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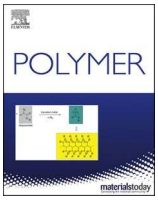

Open-cell PDMS polyHIPEs prepared using polymethylvinylsiloxane to prevent pore collapse

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ABSTRACT

Polymerized high internal phase emulsions (PolyHIPEs) are porous polymers made using an emulsion template. Our group has previously shown that polydimethylsiloxane (PDMS) polyHIPEs prepared using a thiol-ene crosslinking reaction could obtain a maximum total porosity of ~63%. Attempting to increase total porosity by increasing the volume fraction dispersed phase resulted in collapse of the porous material due to the soft nature of PDMS. In this work, polymethylvinylsiloxane (PMVS) was synthesized to impart high crosslinking density in the network. This polymer can be blended with divinyl-PDMS in the continuous phase to obtain a large range of storage moduli (25–900 kPa) in the final polyHIPEs with higher total porosity (74–77%). Finally, the use of these PDMS PolyHIPEs as separation media for oil/water mixtures has been demonstrated.

1. Introduction

Porous polymeric structures can be easily processed into monoliths, films, or beads for various applications including gas storage [1], catalysis [2], and separations [3]. For many porous polymers, the total porosity of the material becomes the defining feature of that material's properties. Therefore, much attention has been devoted to the design and synthesis of porous polymer materials possessing controllable total porosity [4].

One method to synthesize highly porous materials is using an emulsion templated polymerization to prepare polymerized high-internal phase emulsions (polyHIPEs) [5]. PolyHIPEs are used in applications including biomaterials [6], acoustic devices [7], and wearable electronics [8] due to their advantageous materials properties such as high surface area, compressibility, and tunable stiffnesses. *High* internal phase emulsions are defined as those that exceed 74% volume fraction of the dispersed phase with respect to the total emulsion volume, while emulsions with 24–74% dispersed phase are called *medium* internal phase emulsions (polyMIPEs) [5]. The continuous phase of the emulsion template contains the monomers and the dispersed phase is removed following polymerization resulting in a porous material. A wide variety of monomers have been used in the synthesis of poly(HIPES) including acrylates [9], styrenes [10,11], and thiol/alkene pairs [12,13]. Furthermore, as both oil-in-water and water-in-oil emulsion templates have been used in preparing polyHIPEs, this technique has been demonstrated with polymerizing either hydrophilic or hydrophobic monomers [14].

The total porosity and storage moduli of polyHIPEs can be tuned by controlling the properties of the emulsion template. Common strategies include changing the volume fraction of dispersed phase [15], the locus of initiation [16], or tuning the viscosity ratio between the phases [17]. Another strategy is changing the composition of the polymerized phase itself by modifying the molar ratio between monomer(s) and crosslinker to change the crosslinking density of the polymer network. For example, Tunc and coworkers [18] demonstrated that poly(HIPEs) transitioned from brittle to elastomeric by tuning the molar ratio between a set of acrylate monomers and the divinylbenzene crosslinker used in the continuous phase of the emulsion.

In previous work from our group [19], we showed that the storage modulus and total porosity of poly(dimethylsiloxane) (PDMS) polyHIPEs prepared using thiolated PDMS chains and divinyl-PDMS can be controlled using the thiol/ene stoichiometry and volume fraction of the dispersed phase respectively. However, in that work, the maximum total porosity achieved with the PDMS-based polyHIPEs was limited to around 65%. While formally polyMIPEs, we refer to all of our materials as polyHIPEs for simplicity. Achieving high internal porosities (>74%) remains challenging in open-cell PDMS polyHIPEs because PDMSs are typically low T_g polymers, and thus polyHIPEs prepared with these polymers tend to collapse at high porosities [20,21]. One method used to address this challenge has been to stabilize the HIPE template by using

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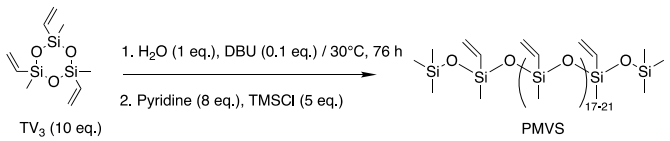


Scheme 1. Synthesis of poly(methylvinyl)siloxane.

Pickering emulsions [16]. Another method to enhance the porosity of a material is through blowing agents. For example, Tebboth and coworkers [22] dissolved $NaHCO_3$ in the aqueous dispersed phase which led to inflatable materials due to formation of CO_2 within pores. However, the porosity of these materials was limited by the fact that only 60% internal phase emulsion templates could produce materials mechanically strong enough to undergo inflation. Kumar and coworkers [23] used a similar approach by adding peroxides to the dispersed phase which would decompose to form O_2 gas while curing. The generation of expanding gas bubbles alleviated the internal stress caused by drying allowing pores to maintain the initial shape of the droplet from the emulsion template. Therefore, there remains a need to prepare high-porosity open-cell PDMS polyHIPEs.

Herein, we report the synthesis of PDMS polyHIPEs with a range of tunable mechanical properties prepared at a variety of constant dispersed phase volume fractions in the emulsion template. The polyHIPEs were able to achieve a total porosity of up to 77%. We show that emulsions with similar rheological properties can lead to varied materials properties by altering the composition of the continuous phase using blends of poly(methylvinylsiloxane) (PMVS) and a commercial divinyl PDMS. Our system takes advantage of a fast, room temperature, thiol-ene "click chemistry" reaction, without requiring additional gas-blowing agents, poragens, or additives. Furthermore, we show the potential of these polyHIPEs as absorbents in oil remediation applications using absorption capacity and recycling tests with common oils.

2. Experimental

Materials The monomer 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane was purchased from AK Scientific (Union City, CA). Pyridine was purchased from Fisher Scientific (Hampton, NH). Chlorotrimethylsilane was purchased from Oakwood Chemical (Estill, SC). The polymers [13−17% (mercaptopropyl) methyl-siloxane]−dimethylsiloxane copolymer ("thiolated-PDMS"), vinyl-terminated PDMS (vinyl-PDMS), and (30−35% dodecylmethylsiloxane-[7−10% hydroxy(propethyleneoxy (6−9) propyl) methylsiloxane] (55−65% dimethylsiloxane) terpolymer (Silube J208-812) were purchased from Gelest (Morrisville, PA, USA). The photo-initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA), reagent-grade dichloromethane (DCM), and the catalyst, 1,8-diazabicyclo[5.4.0]undece-7-ene (DBU) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All the reagents used in this work were used as received.

Synthesis of poly(methylvinylsiloxane) A modified procedure from literature [24] using a ring-opening polymerization of a cyclotrisiloxane initiated by water was used to prepare poly(methylvinylsiloxane) (Scheme 1). In a representative example, a 250 mL round-bottom flask was flame-dried and charged with a magnetic stir bar and septum. The monomer, 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (TV_3), and water were injected into the flask at a 10:1 M ratio of monomer to water and placed under a nitrogen atmosphere. Anhydrous tetrahydrofuran (THF) (0.75 mL per g of monomer) was added to the flask followed by a solution containing 1,8-diazabicyclo[5.4.0]undece-7-ene (DBU) (0.1 equiv. with respect to monomer) dissolved in THF (~0.5 mL/g monomer) and the reaction vigorously stirred for 76 h at 30 °C. After this time, pyridine (8 eq. with respect to water) and chlorotrimethylsilane (TMSCl) (5 eq.) were added to terminate the reaction. Solvents were removed by briefly bubbling nitrogen gas through the flask until constant weight. The crude resin was washed with MeOH (75 mL) three times to yield a colorless oil (61% mass recovery) The polymers were characterized using ^{1}H NMR and ^{13}C NMR spectroscopy and mass spectrometry (Full spectra and assignments are available in Supporting Information). ^{1}H NMR: ($CDCl_3$, 400 MHz), 5.95 ppm (m, 2H), 5.8 ppm (dd 1H), 0.14 ppm (s, 3H). ^{13}C NMR: 136 ppm (s, CH_2), 133 ppm (s, CH), −0.44 ppm (s, CH_3.) Peaks in the mass spectrum were separated by a repeat mass with m/z = 86 Da indicative of the (-OSiMeVi-) repeat unit. The M_n of the PMVS samples used in this study were ~1300–1800 g/mol with narrow molecular weight distributions as determined using mass spectrometry (Table S2, Figs. S1–4).

HIPE Preparation HIPES were prepared following published proceedures [20]. All emulsions in this study were prepared with equal stoichiometric ratios of thiol-to-alkene functional groups in the continuous phase, and the continuous phase was prepared by adding thiolated-PDMS to blends of divinyl PDMS and PMVS in a glass vial ~~and mixed~~ before mixing the polysiloxanes using a vortex shaker. The surfactant, Silube, (5 wt % with respect to total weight of all polymers) was added to the vial and the solution mixed again using a vortex shaker. The dispersed phase consisting of an aqueous 1.5 wt % sodium chloride solution was added dropwise to the continuous phase and the mixture vortexed until a uniform emulsion was formed. Finally, the photoinitiator, 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 0.1 wt % with respect to total weight of all polymers) was dissolved in 0.2 mL dichloromethane and added to the vial. Three separate samples were made for each formulation.

PolyHIPE Synthesis For each sample, 5 g of total emulsion was used for the synthesis of one polyHIPE. The DCM that was added with the photoinitiator was allowed to evaporate and the HIPEs were placed into a square mold and irradiated with UV light (λ_{max} = 365 nm) for 6 min. The resulting polyHIPEs were removed from the molds 5 min after the curing reaction had finished. Once removed from the mold, the polyHIPEs were dried in a fume hood for ~72 h at 24 °C and then rinsed with hexane. The final materials were characterized using total porosity calculations, dynamic mechanical analysis, scanning electron microscopy, and oil uptake capacity tests. Total porosity measurements were performed on dried polyHIPEs using a home-built Archimedes balance. After obtaining the measured density, the total porosity (Φ_{exp}) was calculated using Equation (1) where ρ_0 is the average density of the non-porous PDMS (0.975 g/mL) and ρ^* is the measured density of individual polyHIPE samples.

$$1 - \frac{\rho^*}{\rho_0} = \Phi_{exp} \quad (1)$$

Methods The rheological behavior of each emulsion in the absence of photoinitiator was analyzed by performing oscillatory frequency sweeps (0.1–100 Hz; 24 °C) using Discovery Series Hybrid Rheometer (DHR) (Model HR-2, TA Instruments) with 20 mm diameter parallel plates. The temperature was regulated with a Peltier system. Roughly 0.2 mL samples of emulsion were used. Rheology characterization was performed before adding the photoinitiator for ease of handling.

The shear storage modulus of the dried polyHIPEs were determined using a PerkinElmer dynamic mechanical analyzer (DMA-8000) and processed using Pyris software. Samples of polyHIPEs were cut into strips with dimensions ~3 mm thick, ~7 mm long, and ~3 mm wide. Frequency sweeps were performed in rectangular tension mode (0.1–70 Hz; 0.01 mm strain) on three separate samples for every formulation. The pore morphology of the polyHIPEs was obtained using a scanning electron microscope (Low-Vac) (FEI XL-30) equipped with EDAX detector. The pore diameter was obtained by hand measuring 100 pores on 3 different samples of the same formulation. Cross sectional pieces of the polyHIPEs were cut and fixed to a copper wire and imaged at an accelerating voltage of 10 kV.

^{1}H and ^{13}C{^{1}H} NMR spectroscopy were performed in $CDCl_3$ using a Bruker Ultrashield 400 MHz (100 MHz for ^{13}C NMR) instrument and the data were processed using MestReNova 14 software. Polymer molecular weights were characterized using mass spectrometry. Samples were

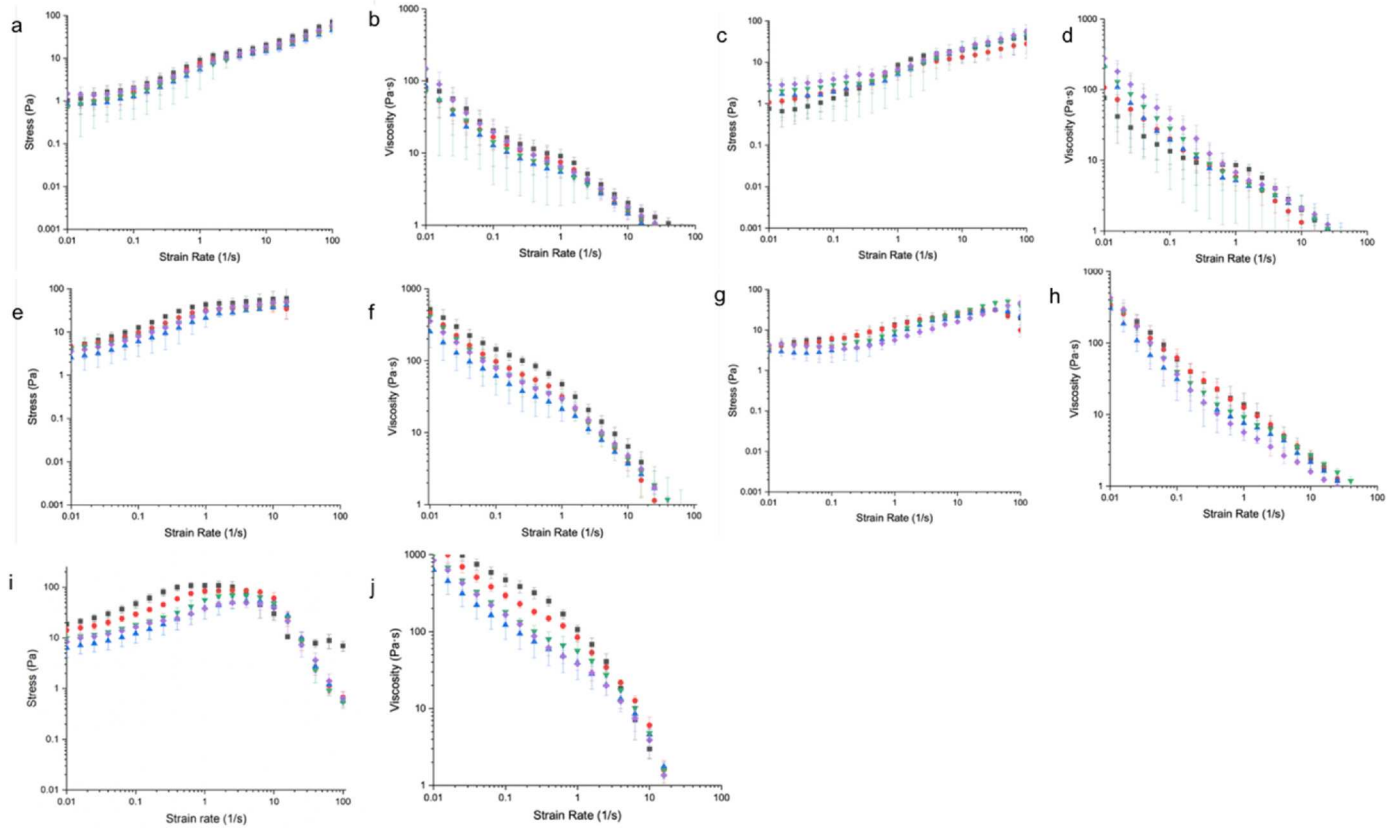
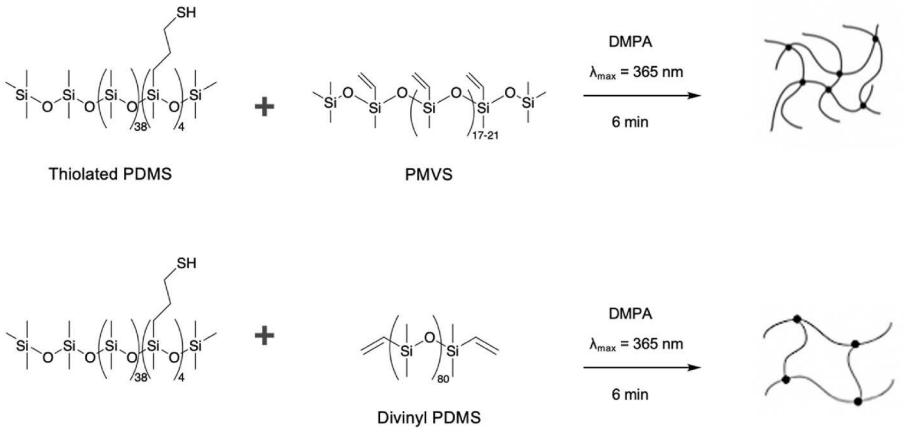


Fig. 1. Stress vs shear rate and viscosity vs shear rate of each of emulsion prepared in this study. Figures a and b = 60% dispersed phase; c and d ~~b~~ = 70% dispersed phase; e and f ~~e~~ = 75% dispersed phase; g and h ~~d~~ = 80% dispersed phase, and i and j ~~e~~ = 85% dispersed phase. The symbols in each figure are different formulations where square = D0-V100, circle = D25-V75, blue triangle = D50-V50, green triangle = D75-V25, and diamond = D100-V0. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Scheme 2. Thiol-Ene crosslinking reactions between thiolated PDMS and PMVS (top) and thiolated PDMS and divinyl PDMS (bottom).

characterized using ultrafleXtreme MALDI-TOF/TOF mass spectrometer from Bruker Daltonics (Billerica, MA). A saturated solution of [2-(4-hydroxyphenylazo)-benzoic acid] HABA in methanol was used as a matrix. A 2:10 sample-to-matrix volumes were mixed using the dried droplet sample preparation method, then 1 μL spotted on the MALDI plate, air dried at room temperature and analyzed. The spectra were acquired in positive ion reflectron mode with accumulation of about 500 laser shots per spectrum. The instrument was calibrated using a poly-alanine standard. The raw data were processed using flexAnalysis software from Bruker.

Oil Uptake Capacity Four formulations: PolyHIPEs 85D0-V100, 85D50-50, 60D100-V0, and 60D0-V100 were chosen to investigate the effect of the total porosity and flexibility on the uptake capacity. For each formulation, three samples were cut into 3 mm thick, 7 × 7 mm squares and placed into a beaker containing 5 mL of oil under slow magnetic stirring. After 10 min, the polyHIPE was removed from the oil and gently squeezed until no more oil could be removed. The material was then washed with hexane and set to dry at room temperature. Finally, the weight of the dried polyHIPE was recorded. The process was repeated for 6 cycles.

Table 1
The total porosity and pore diameter for each sample characterized by SEM (Fig. 2a–e.).

Sample	Total Porosity (± 2%)[a]	Average Pore Diameter (microns)[b]
60D0-V100	59	12.0 ± 4.6
70D0-V100	65	11.1 ± 4.8
75D0-V100	68	9.8 ± 3.9
80D0-V100	72	9.5 ± 3.1
85D0-V100	77	7.6 ± 5.4

[a] Total porosity was measured on a home-built Archimedes balance.
[b] The average pore diameter was obtained by measuring 100 pores in the SEM images of 3 samples of each formulation.

3. Results and discussion

We have previously demonstrated the synthesis of PDMS polyHIPEs using a photoinitated thiol-ene reaction between thiolated PDMS and divinyl PDMS in the continuous phase [19]. The maximum total porosity achieved in those polyHIPEs was ~62–65%. When we attempted to increase the final porosity of the polyHIPEs by adding more volume fraction of dispersed phase we observed pore collapse in the materials, and thus low values of total porosities. In this work, we have targeted materials with higher porosities by blending divinyl-PDMS with PMVS. PMVS was chosen in this study for its high double bond-functionality, which imparts a high crosslinking density in the polymer network. When divinyl-PDMS is used to crosslink with the thiolated-PDMS, crosslinking only occurs at the terminal ends of the divinyl-PDMS chains, leading to a lower crosslinking density in the network and softer mechanical properties in the materials. In contrast, PMVS has a pendant-vinyl repeating unit, therefore crosslinking can occur throughout the polymer backbone. This results in higher crosslinking density in the network and higher storage moduli in the materials. Therefore, by combining divinyl PDMS with PMVS we expected to be able to control the mechanical properties of the materials to provide soft foams with minimal pore collapse at porosities above 74%. PMVS was synthesized using a ring-opening polymerization of vinyl cyclic siloxane (Scheme 1) [24].

We used blends of divinyl-PDMS and PMVS with thiolated-PDMS at a constant 1:1 thiol/ene stoichiometric ratio in the continuous phases of the emulsions, as we have found that a 1:1 stoichiometric ratio results in networks with higher values of storage modulus than off-stoichiometric ratios [25]. We prepared polyHIPEs from 60% volume fraction of dispersed phase in the emulsion increasing to 85% volume fraction of dispersed phase in the emulsion. The details of each emulsion formulation are given in Table S1. Each sample has been named according to the molar ratio of divinyl PDMS (D) to PMVS (V) in the continuous phase of the emulsion. The number preceding the name represents the % volume fraction dispersed phase in the emulsion. For example, 80D50-V50 would represent an emulsion templated sample comprised of an 80% volume fraction dispersed phase and a continuous phase containing 0.5 molar equivalents of both divinyl-PDMS and PMVS with respect to 1 molar equivalent of thiolated PDMS.

We analyzed the rheological properties of the emulsion templates before performing the thiol-ene polymerization to examine if differences in final mechanical properties of the polyHIPEs were due to any differences in the properties of the emulsions, instead of differences in the composition of the vinyl-functionalized PDMS in the final materials. The stress vs. shear rate and viscosity vs. shear rate plots are shown in Fig. 1, and show little difference within each emulsion series. Therefore, for each series emulsions prepared from 60 to 80% of dispersed phase, we conclude that while the compositions of the continuous phase differed at a given volume fraction of dispersed phase, the properties of the

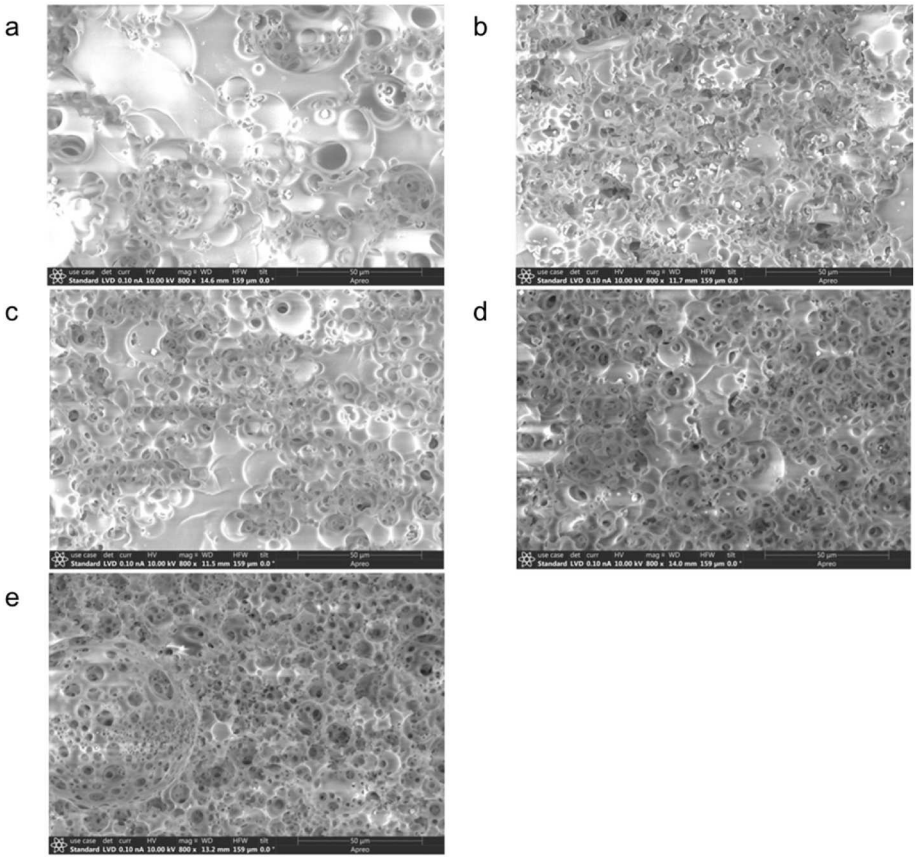


Fig. 2. Scanning electron microscopy of the D0-V100 (hardest) sample from each porosity regime. a = 60%, b = 70%, c = 75%, d = 80%, e = 85% volume fraction dispersed phase.

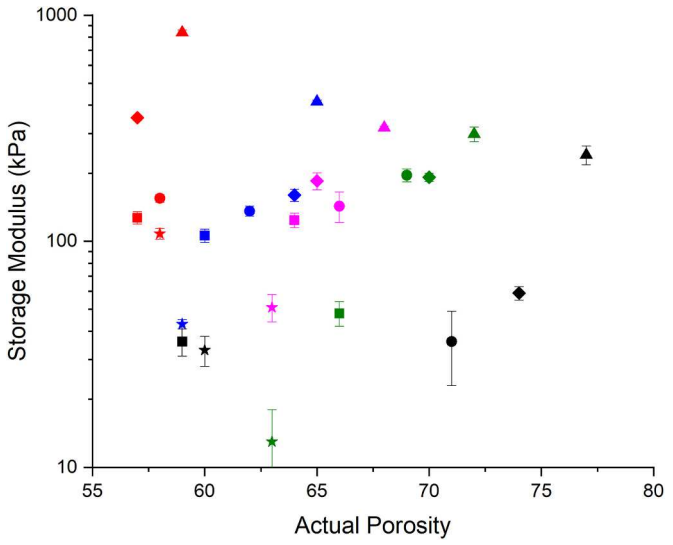


Fig. 3. Storage modulus vs actual porosity of each volume fraction dispersed phase series. Red = 60%, Blue = 70%, Pink = 75%, Green = 80%, = Black = 85%. Symbol shape indicates ratio of divinyl PDMS, (D), and PMVS (V) in the continuous phase of the emulsion precursor. Star = D100-V0, square = D75-V25, circle = D50-V50, diamond = D25-V75, triangle = D0-V100.The standard deviation associated with total porosity is ±2.0% for each formulation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

emulsion template were retained.

In this work, we crosslinked the networks using a photoinitiated thiol-ene reaction using UV-wavelength light at room temperature. We observed that 6 min of reaction time was sufficient to prepare a fully polymerized monolith with 97–99% mass recovery for each emulsion template. The crosslinking reactions are shown in Scheme 2.

We initially attempted Soxhlet extraction with THF for the purification of the polyHIPEs, however, this process resulted in damage to the materials. Furthermore, drying the materials in a vacuum oven at room temperature resulted in cracks forming in the stiffer polyHIPEs, so we allowed the polyHIPEs to dry at room temperature in a fume hood for three days until constant weight. The polyHIPEs were then thoroughly rinsed with hexane to remove unreacted starting material or leftover surfactant. Finally, the polyHIPEs were left to dry in the fume hood at room temperature for 24 h.

We determined the total porosity of the dry polyHIPEs (Table 1) and analyzed the pore morphology of the materials with only PMVS and thiolated-PDMS in each series, i.e. D0-V100 (triangles in Fig. 3), using SEM imaging (Fig. 2).

The pore diameter decreases and the total porosity of the material increases as the volume fraction of dispersed phase in the emulsion template is increased. For 85D0-V100 formulation which possessed a total porosity of 77%, there is a drastic change in pore morphology as the materials transition from the formally defined polyMIPE regime to the polyHIPE regime. Specifically, we observed that the number of pore throats increases and there are minimal regions of non-porous crosslinked PDMS compared to materials prepared at lower volume fractions of dispersed phase in the emulsion template.

The results from mechanical testing using DMA are shown with total porosity in Fig. 3.

The storage moduli of the polyHIPEs increased with increasing PMVS content at a constant volume fraction of dispersed phase used in the emulsion template, as expected due to the higher crosslinking density resulting from the high vinyl-functionality of the polymer. For example, the storage moduli increased from ~100 kPa to ~850 kPa in polyHIPEs prepared at 60% volume fraction of the dispersed phase. As the volume fraction of the dispersed phase increases from 60%–85% the total porosity of the materials increases only when sufficient PMVS is present to provide the material with enough stiffness to prevent pore collapse. For example, in the 60% dispersed phase series, all materials achieve roughly 60% total porosity because divinyl-PDMS produces stiff enough materials to maintain this total porosity. In contrast, at volume fractions of the dispersed phase over 60%, the polyHIPEs crosslinked with only divinyl-PDMS (stars in Fig. 3) produced materials possessing lower porosities relative to the volume fraction of the dispersed phase in the emulsion template. The porosity of the polyHIPEs increases as PMVS content increases in polyHIPEs prepared from emulsion templates with higher than 60% volume fraction of dispersed phase. For example, the polyHIPEs prepared with 85% volume fraction dispersed phase range from 58% porosity to 77% porosity. This is because at least 0.75 molar equivalents of PMVS with respect to thiolated-PDMS are required for reproducible materials (85D0-V100 and 85D25-V75 in Fig. 3) Taken together, all the polyHIPEs prepared in this study retain their elastic properties, despite the increased crosslinking in these samples compared to ones prepared with only divinyl-PDMS, and remain softer than polyHIPEs made from styrenic monomers at similar porosities [26–30]. Overall, this represents an expansion of available materials properties for PDMS polyHIPEs using this system, where the limit on total porosity has been increased from ~62% to ~ 77%. This now means that formally-defined *poly(HIPEs)* rather than only *poly(MIPEs)* with open cell pore structures are achievable with this synthesis route. Furthermore, the porosities of our materials are approaching the porosities recently observed in closed-cell PDMS polyHIPEs [16,17,31].

It is known that hydrophobic porous polymer materials have the ability to separate oil from water [32–35]. Therefore, we investigated the ability of our materials to separate oil from water, we expect that this may have potential uses in oil remediation applications. We chose polyHIPEs prepared using 85D0-V100, 85D50-V50, 60D0-V100, and 60D100-V0 formulations, and tested their oil sorption capacity by placing them in containers at room temperature that contained a mixture of either white paraffin oil, vacuum pump oil, or commercial PDMS oil in water. We chose these formulations to test the dependency of the oil uptake on both porosity and flexibility of the polyHIPEs. An example of the separation behavior using the 85D0-V100 sample is shown with static images in Fig. 4, and the absorption results of each oil is are presented in Fig. 5.

In all cases, the porous PDMS foams could uptake ~3 g oil per 1 g of polyHIPE on the first use, and then ~1.5 g per 1 g material throughout

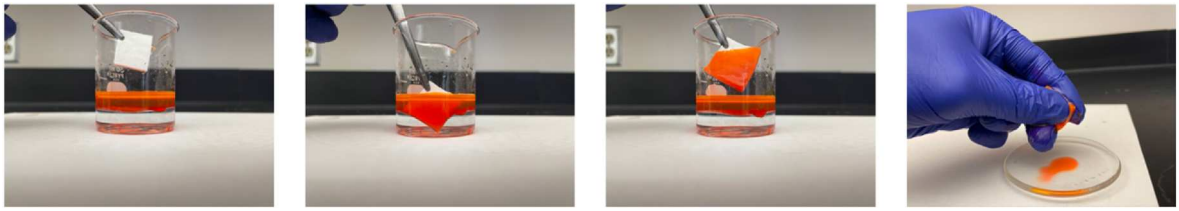


Fig. 4. Representative images of the oil absorption behavior of a pristine PDMS polyHIPE. The white paraffin oil was dyed with Nile red for clarity. Left to right: PolyHIPE before being immersed in the oil/water mixture; polyHIPE wicks up the oil; polyHIPE after being partially filled with oil; polyHIPE being squeezed and releasing the oil. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

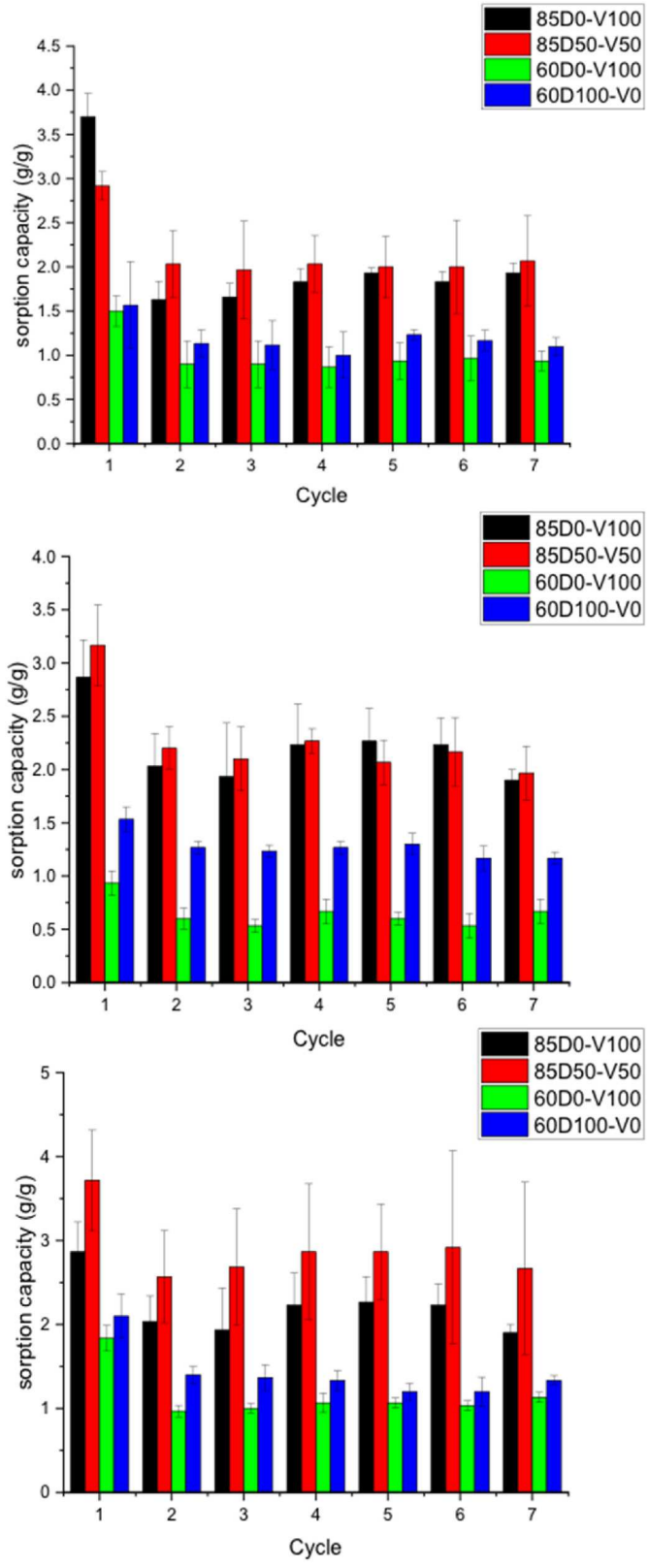


Fig. 5. Uptake capacity of 85D0-V100, 85D50-V50, 60D0-V100, and 60D100-V0 polyHIPEs vs cycle for (top) paraffin oil, (middle) pump oil, and (bottom) PDMS oil.

the next 6 cycles. This initial loss in uptake capacity may be a result of some oil becoming trapped in the polymer network and unable be squeezed out or washed away [36]. However, the material maintains the ability to uptake oil and release it under compression. Further, the sorption capacity was reached within 5 min in all cases suggesting a quick adsorption rate.

The results in Fig. 5 show that the more porous polyHIPEs possess higher uptake capacities. Furthermore, we observed a slightly increased uptake capacity for more flexible materials. Considering this, combined with more flexible polyHIPEs being more resilient to cracks forming during squeezing the oils out of the materials, the optimal choice for oil separation applications appear to be those that are more flexible with the highest porosity.

4. Conclusions

We have demonstrated the ability to prepare highly porous, open-cell, PDMS polyHIPEs possessing actual porosities of over 74%. This has been achieved by preparing a polysiloxane possessing pendant-vinyl functional groups rather than vinyl-groups at the chain-ends as used in our previous work. This has the result of increasing the crosslinking density in the PDMS network and preventing pore collapse at higher porosities. PolyHIPEs with storage moduli ranging from ~20 kPa to 850 kPa are able to be prepared by changing the ratio of polysiloxanes used in the continuous phase and volume fraction of the dispersed phase in the emulsion template. We anticipate multiple applications for these PDMS-based polyHIPEs including as acoustic materials and potential biomedical uses. Furthermore, we showed that these materials can efficiently separate 2–3 times their own weight of oil from water repeatedly without the loss of their sorption capacity, meaning they could be used in oil remediation applications.

CRediT authorship contribution statement

Anthony Smith: Methodology, Investigation, Writing – original draft, Visualization. **Neil Ayres:** Conceptualization, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2023.125787.

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