

The microscope imaging was performed to determine the pore size distribution and obtain the average pore size of the fabricated samples. Accordingly, the Leica SP8 laser scanning confocal microscope was utilized to take the images. For each case, several microscope images were captured from different locations of multiple samples. The number of pores explored in each sample was different based on the size of the pores. Generally, at least 30 pores were analyzed for each case. The captured images were evaluated using ImageJ open-source software. The area of the pores in the microscope images was obtained. Then, the post-processing analysis was performed to calculate the average equivalent diameter and the SD.

2.3.2 | Mechanical properties

The mechanical properties of the porous PDMS structures were evaluated by tensile tests. The dogbone-shaped samples following ASTM standard D412$^{23}$ were cut from the porous sheets by utilizing a customized cutting die and mechanical press. Photograph of the cutting die and the schematic of the samples with the dimensions (in mm) are depicted in Figure 2(a),(b), respectively. The tensile displacement loading with the rate of 500 mm/min was carried out using the Instron uniaxial test machine until complete fracture.
2.3.3 | Porosity

The porosity (void fraction) of the porous samples was characterized using an analytical balance and measuring tools. In this regard, the volume of the samples with the mass of \( M \), thickness of \( h \), length of \( l \), and width of \( b \) was calculated by measuring the dimensions from multiple points utilizing a digital micrometer. The porosity \( \varepsilon \) of the specimens was determined using Equation (1).

\[
\varepsilon = \frac{V_{\text{pores}}}{V_{\text{tot}}} = 1 - \frac{\rho_{\text{porous}}}{\rho_{\text{polymer}}},
\]

where \( V_{\text{tot}} \) and \( V_{\text{pores}} \) are the total volumes of the specimens and the volume of the pores, \( \rho_{\text{porous}} \) is the density of the porous sample calculated from the volume and mass of the specimens, and \( \rho_{\text{polymer}} \) is the PDMS density obtained using a pycnometer (AccuPyc II 1340, Micromeritics Instrument Corp., GA), respectively. The relative uncertainty of the porosity measured using Equation (1) can be calculated based on the following equation.

\[
\frac{\Delta \varepsilon}{\varepsilon} = \left( \frac{1}{\rho_{\text{polymer}}} \right) \left( \frac{\Delta M}{M} + \frac{\Delta h}{h} + \frac{\Delta l}{l} + \frac{\Delta b}{b} \right),
\]

where \( \Delta M = 0.0001 \) g and \( \Delta h = \Delta l = \Delta b = 0.002 \) mm based on the accuracy of the analytical balance and the digital micrometer used for the measurement.

### Table 1

<table>
<thead>
<tr>
<th>Category</th>
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<th>PDMS (wt%)</th>
<th>Water/THF ratio</th>
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Abbreviations: PDMS, polydimethylsiloxane; THF, tetrahydrofuran.

2.4 | Ternary phase diagram

The analytical ternary phase diagram describing the possible miscible, unstable, and composition change of water/THF/PDMS was constructed. The thermodynamic behavior of the polymer solution can be described with the classical Flory-Huggins model. Tompa extended this approach to mathematically explain the ternary mixture containing nonsolvent (1), solvent (2), and polymer (3) phases. Based on this method, the Gibbs free energy for such a mixture can be written as,

\[
\frac{\Delta G_M}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1 \phi_1 \chi_{12} + n_2 \phi_2 \chi_{23} + n_3 \phi_3 \chi_{13},
\]

where \( T \) is the absolute temperature, \( R \) is the gas constant; \( n_i \) and \( \phi_i \) (i = 1, 2, 3) describe the number of moles, and the volume fraction of component \( i \), respectively; \( \chi_{ij} \) denotes the interaction parameter of a binary phase \( i \)/phase \( j \). The nonsolvent, solvent, and polymer phases are described with the subscripts 1, 2, and 3, respectively. By knowing the interaction parameters for a ternary polymer solution, the phase diagram map containing binodal and spinodal curves can be obtained. The chemical potential of components in a mixture can be extracted from Equations (4–6).
In order to calculate the six unknowns from the five coupled-nonlinear equations, one parameter can be considered as an independent variable ($\phi_1^I$ in this study), and the remaining parameters can be solved using the numerical method (i.e., LSqnonlin function in MATLAB program). More information about the mathematical calculations can be found in ref. 28.

### 2.4.2 Spinodal curve

The spinodal curve representing the boundary between metastable and unstable regions can be obtained by Equation (9).

$$G_{22}G_{33} = G_{23}^2,$$  

where $G_{ij} = \frac{\partial^2 G}{\partial \phi_i \partial \phi_j}$, is the second derivative of the Gibbs free energy with respect to the composition. Using Equation (1), the spinodal relations lead to Equations (10)–(12).

$$G_{22} = \frac{1}{\phi_1} + \frac{\nu_1}{\nu_2\phi_2} - 2\chi_{12} + 2\left(\frac{d\chi_{12}}{du_2}\right)u_1 - u_2 + \left(\frac{d^2\chi_{12}}{du_2^2}\right)u_1u_2,$$  

$$G_{23} = \frac{1}{\phi_1} - (\chi_{12} + \chi_{13}) + \frac{\nu_1\chi_{23}}{\nu_2} + \left(\frac{d\chi_{12}}{du_2}\right)u_2(u_1 - 2u_2),$$  

$$G_{33} = \frac{1}{\phi_1} + \frac{\nu_1}{\nu_3\phi_3} - 2\chi_{13} - 2\left(\frac{d\chi_{12}}{du_2}\right)u_2^2(1 - u_1) + \left(\frac{d^2\chi_{12}}{du_2^2}\right)u_1u_2^2 + 2(\phi_1 - \phi_3)\left(\frac{d\chi_{13}}{d\phi_3}\right) + \phi_1\phi_3\left(\frac{d^2\chi_{13}}{d\phi_3^2}\right) + 2\frac{\nu_1}{\nu_2}\phi_2\left(\frac{d\chi_{23}}{d\phi_3}\right) + \frac{\nu_1}{\nu_2}\phi_2\phi_3\left(\frac{d^2\chi_{23}}{d\phi_3^2}\right).$$  

There are three unknowns required for constructing the spinodal curve. Two coupled-nonlinear equations come from the substitution of Equations (10)–(12) in Equation (9), and the other is the material balance ($\sum_1 = 1$). Similar to the binodal calculation, one parameter (i.e., $\phi_3$) can be considered as an independent variable, and the other two parameters can be solved using numerical methods.
2.4.3 Interaction parameters

As described above, three interaction parameters are required to find the binodal and spinodal curves. Generally, the solvent-polymer binary interaction parameter ($\chi_{23}$) is not dependent on the volume fraction of the components. There are several experimental techniques to measure $\chi_{23}$, including gas–liquid equilibrium, osmotic pressure, and light scattering. The value of $\chi_{23} = 0.48$ is reported in the literature for the THF/PDMS system at 20°C.31 The nonsolvent-polymer binary interaction parameter ($\chi_{13}$) is usually calculated by the equilibrium swelling measurement.32 The nonsolvent phase diffuses in the polymer phase until the equilibrium state between the chemical potential of the liquid inside the polymer and the liquid phase is achieved. According to the Flory-Rehner theory, $\chi_{13}$ is dependent on the polymer concentration and can be expressed with Equation (13).33,34

$$
\chi_{13} = \frac{-\ln(1 - \phi_3) + \phi_3}{\phi_3^2}
$$

(13)

The non-solvent/solvent binary interaction parameter ($\chi_{12}$) depends on the $u_2$ pseudo-binary mixture at different temperatures, which can be calculated from Equation (14).35

$$
\chi_{12} = \alpha_0 + \frac{\beta_0}{1 - \gamma_0 u_2}
$$

(14)

where $\alpha_0$, $\beta_0$, and $\gamma_0$ are temperature-dependent parameters. The value of 0.720, 0.764, and 0.531 are reported for water/THF system at 20°C, respectively.35

3 RESULTS AND DISCUSSIONS

3.1 Phase diagram

The parameters required for constructing the phase diagram were calculated based on the numerical method described before. The thermodynamic ternary phase diagram for water/THF/PDMS is illustrated in Figure 3. The binodal and spinodal curves divide the phase map into three different regions. Region (A) is the homogenous domain where the mixture is stable. The area between spinodal and binodal curves (B) is called the metastable zone, while region (C) indicates the unstable area. The intersection of these two curves, called critical point (CP) is shown in this figure. The CP for the water/THF/PDMS system was obtained as 39.6/52/8.4. The region above the CP is related to the polymer-rich zone, and the underneath area is the polymer-lean phase.

Two scenarios can be attributed to the phase separation mechanism based on the phase diagram’s precipitation path, as demonstrated in Figure 3. The NG is the primary mechanism in the first scenario, where the composition slowly passes a line from a homogeneous region to the metastable domain (Path 1). The composition follows path 1 until all the solvent is evaporated (zero-THF edge). Then, water is removed from the system, and the composition moves toward the polymer section of the phase diagram on the zero-THF edge. The final porous structure, in this case, is the isolated cellular pores in the polymer matrix.35 The nature of the phase separation is different based on the composition change path on the binodal curve. If the path is above the CP, the nonsolvent enriched droplets are formed in the polymer-lean area. Then, these droplets merge and grow by the concentration gradient until the polymer-rich phase solidifies. If the composition path is located below the CP, the isolated droplets of the polymer-rich phase are formed. Similarly, the droplets are driven to grow until the polymer phase solidifies.36

In the second scenario, the mechanism of the pore formation is spinodal decomposition (SD) if the composition path passes the CP (Path 2) leads to the liquid–liquid demixing in the unstable region. The composition path reaches the zero-THF edge and then moves up to the polymer section during the water removal. Continuous pore structure with interconnected networks is formed by the SD mechanism.37 Considering the solvent evaporation procedure and the location of the CP in the ternary diagram, it can be claimed that NG is the pore formation.

FIGURE 3 Ternary phase diagram for water/THF/PDMS system showing the possible mass-transfer path leading to porous structures. PDMS, polydimethylsiloxane; THF, tetrahydrofuran [Color figure can be viewed at wileyonlinelibrary.com]
mechanism of the water/THF/PDMS formulations used in this study. For the same reason, it can be claimed that the NG of water-enriched droplets occurs in the polymer-rich domain.

3.2 | Pore size distribution

The microscope images captured from the porous samples for groups 1 and 2 with different $\alpha$ are illustrated in Figures 4 and 5, respectively. The isolated pores with the circular shape in dark colors are observed in these images, while the cured PDMS is the continuous shape in the bright color. It can be seen that NG of the water-enriched droplets was the mechanism of the pore formation. The pore formation mechanism can also be explained by the ternary phase diagram (Figure 3), as all the formulations used in this study have a polymer concentration far above the CP (PDMS>8.4%). The droplets were formed in the polymer-rich domain during the phase separation procedure, leading to the isolated porous structure. After coalescence and creating larger droplets, a thin film of PDMS covered the droplets due to the higher surface tension of the water compared to the polymer-rich solution. Then, the water was removed during the heat treatment resulted in hollow cellular pores in the structure.

Based on the microscope images, a higher water/THF ratio caused larger pore sizes in both 40% and 60% PDMS categories. Multiple pores were seen through the thickness for the samples with $\alpha = 3, 4, 6,$ and 8, while only one pore was observed through the thickness for the samples with $\alpha = 1$ and 2. The equivalent diameter of the pores was measured using the ImageJ software. The average pore size for the samples with 40% and 60% with different $\alpha$ are given in Figure 6(a),(b), respectively. It can be observed that the average pore size in both groups was decreased by increasing the parameter $\alpha$. The increased amount of solvent in a smaller value of $\alpha$ reduced the viscosity of the solution. Hence, the water droplets had more mobility to coalesce and create larger droplets, leading to larger pore sizes. It should be noted that there was a limitation in increasing the water/THF ratio. Both experiments and the ternary phase diagram showed that the value of $\alpha$ greater than 8 resulted in an unstable mixture.

Similar pore sizes can be seen in Figure 6(a),(b) by keeping the water/THF ratio consistent in the samples with 40% and 60% PDMS concentrations. In order to prove this claim, the average pore size for the third group of the formulation is calculated, as shown in Figure 7. Various PDMS concentrations with $\alpha = 2$ resulted in similar pore sizes. Hence, it can be concluded that the water/THF ratio is the parameter controlling the pore size in

FIGURE 4 Microscope images showing the pore distribution for the samples with 40% PDMS and (a) $\alpha = 8$, (b) $\alpha = 6$, (c) $\alpha = 4$, (d) $\alpha = 3$, (e) $\alpha = 2$, (f) $\alpha = 1$. PDMS, polydimethylsiloxane
different polymer concentrations. A slight increase in pore size for lower PDMS could be due to the lower viscosity of the mixture compared to higher polymer weight. Moreover, the pore size distribution for the samples with 40% PDMS and $\alpha = 3, \alpha = 4$ are shown as examples in Figure 8(a), (b), respectively. Both larger and smaller pores compared to the average size were observed, while the majority of the pores are in the average range.

It should be noted that three samples of the 19 prepared water/THF/PDMS mixture did not result in a porous structure. There was not a stable solution in case number 13 (PDMS = 20%, $\alpha = 2$), while no pores were created by solvent evaporation in case numbers 18 (PDMS = 70%, $\alpha = 2$) and 19 (PDMS = 80%, $\alpha = 2$). In order to justify the failure of these points, their formulations were plotted in the ternary diagram, as shown in Figure 9. It is obvious that case number 13 is located in an unstable region and could not result in a stable solution. Besides, the possible composition path change for case numbers 18, 19 shown in Figure 9 did not intercept

**FIGURE 5** Microscope images showing the pore distribution for the samples with 60% PDMS and (a) $\alpha = 8$, (b) $\alpha = 6$, (c) $\alpha = 4$, (d) $\alpha = 3$, (e) $\alpha = 2$, (f) $\alpha = 1$. PDMS, polydimethylsiloxane

**FIGURE 6** The average pore size obtained for (a) 40% PDMS and (b) 60% PDMS with different water/THF ratio ($\alpha$). PDMS, polydimethylsiloxane; THF, tetrahydrofuran [Color figure can be viewed at wileyonlinelibrary.com]
the binodal curve, leading to PDMS solidification without any pore formation.

3.3 | Mechanical behavior

The dogbone-shaped samples were tested under tensile loading, and the mechanical behavior of the porous structures was determined. As an example, prepared samples with 40% PDMS and $\alpha = 1, 2, 3, 4$, and the nonporous PDMS before and after the tensile test are shown in Figure 10(a),(b), respectively. The stress–strain curves showing the mechanical behavior of the porous structures with 40% PDMS, 60% PDMS and different $\alpha$ are illustrated in Figure 11. According to this figure, the porous PDMS samples in both groups became stiffer as the water/THF ratio increased. The elastic modulus of the samples was calculated from the stress–strain curves. It was observed that for the samples with the same polymer concentration (40% PDMS), a wide range of elastic modulus increasing from 0.49 MPa ($\alpha = 1$) to 1.05 MPa ($\alpha = 8$) was achieved by raising the nonsolvent/solvent content.

For a better comparison, the strain of the samples with 40% PDMS at the 0.18 MPa stress is shown in Figure 12(a). Higher deformation in the samples with a lower water/THF ratio (larger pore size) can be seen in this figure. Moreover, the stress of the specimens with 60% PDMS at the 0.4 mm/mm strain is compared in Figure 12(b). A higher stress value can be observed for the porous PDMS samples with a smaller pore size (higher water/THF ratio). The stiffness is controlled by the solid phase, which is the pore's wall in the porous network. The porous structure with smaller pores had a higher ability to sustain the flow stress as the number of pores along the width was improved by increasing the water/THF ratio. In other words, the samples with larger pore sizes showed higher deformation, indicating more flexible behavior than the specimens with small pore sizes.

In order to demonstrate the effect of PDMS concentration on the mechanical performance of the porous sheet, the stress–strain of specimens with constant $\alpha = 2$ and different PDMS concentrations is displayed in Figure 13(a). According to this figure, higher PDMS concentration resulted in increased stiffness. By comparing the strain of the samples at 0.2 MPa stress in Figure 13(b), it was revealed that lower PDMS concentration showed higher deformation. For example, the strain of

**FIGURE 7** The average pore size for the samples with $\alpha = 2$ and different PDMS concentrations. PDMS, polydimethylsiloxane; THF, tetrahydrofuran [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 8** The pore size distribution for samples with 40% PDMS and (a) $\alpha = 3$, (b) $\alpha = 4$. PDMS, polydimethylsiloxane [Color figure can be viewed at wileyonlinelibrary.com]
0.43 mm/mm was observed for the sample with 30% PDMS, which was 34.8% higher than the strain in the sample with 60% PDMS. Besides, the strain in the sample with 30% PDMS was 258% higher than the nonporous PDMS, indicating the enhanced flexibility of the porous PDMS structure.

### 3.4 | Porosity measurement

The porosity of the fabricated specimens was calculated using Equation (1). The porosity and the relative uncertainty of the measurement for a representative sample with $l = 10.014$ mm, $b = 10.113$ mm, $h = 1.434$ mm, and $M = 0.0598$ g were calculated as $\varepsilon = 0.6002$ and $\Delta\varepsilon/\varepsilon = 0.0034$ based on Equation (1) and (2). Hence, the uncertainty of the measurement for this representative sample was found as $\Delta\varepsilon = 0.0020$. The porosity measurements for the samples with 40% and 60% PDMS and various $\alpha$ are illustrated in Figure 14. Multiple samples were explored, and the standard deviation is obtained, as shown in this figure. Based on this figure, the porosity of the PDMS samples did not change by altering the water/THF ratio in both groups.

It can be concluded that a larger number of pores were formed in the sample with larger $\alpha$ (smaller pore size)
size), making the void fraction a constant value. As it was shown in the microscopy images, larger spaces with no pores were seen for the samples with lower PDMS concentration. This can be verified from Figure 14, as the porosity of the samples with 40% PDMS is higher than 60% PDMS.
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REFERENCES


CONCLUSION

The fabrication and analysis of porous PDMS structures formed by solvent EIPS were discussed in this article. Different formulations of polymer solutions with various PDMS concentrations and water/THF ratios were investigated. The analytical ternary phase diagram in the water/THF/PDMS system was constructed to determine the stable, unstable, and metastable regions and the binodal, spinodal curves. It was shown that a phase diagram is an effective tool for predicting the stable/unstable formulations and the possible mass transfer path leading to PDMS samples with various porosity levels and pore sizes. The fabricated porous samples were analyzed to evaluate the pore size distribution, mechanical properties, and porosity microstructure. The isolated pores with the average pore size ranging from 330 to 1900 μm were obtained from NG of the water enriched droplets in the PDMS-rich domain. It was observed that in the formulations with the same PDMS concentration, the average pore size was decreased by raising the water/THF ratio. However, a similar pore size was achieved by changing the PDMS concentrations from 30% to 60% and keeping the water/THF ratio a fixed parameter.

Besides, the tensile tests of prepared samples revealed that increasing the water/THF ratio at a constant PDMS concentration can increase the stiffness of the porous PDMS structures. The porous structure with smaller pores had a higher ability to sustain the flow stress as the number of cells across the width was improved by increasing the water/THF ratio. In other words, the samples with larger pore sizes showed higher deformation, indicating more flexible behavior than the specimens with small pore sizes. This study showed that a wide range of elastic modulus ranging between 0.49 and 1.05 MPa could be achieved in the samples with the same density by adjusting the solvent and non-solvent content in the solution. Comparing the samples with different PDMS concentrations and the same water/THF ratio, it was evident that higher polymer weight can result in increased stiffness. It was shown the strain in a sample with 30% PDMS is 34.8% higher than the sample with 60% PDMS and 258% higher than the bulk, nonporous PDMS. Moreover, the porosity of the fabricated structure was evaluated by measuring the void fraction of the samples. It was observed that higher PDMS concentration leads to lower porosity. The results indicated that the porosity of the samples could be controlled by the polymer concentration, while a negligible effect was observed from changing the non-solvent/solvent ratio.

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