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# Inflatable Elastomeric Macroporous Polymers Synthesized from Medium Internal Phase Emulsion Templates

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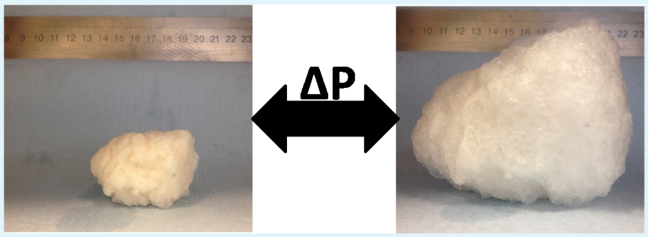
Supporting Information



**ABSTRACT:** Closed cell elastomeric polydimethylsiloxane (PDMS) based polymerized medium internal phase emulsions (polyMIPEs) containing an aqueous solution of sodium hydrogen carbonate ($NaHCO_3$) have been produced. Via thermal decomposition of $NaHCO_3$, carbon dioxide was released into the polyMIPE structure to act as a blowing agent. When placed into an atmosphere with reduced pressure, these macroporous elastomers expanded to many times their original size, with a maximum expansion of 30 times. This expansion was found to be repeatable and reproducible. The extent of volume expansion was determined primarily by the dispersed phase volume ratio of the emulsion template; polyMIPEs with 60% dispersed phase content produced greater volume expansion ratios than polyMIPEs with 50% dispersed phase. Increasing the concentration of $NaHCO_3$ in the dispersed phase also led to increased expansion due to the greater volume of gas forming within the porous structure of the silicone elastomer. The expansion ratio could be increased by doubling the agitation time during the emulsification process to form the MIPEs, as this decreased the pore wall thickness and hence the elastic restoring force of the porous silicone elastomer. Although MIPEs with 70% dispersed phase could be stabilized and successfully cured, the resultant polyMIPE was mechanically too weak and expanded less than polyMIPEs with a dispersed phase of 60%. It was also possible to cast the liquid emulsion into thin polyMIPE films, which could be expanded in vacuum, demonstrating that these materials have potential for use in self-sealing containers.

**KEYWORDS:** *PolyHIPE, macroporous polymer, elastomer foam, emulsion templating, inflatable foam*

## 1. INTRODUCTION

Emulsion templated macroporous polymers are produced by the polymerization of the continuous phase of an emulsion with the emulsion droplets acting as templates for macropores within the polymers. Emulsion templates are characterized by their internal phase volume ratio; high (HIPE), medium (MIPE), and low internal phase emulsions (LIPE), which have internal phase volume ratios of above 70%, between 70 and 30%, and below 30%, respectively.[1] After polymerization of the emulsion templates they are known as poly(merised)HIPEs, polyMIPEs, and polyLIPEs, respectively, and their porosity is largely determined by the internal phase volume ratio of the emulsion templates.[2] Commonly, these macroporous polymers are synthesized from water-in-oil emulsion templates;[3] however, oil-in-water emulsions[4,5] have been used, too, as have emulsions with ionic liquid[6] or supercritical carbon dioxide internal phases.[7] Multiple emulsions can also be used to create macroporous beads.[8] Emulsion-templated macroporous polymers are often open celled, having appreciable permeability due to the breakdown of the polymer walls in between the droplets (which become pores upon removal of the template phase) during[9] or after polymerization.[10] These openings in the pore walls we call pore throats. Much research has been carried out on polyHIPEs because their high porosity and open celled nature allows for flow-through applications.[11−13] Moreover, many emulsion templated macroporous polymers are rigid and brittle; however, elastomeric versions have been created by the use of flexible monomers.[14,15] Potential applications for emulsion templated macroporous polymers include fluid separation,[16] such as chromatography,[17] filtration,[18] membranes,[14,19,20] emulsion breaking,[21] and adsorbents.[22−24] PolyHIPEs have also been explored as structural materials,[25] scaffolds to support cell growth,[26] bone grafts,[27] electrodes,[28] and supports for chemical reactions.[12,29]

This being said, our work reports the synthesis of closed-celled silicone elastomer polyMIPEs based on polydimethylsiloxane (PDMS). Grosse et al.[30] previously prepared open-celled PDMS-based polyHIPEs to be used for the detection of benzenic pollutants. We explored the synthesis of closed celled elastomeric polyMIPEs, which contain a blowing agent in the dispersed phase that can be activated subsequent to polymerization to expand the porous polymer structure many times its

**Received:** June 10, 2015
**Accepted:** August 6, 2015
**Published:** August 6, 2015

DOI: 10.1021/acsami.5b05123
ACS Appl. Mater. Interfaces 2015, 7, 19243−19250

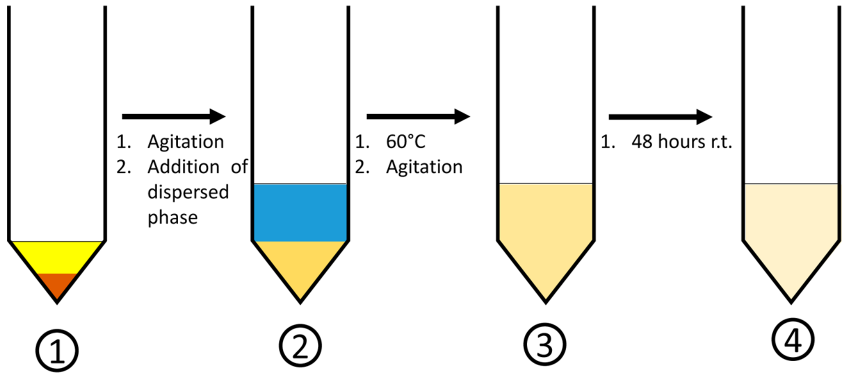


**Figure 1.** Schematic of polyMIPE production. (1) Addition of continuous phase consisting of surfactant and Sylgard 184 silicone base and hardener followed by agitation until homogeneous then addition of $NaHCO_3$ solution dispersed phase (blue). (2) Heating both phases to 60 °C to reduce viscosity of the continuous silicone phase then agitation to form emulsion. (3) MIPE template then left to cure for 48 h. (4) Fully cured PolyMIPE material.

original volume. This could have potential uses in structures such as self-sealing vessels or puncture resistant materials.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** PDMS in the form of Sylgard 184 silicone elastomer kit (containing base and hardener), Rhodorsil silicon oil 47 and sodium hydrogen carbonate ($NaHCO_3$) were purchased from VWR. Nonionic polymeric surfactant Hypermer 2296 (HLB = 4.9) was kindly supplied by Croda (New Castle, DE). Sunflower oil was purchased from Tesco. Hydrophobic pyrogenic silica particles HDK H20 were kindly provided by Wacker Chemie AG (Germany). All materials were used as received.

**2.2. Preparation of Macroporous Silicone Elastomers.** The continuous phase of all emulsion templates consisted of 4 mL Sylgard 184 silicone base, 0.5 mL Sylgard 184 hardener and 0.5 mL Hypermer 2296 was filled in to 50 mL polypropylene centrifuge tubes (Fisherbrand) and briefly agitated using a vortex mixer (Vortex-Genie 2) at the maximum setting until it was homogeneous (Figure 1). To this a volume of 5 mL, 7.5 or 11.7 mL dispersed phase of an aqueous solution of sodium hydrogen carbonate ($NaHCO_3$) was added to create emulsions with 50, 60, and 70% dispersed phase, respectively. The concentrations of $NaHCO_3$ in the aqueous phase were 30, 50, and 70 g $L^{-1}$ (0.36, 0.60, and 0.83 mol $L^{-1}$), respectively.

The centrifuge tube was then transferred to a water bath heated to 60 °C for 2 min to decrease the viscosity of the continuous phase to enable emulsification. The mixture was then agitated using a vortex mixer at the maximum setting for 45 or 90 s to produce an emulsion. The resulting emulsions were allowed to cure for 48 h at room temperature.

After curing, the polyMIPE samples were removed from the centrifuge tube and placed in a convection oven at 70 °C for 45 min to thermally decompose $NaHCO_3$ and release carbon dioxide. The porous silicone was more easily handled when coated with silica particles to prevent unwanted adhesion to surfaces.

**2.3. Polymer Morpology.** Cryo-Scanning Electron Microscopy (SEM; Hitachi S-3400N) was used to image the polyMIPE structures before expansion. The polyMIPEs were frozen in a liquid nitrogen slusher before a vacuum transfer system was used to insert them into a sputter coater connected to the SEM. The sample was fractured with a knife, mounted in the wall of the chamber, to coat the surface to be inspected with gold. Then, the sample was transferred into the main chamber and imaged (beam voltage 15.0 kV, working distance 16.4 mm).

**2.4. Quantification of Expansion Ratio of Porous Silicone Elastomers.** PolyMIPE samples of known volume (from the sum of the emulsion components; 50% dispersed phase volume = 10 mL, 60% dispersed phase volume = 12.5 mL and 70% dispersed phase volume = 16.7 mL) were placed at the bottom of a measuring cylinder, which was filled with sunflower oil. A mesh was then fitted into the cylinder to ensure the sample remained fully immersed in the oil (Figure 2). The measuring cylinder was then placed into a vacuum oven (at room temperature), which was evacuated to a reduced pressure of 10 mbar, causing the sample to expand and the liquid level to rise. The change in volume was read from the measuring cylinder. Repeated cycles of depressurization and pressurization where carried out to determine the average volume increase.

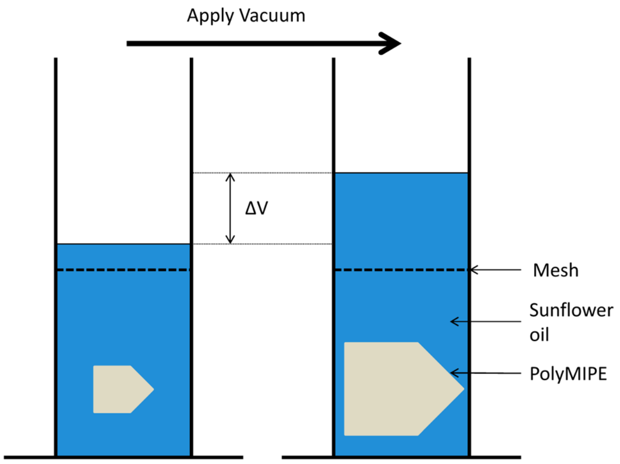


**Figure 2.** Measurement of the expansion of emulsion template macroporous elastomers under reduced pressure.

The extent of expansion was calculated using eq 1:

$$\text{average increase in volume} = \frac{V_{\text{init}} + \Delta V}{V_{\text{init}}} \quad (1)$$

where $V_{\text{init}}$ is the initial volume of the polyMIPE and $\Delta V$ the volume change during expansion under vacuum.

**2.5. Dynamic Mechanical Analysis of PolyMIPEs.** PolyMIPE samples with a diameter of 25 mm and a height of 11 mm were tested using Dynamic Mechanical Analysis (DMA, RSAG2, TA Instrument, Germany) in compression to assess their mechanical properties. Oscillated compression of the samples was carried out between 0 and 10% applied strain in the frequency range from 0.1 to 20 Hz at a set temperature of 25 °C. The storage, loss modulus, and tan $\delta$ were recorded. The DMA tests had to be preformed in compression as it was impossible to load these soft samples otherwise.

## 3. RESULTS AND DISCUSSION

**3.1. Production of Macroporous Silicone Elastomers.** A silicone elastomer was chosen because of its elasticity and the ability to cure at room temperature. Aqueous sodium hydrogen carbonate ($NaHCO_3$) solution was chosen as internal phase because it stabilizes the emulsion,[31,32] acts as blowing agent and is simple to use. $NaHCO_3$ in aqueous solution undergoes thermal decomposition eq 2 above 50 °C releasing carbon dioxide. This allows for the continuous silicone phase to fully cure before the carbon dioxide is released ensuring it is contained within the macroporus structure of the poly(silicone)MIPE.

$$2NaHCO_3 \xrightarrow{T > 50\,^\circ C} Na_2CO_3 + H_2O + CO_2 \qquad (2)$$

During the emulsification, the size of the vortex produced in the centrifuge tube decreased with time until it disappeared, which is consistent with the increase in viscosity occurring during the production of concentrated emulsions.[33] The emulsion templates were very stable and underwent no noticeable phase separation between emulsion formation and curing of the silicone. This is in part due to the emulsion cooling from 60 °C to room temperature leading to a significant increase in the viscosity of the continuous phase, which in turn resulted in an increased stability of the emulsion.[34] Prior to heating the emulsion to 60 °C the continuous phase was too viscous to allow emulsification of the aqueous phase. A stable emulsion could not be formed if no $NaHCO_3$ was present in the dispersed phase likely due to the salt acting to increase the surfactant affinity to the interface.[31] Under these emulsion formulation and templating conditions, no stable emulsion with an internal phase percentage above 70% could be formed. A stable MIPE containing 70% internal phase could be produced but this required a high $NaHCO_3$ concentration of 70 g $L^{-1}$ in the dispersed phase and an agitation time of 90 s. Negligible $NaHCO_3$ decomposition was observed during the agitation despite the elevated temperature (60 °C). After curing, the resulting macroporous silicone elastomer was very flexible and had the texture of a marshmallow. When the elastomer was removed from the centrifuge tube, the surface was very tacky.

The structure of the polyMIPEs is typical of an emulsion templated polymer with individual pores created around the template of emulsion droplets (Figure 3). Many of these frozen droplets can still be seen in place, their diameters are between 2 and 8 $\mu$m. We found no evidence for the formation of pore throats, indicating the structure is close celled. This allows for the entrapment of carbon dioxide released into the macroporous elastomer by the decomposition of $NaHCO_3$ in the dispersed phase.

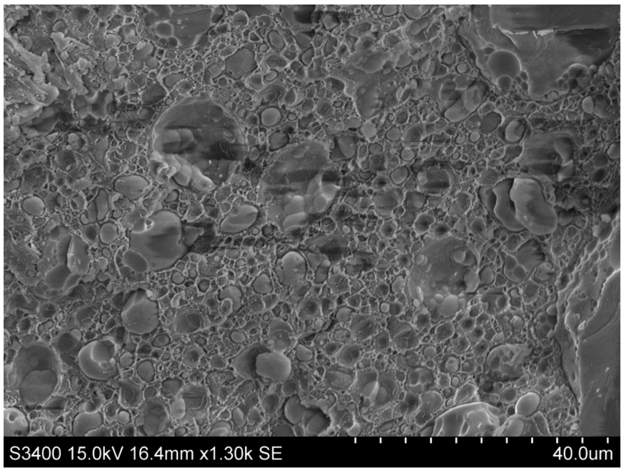


**Figure 3.** Characteristic cyroSEM image of poly(silicone)MIPEs produced from an emulsion template with 50% internal phase volume ratio containing 30 g $L^{-1}$ $NaHCO_3$ solution, agitated for 45 s.

### 3.2. Expansion of Emulsion Templated Silicone Elastomers in Vacuum.

After the $NaHCO_3$ decomposed at elevated temperatures (70 °C), gas could be seen trapped in large bubbles at the very surface of the macroporous polymers (Figure 4b), but no bulk expansion was observed. This is due to the carbon dioxide released by the decomposition of the $NaHCO_3$ remaining in solution due to the high pH of the resulting sodium carbonate solution (≈ pH 12) and the closed-celled nature of the polymer inhibiting escape of the gas. The pores at the very surface did expand as the polymer exerted a lower elastic restoring force than the polymer, enclosing the pores in the bulk macroporous silicone. The $NaHCO_3$ present in polyMIPEs 1, 5, 9, and 13 was not thermally decomposed so we could investigate whether the polyMIPEs would expand without trapped carbon dioxide present—they served as control samples. When placed into a reduced pressure atmosphere, the polymers expanded significantly in size, with a possible increase in volume well over an order of magnitude. Upon repressurization to atmospheric pressure, the polymer rapidly returned to its original size. On the first expansion, the pockets of gas trapped at the surface of the polymer burst open, giving the surface a rougher texture compared to the monolith before thermal decomposition of the $NaHCO_3$ (Figure 4a,c).

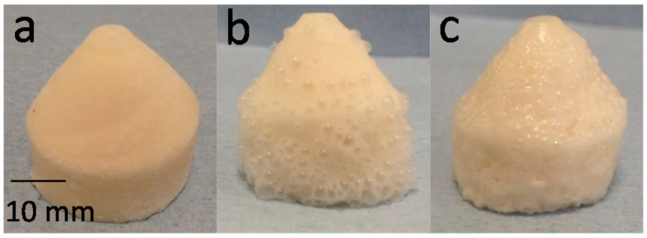


**Figure 4.** Photographs of poly(silicone)MIPE produced from an emulsion template with 50% internal phase volume ratio containing a 70 g $L^{-1}$ $NaHCO_3$ solution (Sample 4) (a) after curing and removal from a 50 mL centrifuge tube, (b) after heating to 70 °C for 45 min to decompose $NaHCO_3$ in aqueous solution, and (c) after an expansion cycle in vacuum under sunflower oil.

It was possible to produce stable water-in-silicone MIPEs and cure them when only 5% surfactant was used in the continuous phase. However, this resulted in a macroporous silicone elastomer, which did not undergo significant expansion in vacuum (less than doubling in size). However, when 10% surfactant was used to stabilize the water-in-silicone MIPEs followed by curing them into macroporous silicone elastomers, a massive expansion in vacuum was observed. It is known that surfactants do act as plasticizers[35,36] in polyHIPEs, decreasing the surfactant content used to stabilize the emulsion template resulted in an increase of the elastic modulus of the synthesized polyHIPEs. In analogy, in the case of the macroporous silicones, a decrease of the expansion under reduced pressure was observed with decreasing surfactant content.

Significant expansion was not observed until the pressure dropped below 200 mbar. Below this threshold pressure, rapid expansion occurred. It was only at these low pressures that the force exerted by the expanding encapsulated gas was able to overcome the elastic restoring force of the silicone elastomer in the polyMIPEs structure. Expansion continued until an equilibrium point was reached where the pressure of the entrapped gases was equal to tensile stress exerted by the polyMIPE structure. By repeatedly (20 times) expanding and contracting the polyMIPE structure by cycling the pressure, the final (original and expanded) volumes of the structure were found not to change with each cycle, as can be seen by the magnitude of the standard deviation in Table 1. Upon reaching the full expanded volume under reduced pressure (≈ 10 mbar), gas bubbles began to be released into the sunflower oil from the polymer structure, indicating that damage to the pore structure was occurring.

Table 1. MIPE Template Formulations and Preparation Conditions and Increase in Volume in Vacuum

| sample | dispersed phase vol (%) | agitation time (s) | $[NaHCO_3]$ in the dispersed phase ($g\ L^{-1}$) | av increase in volume (inflated vol/original vol) |
|---|---|---|---|---|
| 1 | 50 | 45 | 30[a] | 3.7 ± 0.3 |
| 2 | | | 30 | 6.8 ± 0.3 |
| 3 | | | 50 | 9.0 ± 0.0 |
| 4 | | | 70 | 13.0 ± 0.0 |
| 5 | | 90 | 30[a] | 4.2 ± 0.3 |
| 6 | | | 30 | 9.7 ± 0.4 |
| 7 | | | 50 | 14.3 ± 1.6 |
| 8 | | | 70 | 20.3 ± 0.0 |
| 9 | 60 | 45 | 30[a] | 3.8 ± 0.0 |
| 10 | | | 30 | 17.8 ± 0.0 |
| 11 | | | 50 | 21.3 ± 0.9 |
| 12 | | | 70 | 23.1 ± 0.5 |
| 13 | | 90 | 30[a] | 4.3 ± 0.2 |
| 14 | | | 30 | 20.1 ± 1.1 |
| 15 | | | 50 | 26.1 ± 0.4 |
| 16 | | | 70 | 30.0 ± 1.4 |
| 17 | 70 | 90 | 70 | 15.5 ± 0.2 |

[a] Undecomposed.

From Figure 5, it is clear that expansion is homogeneous (Figure 5, image a to b and image c to d); the closed celled structure of the polyMIPE expanded evenly maintaining the original shape of the monolith. Large gas bubbles were seen to form throughout the structure when fully expanded. These large bubbles are of similar dimensions to each other and are clearly separated by a layer of silicone elastomer. The polyMIPEs containing 50% dispersed phase more closely maintained their original shape both during and after expansion than those produced with 60% dispersed phase (both originally had the shape shown in Figure 4a before expansion). This can be seen clearly in Figure 5c where the sample (60% internal phase) collapsed to some extent, compared to Figure 5a (50% internal phase), which well maintained its original shape after four expansion cycles. It should be noted that this loss of shape did not affect the maximum expanded volume of these polyMIPEs.

The expanded size of the polyMIPEs (calculated from eq 1) depends on both the dispersed phase volume ratio in the emulsion template, the concentration of $NaHCO_3$ in the dispersed phase and the agitation time used to prepare the MIPE template (Table 1). The extent of the volume expansion increased with increasing dispersed phase volume ratio and higher $NaHCO_3$ concentration, and agitation time, i.e. the energy input into the MIPE template prior to curing. However, the overriding dependence is clearly the dispersed phase percentage of the emulsion template. An increase of the dispersed phase volume ratio of the MIPE from 50 to 60% significantly increased the extent by which the polyMIPE

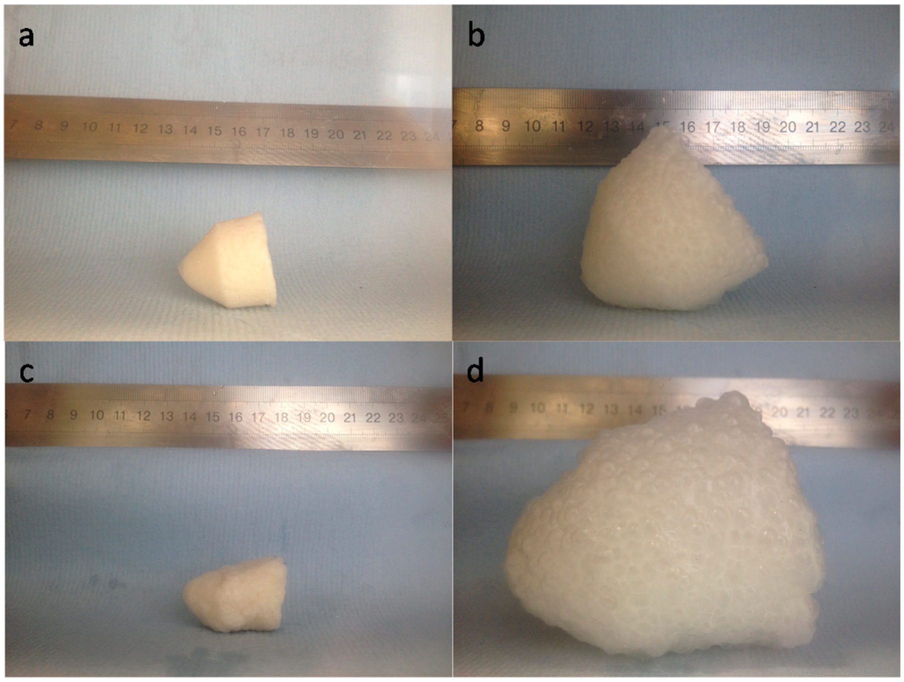


Figure 5. (a and b) Photographs showing polyMIPE 2 synthesized by curing a MIPE with 50% dispersed 30 $g\ L^{-1}$ $NaHCO_3$ phase produced by 45 s agitation at atmospheric pressure and under reduced pressure, respectively. (c and d) Photographs showing polyMIPE 12 synthesized by curing a MIPE with 60% 70 $g\ L^{-1}$ $NaHCO_3$ dispersed phase produced by 45 s agitation at atmospheric pressure and in a reduced pressure environment, respectively. Both polyMIPEs shown underwent four expansion cycles under reduced pressure.

monolith expanded in a reduced pressure atmosphere. This is due to a decrease in the elastic restoring force of the polymer walls, separating the encapsulated liquid droplets in the polyMIPE monolith, required to be overcome by the entrapped gases. This is because an increase in the internal phase volume results in thinner pore walls. Moreover, increasing the amount of $CO_2$ that is released due to the increase in $NaHCO_3$ solution volume resulted in an increased gas volume entrapped in the pores that could expand and perform work on the polyMIPE. A maximum expansion of just under 30 times the original volume was observed for polyMIPEs produced from a MIPE containing 60% 70 g $L^{-1}$ $NaHCO_3$ solution prepared by 90 s agitation. This equates to a polyMIPE originally with 60% dispersed phase transitioning to a macroporous polymer with 98.6% dispersed phase.

Increasing the agitation time of the emulsion templates from 45 to 90 s, which were subsequently cured into polyMIPEs resulted in an increase of their volume expansion in vacuum (Table 1); increasing the agitation time and, therefore, the energy input during emulsification resulted in a decrease of the droplet size in the emulsion template,[37] this in turn will result in thinner pore walls in the polyMIPEs.[38,39] These thinner pore walls in the produced macroporous silicone elastomers are more easily stretched by the expanding gases under reduced pressure leading to the greater expansion observed.

The polyMIPEs 1, 5, 9, and 13, which still contained the 30 g $L^{-1}$ aqueous solution of $NaHCO_3$ originally used as dispersed phase, expanded but to a much lesser extend in a reduced pressure environment than polyMIPEs 2, 6, 10, and 14, which were produced by curing MIPEs with an identical internal phase but the dissolved $NaHCO_3$ entrapped in their pores after curing was thermally decomposed to release $CO_2$. Expansion in this case must have been caused by the reduced pressure causing the water present within the pores to partly boil. Even without thermal decomposition of the $NaHCO_3$ it was still observed that both increasing the dispersed phase volume ratio in the emulsion template and the longer agitation time increased the volume expansion of polyMIPEs under reduced pressure.

A linear dependence between volume expansion and the $NaHCO_3$ concentration in the dispersed phase before thermal decomposition was observed. This is unsurprising, as a higher $NaHCO_3$ concentration in the encapsulated aqueous phase within the macroporous silicone elastomer will result in more $CO_2$ being released and trapped inside the pore structure. It is interesting to note that the average volume increase of silicone elastomer polyMIPEs is more rapid for those polyMIPEs produced from a 60% emulsion template compared to those made from a MIPE containing 50% internal phase as the $NaHCO_3$ concentration increases (shown graphically in the Supporting Information, Figure S1). This again suggests that the increased agitation of the MIPE template, which was subsequently cured into the macroporous elastomers, resulted in polyMIPEs with thinner and, therefore, more flexible pore walls that responded to a greater extent to the introduction of more $CO_2$ by increasing the $NaHCO_3$ concentration.

An attempt was made to produce a polyMIPE (sample 17) from an emulsion template with a dispersed phase volume ratio of 70%. This could only be achieved when the agitation time of the MIPE template was increased from 45 to 90 s. The resulting polyMIPE was fragile and could not easily be removed from the mold without causing significant tearing damage to the (internal) structure of the polyMIPE (Figure 6). Despite this damage, the polyMIPE was still able to undergo a significant volume expansion and remain expanded under reduced pressure. The polyMIPE volume increased over 15 times, and the structure did not deflate under reduced pressure, suggesting that the pores remained intact and are closed celled. However, this expansion is much lower than expected (due to the tearing damage to the pore structure) from the trends observed for polyMIPEs containing 50 and 60% internal aqueous $NaHCO_3$ solution. This proves that these polyMIPEs possess indeed truly closed celled structures.

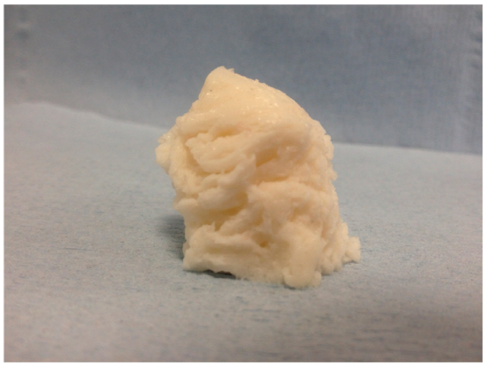


**Figure 6.** Damaged polyMIPE produced by curing an MIPE template with 70% internal phase (sample 17) after removal from the mold. Compare this polyMIPE to the polyMIPE monoliths produced by curing MIPEs with an internal phase of 50 and 60% (Figure 3).

Once the $NaHCO_3$ was thermally decomposed, it was possible store the polyMIPEs on the benchtop for over a month and to retain the ability to expand the polyMIPEs in a reduced pressure environment. However, when the polyMIPEs are exposed to reduced pressure for a period of 24 h a significant loss of $CO_2$ and water vapor did occur. In this case when atmospheric pressure was restored the polyMIPE collapsed due to the loss of carbon dioxide and water from within the structure.

**3.3. Mechanical Properties of Emulsion Templated Silicone Elastomers.** DMA analysis showed that the storage modulus, a measure of elastic energy stored, measured in compression as a function of frequency at 25 °C of the polyMIPEs decreased with increasing dispersed phase percentage (Figure 7). The tests were performed at constant temperature to avoid phase transitions and expansion of the aqueous internal phase. The storage modulus increased with increasing test frequency as expected as the polymer network has less time to respond to the applied load. The discontinuities in the storage modulus−frequency plots occur in multiple runs but are shifted to higher frequencies are probably caused by structural rearrangement of aqueous phase filled pores within the samples. Please note that the compression storage moduli of the macroporous elastomers are about 10 times larger than those of monolithic PDMS materials because the aqueous phase entrapped in the pores acts as incompressible inclusion within the porous elastomer. Nevertheless, it becomes apparent that increasing the internal phase volume results in a decrease of the storage moduli, explaining why the polyMIPEs produced from template emulsions with 60% internal phase expanded more than those produced from template emulsions with 50% internal phase. It also explains the damage to sample 17 upon removal from the mold, as it had an extremely low modulus. The samples produced with 45 s of agitation had moduli similar to those of samples produced with 90 s of agitation.

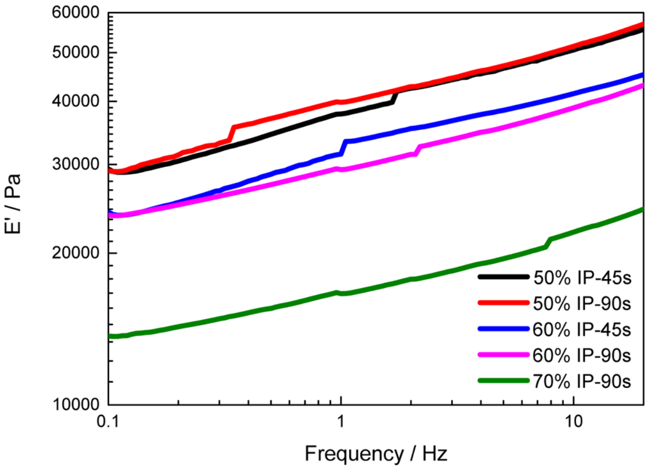


**Figure 7.** Storage modulus ($E'$) as a function of compression frequency for polyMIPEs. The legend refers to the internal phase percentage (IP) and the template emulsion agitation time. The $NaHCO_3$ concentration of the dispersed phase for all samples was 30 g $L^{-1}$, with the exception of the sample with 70% internal phase percentage, which had a dispersed phase concentration of 70 g $L^{-1}$.

### 3.4. Demonstration of the Self-Sealing Potential of Inflatable Macroporous Silicone Elastomers.

A pressure-sensitive inflatable elastomer could potentially be used to create self-sealing pressure vessels, such as airplane fuel tanks or cabins, which operate in a reduced pressure environment. If a thin layer of an inflatable polymer were sandwiched between two container walls, then the polymer would expand and seal any potential leak in the event of the structure being penetrated. To test this hypothesis, we formed a MIPE with 60% dispersed phase containing 70 g $L^{-1}$ $NaHCO_3$ in the dispersed phase using the method described in section 2.2. However, the MIPE was then poured out of the centrifuge tube and allowed to cure between two aluminum plates 2 mm apart. This created a flexible polyMIPE film that, after decomposition of the $NaHCO_3$ dissolved in the aqueous phase, was able to expand in reduced pressure.

Decomposition of the $NaHCO_3$ was carried out after removal of the film from between the aluminum plates. This resulted in the formation of many surface bubbles (similar to those in Figure 4b), which caused the polymer film to curl. These bubbles burst upon first expansion, leading to a loss of carbon dioxide. The macroporous elastomer seemed to expand isotropically, and its side length increased from 65 to 120 mm (Figure 8a,b).

To demonstrate the potential of an elastomeric expandable polyMIPE for use in self-sealing vessels, we placed the film back in between the aluminum plates with a thin coating of Rhodorsil on the aluminum to act as a lubricant. The edges of the plates where glued together. A 5 mm hole was then drilled through both plates and the polyMIPE film sandwiched between the plates. Under reduced pressure (≈ 10 mbar), the polyMIPE film expanded, blocking the 5 mm hole so that no light could be seen through it (Figure 8c). The polyMIPE film expanded gradually as the pressure slowly dropped in the vacuum oven, the process would be more rapid if the polyMIPE film was instantaneously exposed to a low-pressure environment. Upon repressurization to atmospheric pressure, the polyMIPE film retracted, thereby unblocking the hole.

The potential of expandable, emulsion-templated macroporous elastomers for use in self-sealing fuel tanks could be further improved if the dispersed phase were replaced with supercritical carbon dioxide such that volume expansion would occur at atmospheric pressure rather than reduced pressure. In this case, puncturing the fuel tank would cause the polymer to expand rapidly, sealing any damage and, therefore, preventing significant fuel loss.

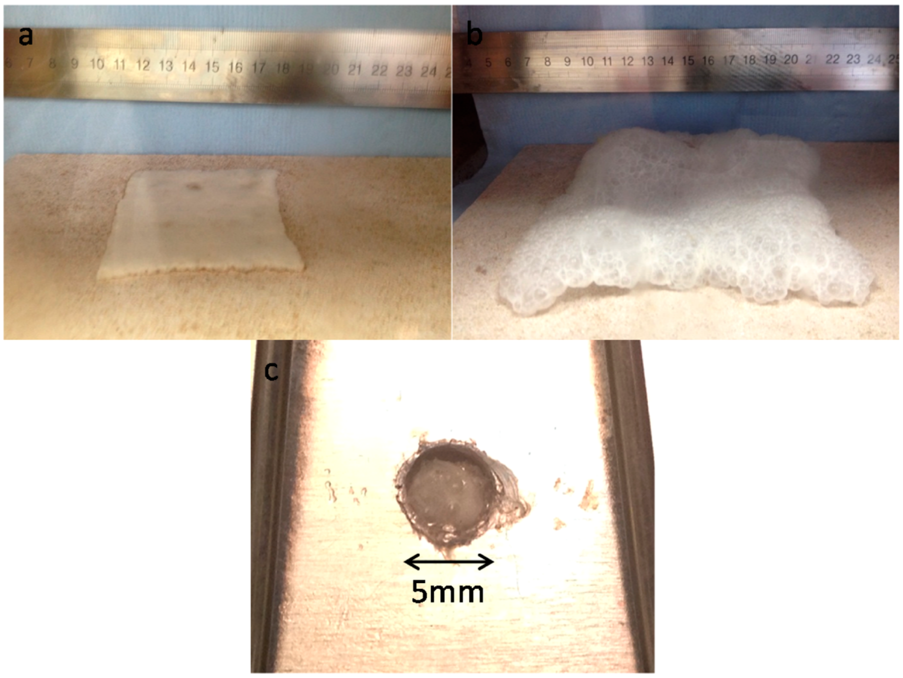


**Figure 8.** Expansion of a silicon elastomer polyMIPE film in vacuum: (a) the film at atmospheric pressure and (b) the film under vacuum. (c) The film between two aluminum sheets expanded to block a 5 mm bore hole.

## 4. CONCLUSION

We demonstrated that it was possible to create macroporous, closed-celled silicone elastomers (polyMIPEs) from water-in-PDMS MIPEs containing a $NaHCO_3$ solution in their macropores. By thermally decomposing the $NaHCO_3$ dissolved in the encapsulated aqueous phase to release carbon dioxide, it was possible to expand the polyMIPEs (but only in a reduced pressure atmosphere) to many times their original volumes, with a maximum of 30 times the original size. The polyMIPE structure was confirmed by cyroSEM.

PolyMIPEs created from emulsion templates with dispersed phase percentages of 60% were found to expand significantly more than those produced by curing MIPE templates containing dispersed phase percentages of 50% due to their thinner pore walls reducing the elastic restoring force to be overcome by the expanding gas. Increasing the entrapped carbon dioxide content by increasing the concentration of $NaHCO_3$ in the aqueous internal emulsion phase also increased the expansion. Increasing the time of agitation of the emulsion template from 45 to 90 s created smaller pores in the original polyMIPEs; these pores were separated by thinner pore walls, which also led to an increased expansion ratio. It was possible to create an emulsion template with 70% dispersed phase; however, once cured the polyMIPE was mechanically very weak and expanded to a lesser extend under reduced pressure than the polyMIPEs containing lower dispersed phases percentages due to damage caused by removing it from the mold. Expansion of the polyMIPEs was found to be repeatable; however, prolonged exposure to vacuum caused a significant gas loss. Such PolyMIPEs can be produced in the form of monoliths and thin flexible films.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b05123.

> Increase in volume of silicone elastomer polyMIPEs under reduced pressure as function of $NaHCO_3$ concentration in the dispersed phase before thermal decomposition (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors would like to acknowledge a Doctoral Trainee Award of the UK Engineering and Physical Sciences Research Council (EPSRC) for funding M.T. and the FP7 project MATFLEXEND (Grant # 604093) for funding Q.J. We thank Dr. Ruth Brooker and Dr. Judith Thei for their CryoSEM expertise.

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DOI: 10.1021/acsami.5b05123
*ACS Appl. Mater. Interfaces* 2015, 7, 19243−19250