

CONSTRUCTION OF A 3-D DROPLET ARRAY IN A METABOLIC ELASTOMER

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Summary: *This article reviews our experiments on flexible liquid-solid composites that use polydimethylsiloxane elastomer as a host matrix. A metabolic self-healing function was realized by dispersing nonpolar toluene uniformly in the matrix for enhancing the molecular diffusivity. Polar methanol created microspheres that yielded laser emission. A composite with a 3-D droplet array was fabricated by using an ultrasonic trapping method.*

1 INTRODUCTION

Liquids exhibit various useful functions that are unattainable with solids. Handling difficulty, however, restricts uses of liquids in components and devices. Construction of a liquid-solid composite is therefore essential for creating a stable material that exhibits an excellent function of a liquid. Host-guest composites are usually fabricated with rigid materials (glasses, ceramics, and polymers), whereas useful characteristics of liquids are generally based on fluidity or deformability. Excellent functions are therefore spoiled by enclosing a liquid in a solid matrix.

Polydimethylsiloxane (PDMS) rubbers provide a suitable matrix for solving this problem. As Fig. 1 shows, PDMS rubbers are transparent polymers that consist of long molecules [1]. These molecules originally take a liquid phase and yield viscous oil. When a curing agent is added to this oil, the molecules are bridged with one another, creating a flexible network or a rubber. As regards a PDMS rubber that we used in the current experiments, this curing process is complete in 8 h after mixing a raw liquid (oil) and a curing agent (Shin-Etsu Chemical, KE-103) [2]. This simple solidification process is advantageous for attaining a uniform dispersion of various molecules, e.g., drugs and dyes, since their solution is readily mixed with the raw liquid. In addition the curing (bridging) reaction requires neither heating nor ultraviolet irradiation that possibly damages the functional molecules. Another important advantage is that the curing process accompanies no phase transition from liquid to solid; i.e., although PDMS apparently changes from liquid (oil) to solid (rubber), little change takes place in physical properties (volume, density, compressibility, sound velocity, etc.). In other words, the PDMS rubber macroscopically acts as a solid matrix, although it microscopically acts like a liquid (solvent). These features are useful when creating metabolic composites (Section 2) and droplet arrays (Sections 3 and 4). In this article, we first summarize our research on liquid-solid composites and demonstrate their useful functions (self-healing of damaged molecules and tuning of laser emission). Then we describe a novel ultrasonic technique for creating a 3-D droplet array in a PDMS composite.

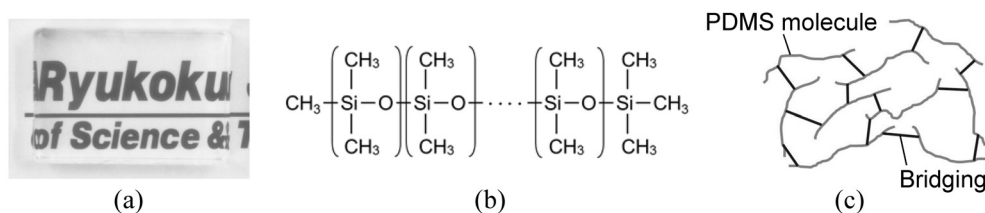


Figure 1: (a) Photograph, (b) molecular structure, and (c) molecular network of a PDMS rubber.

2 METABOLIC LIQUID-SOLID COMPOSITES

A flexible network structure of PDMS rubbers creates a large free volume in which solvents and solutes stay or circulate. Diffusion coefficients of various molecules are therefore higher in PDMS rubbers than other materials (polymers, glasses, and crystals) [3–5]. Figure 2(a) shows a process of toluene diffusion into a PDMS rubber. Toluene was colored with a dye (dicyanomethylene) for visualization and then poured on a PDMS rubber in a glass vessel (20 mm diameter). The toluene solution on the rubber top (the dark portion) decreased in volume as it penetrated into the rubber (12 h later), while the rubber got colored gradually from the upper portion to the bottom. The entire rubber was colored uniformly in 60 h, and the rubber top expanded upward forming a dome.

Medical doctors use this phenomenon for drug delivery [6, 7]. Drugs like chloroform and steroid, for example, are delivered to a diseased part continuously for a few months by dispersing them in a PDMS rubber; i.e., drugs diffuse in the rubber and leak out slowly from the surface. This phenomenon is also useful in technical fields to develop a metabolic material that self-heals a deteriorated function by substituting fresh molecules for damaged ones. Figure 2(b) shows a scheme of the metabolic material, taking a laser medium as an example [8]. Although organic dyes are used widely as a light emitter, they occasionally suffer a photochemical damage by a strong laser beam, which leads to a short lifetime of organic dye lasers. If dye molecules are dispersed in a PDMS rubber with a large volume, damaged molecules in the operation region (fluorescence region) are replaced by fresh molecules in the surrounding region (reservoir).

We measured diffusion coefficients by using photochromic diarylethene as a tracer. This dye takes two different molecular states (isomers); i.e., one is transparent and the other exhibits red color due to green light absorption. When exposed to violet light, the transparent isomer turns to red. Conversely the red isomer is decolored when it is exposed to green light [8, 9]. Both isomers are stable enough at room temperature, and hence, no color change takes place without light irradiation. This coloration phenomenon is useful to trace the molecular diffusion process. Figure 3(a) illustrates a sample that we used for observing the diffusion

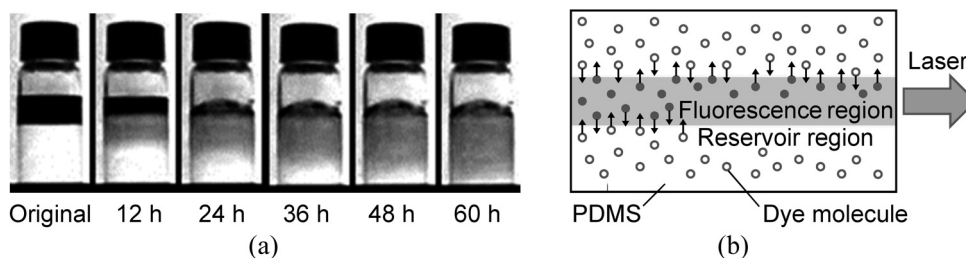


Figure 2: (a) Penetration of a toluene solution (the upper dark portion) into a PDMS rubber (the lower transparent portion). (b) Schematic illustration of molecular metabolism in PDMS [8].

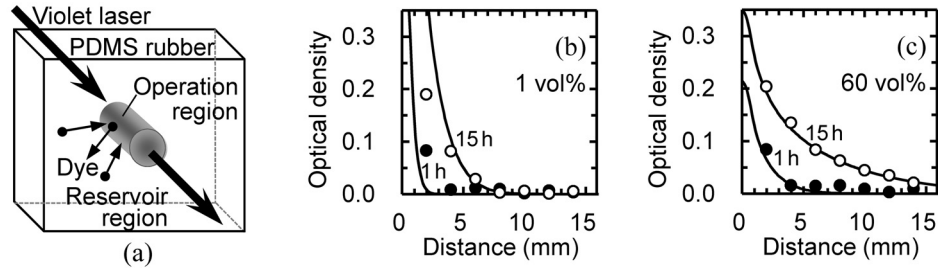


Figure 3: (a) Diffusion of dye molecules in a PDMS rubber. (b), (c) Distributions of colored molecules in PDMS rubbers that contained 1 or 60% toluene. The circles show optical densities that were measured at 1 or 15 h after start of coloration. The lines show theoretical values.

process. Diarylethene (Tokyo Kasei Kogyo, B1535) was dispersed uniformly in a PDMS rubber at a concentration of 10^{-4} mol/l. This PDMS rubber (3 mm thickness) contained 1-vol% toluene to avoid aggregation of diarylethene molecules. The entire sample was first exposed to green laser (532 nm wavelength) for decoloration of the dye. Then a violet laser beam (405 nm) of 1.5 mm diameter was irradiated on the sample center. Consequently, the central portion of the PDMS rubber turned to red, since an absorption band appeared at around 530 nm wavelength. This colored portion expanded gradually as colored molecules diffused outward. Figure 3(b) shows distributions of the optical density (absorbance at 530 nm) that corresponds to the number of colored molecules. The horizontal axis shows the distance from the irradiation point. When 1 h passed from the start of laser irradiation (●), colored molecules still stayed within ~ 2 mm from the irradiation point. The colored portion, however, expanded to ~ 6 mm radius in 15 h (○). The concentration of colored molecules (c), which is a function of radius r and time t , follows Fick's law; i.e.,

$$\partial c / \partial t = -D \operatorname{div}(\operatorname{grad} c), \quad (1)$$

where D is a diffusion coefficient. We calculated $c(r, t)$ by assuming various D values and drew fitting curves for the measured values. As the lines in Fig. 3(b) show, the best fitting was attained when the diffusion coefficient was assumed to be $0.0001 \text{ mm}^2/\text{s}$.

We tried to attain a higher diffusion coefficient by swelling a PDMS rubber with toluene. PDMS oil was mixed with toluene (60 vol%) in a glass cell, and then a curing agent was added to this mixture. Although toluene slowed down the curing reaction, solidification was complete in 24 h at room temperature. (The solidification process became faster by heating the mixture.) The toluene-PDMS composite that was prepared in this manner was transparent in the visible spectral range. The diffusion coefficient in this composite was evaluated by using a sample in which diarylethene was dispersed uniformly before the solidification process. As the circles in Fig. 3(c) show, expansion of the colored region became faster by increasing the toluene content. The measured values were fitted well by theoretical curves when the diffusion coefficient was assumed to be $0.0015 \text{ mm}^2/\text{s}$. This diffusion coefficient was 15 times larger than that in the original PDMS rubber.

This toluene-PDMS composite was used to fabricate a metabolic optical device. Diarylethene, which was used as a tracer in the above experiment, is useful for fabricating all-optical switches that control optical signal transmission by using another optical signal [10, 11]. Figure 4(a) shows transmission spectra of a PDMS rubber containing diarylethene (10^{-4} mol/l) and toluene (1 vol%). As the gray lines show, an absorption band grows on the occasion of violet laser irradiation and disappears by green laser irradiation. Although this photochromic process is reversible at the beginning, the color change becomes faint after the

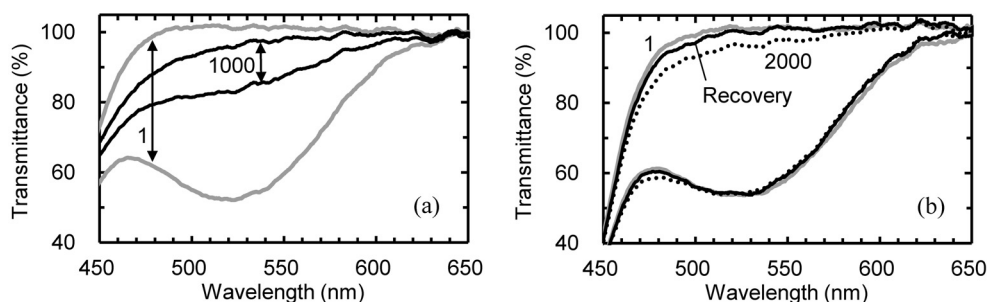


Figure 4: (a) Transmission spectra of a photochromic PDMS rubber in the transparent and colored states. The gray and black lines show spectral changes at the first and 1000th cycle, respectively. (b) Improved photochromic reactions in a metabolic toluene-PDMS composite. The black spectra were measured 1h later after finishing 2000 photochromic cycles [8, 11].

coloration-decoloration process is repeated about 1000 times, as shown by the black lines in Fig. 4(a). This degradation is attributed to photobleaching of diarylethene by the laser irradiation. The lifetime of organic devices is generally shorter than that of inorganic devices, since, as this example shows, organic materials exhibit poor durability against thermal or photochemical damages. The high diffusivity of the toluene-PDMS composite seems useful to avoid such degradation. Figure 4(b) shows photochromism of diarylethene (10^{-4} mol/l) in the composite with 60-vol% toluene. The original transmission spectra (the gray lines) changed little even after the coloration-decoloration process of 2000 cycles (the dotted lines). A slight decrease in transmittance recovered when the sample was preserved in darkness for 1 h (the black lines). This improved durability was induced by circulation of dye molecules.

3 DROPLET-ELASTOMER COMPOSITES

As described in Section 2, toluene disperses uniformly in a PDMS rubber, filling and expanding nano-sized free volume between long molecules. By contrast, polar liquids like methanol and ethanol form droplets in PDMS oil owing to the surface tension. These droplets are fixed in the PDMS rubber after solidification. Figure 5(a) shows a droplet-elastomer composite that was prepared by curing a mixture of methanol and PDMS oil. Methanol was colored with a fluorescent dye (rhodamine 6G) for visualization. The droplet size ranged between 10 and 100 μm . These droplets, however, shrank gradually in a few days, as shown in Fig. 5(b). It was assumed that methanol diffused out of droplets leaving dye molecules behind. This shrinkage was healable by dipping the composite in methanol; i.e., shrunk droplets expanded again to the original size owing to methanol penetration. Droplets remained stable (no shrinkage), when a surfactant (Merck, Tween 20) was added to the mixed solution before solidification. The surfactant probably created a protection coating around droplets, as shown in Fig. 5(c), and prevented the diffusion of methanol.

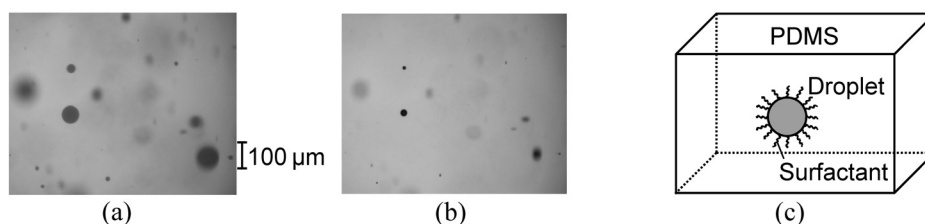


Figure 5: (a) Dye-doped methanol droplets in a PDMS rubber. (b) Droplet shrinking (darkening) due to methanol diffusion. (c) Stabilization of droplets by the use of a surfactant.

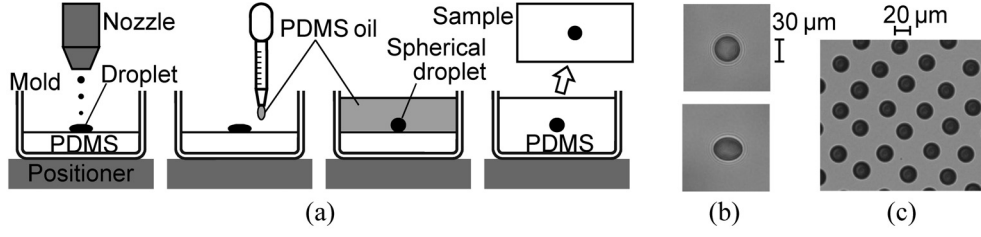


Figure 6: (a) Inkjet method for creating a droplet in a PDMS rubber. (b) Spherical droplet and its deformation during the rubber pressing process. (c) 2-D droplet array in a PDMS rubber [12].

Droplet size and arrangement were controllable by using an inkjet technique [12]. Figure 6(a) shows the fabrication process of the droplet-elastomer composite. A solution, e.g., methanol that contained dye and surfactant, is shot on a PDMS rubber (base) that has been cured in a plastic mold. The droplet volume (1–1000 p l) is adjustable by changing the shot number. Then PDMS oil with a curing agent is poured on the PDMS rubber. As the oil encloses the droplet, its shape changes from an ellipsoid to a sphere owing to the surface tension. The oil solidifies in 8 h and creates a uniform PDMS rubber together with the original rubber in the bottom. In this manner, a spherical droplet with a smooth surface is formed in the PDMS rubber. As Fig. 6(b) shows, this spherical droplet deforms into an ellipsoidal shape by pressing the rubber. Figure 6(c) shows a droplet array that was created in a PDMS rubber by shooting multiple droplets on the PDMS rubber (base) as it was moved on a motor-driven positioner.

Deformability of a droplet was examined by pressing the PDMS rubber. As Fig. 7(a) shows, the sample, 30×30 mm² in area and 10 mm in thickness (h_0), was sandwiched between two glass plates (on the top and bottom) for attaining uniform deformation. A droplet was observed through the glass plate by using a microscope. Figure 7(b) shows photographs of a droplet with an original diameter of $d_0=100$ μm. As the sample pressed in the vertical direction, the droplet expanded in the horizontal plane (the dotted lines in Fig. 7(a)). When the sample deformed by $\Delta h=2$ or 3 mm, the droplet diameter increased to 120 or 140 μm, respectively. Figure 7(c) shows a relation between the sample and droplet deformation. Regardless of the original droplet diameter ($d_0=80$ –120 μm), the expansion ratio ($\Delta d/d_0$) exhibited a similar dependence on the sample deformation ($\Delta h/h_0$). The reduction curve for these data points followed a quadratic equation; i.e.,

$$\Delta d/d_0 = 4 \times (\Delta h/h_0)^2. \quad (2)$$

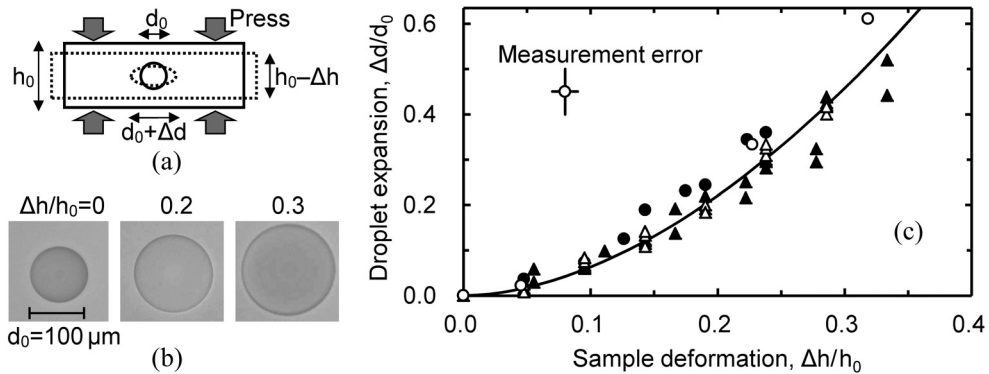


Figure 7: (a) Deformation of a PDMS rubber and a droplet. (b) Micrographs of an expanding droplet during a deformation process. (c) Relation of the rubber deformation and the droplet expansion. The original droplet diameter (d_0) is 80 (●), 90 (○), 100 (▲), or 120 μm (Δ) [17].

Let us consider the droplet deformation process on the basis of a simple theoretical model. The droplet volume is assumed to be unchanged during the pressure process, since the compressibility of liquids is too small ($<10^{-9} \text{ Pa}^{-1}$) to induce a volume change. If this is the case, a relation (conservation of the droplet volume)

$$(\pi d_0^3/6) = (\pi/6)(d_0 + \Delta d)^2(d_0 - \Delta z) \cong (\pi d_0^3/6)(1 + 2\Delta d/d_0 - \Delta z/d_0) \quad (3)$$

holds, where Δd and Δz denote diameter changes in the horizontal and vertical directions, respectively. Consequently, if the droplet deformation ratio $\Delta z/d_0$ is the same as the sample deformation ratio $\Delta h/h_0$, a relation

$$\Delta d/d_0 = (1/2) \times (\Delta z/d_0) = (1/2) \times (\Delta h/h_0) \quad (4)$$

is derived. The data in Fig. 7(c) follows Eq. (4) in the small pressure range ($\Delta h/h_0 < 0.1$). The droplet deformation ratio ($\Delta d/d_0$), however, becomes larger than this theoretical prediction, as the pressure increases. This fact indicates that droplets deform more heavily than the PDMS rubber because of difference in their compressibilities.

Dye-doped microspheres act as a microlaser in which fluorescence is amplified as it circulates along the periphery (the whispering gallery mode) [13, 14]. Although solid spheres (glasses and polymers) are usually used for creating microlasers, droplets have some advantages over them. One is a self-formation of a smooth surface, which is an important factor for reducing a scattering loss. Deformability is another advantage, since it realizes spectral tuning of the laser emission. In conventional studies, measurements were conducted with droplets that were floating in air or adsorbing on a glass plate [15, 16]. Droplets were therefore unstable and difficult to handle. PDMS rubber is a suitable solid matrix for fixing a droplet without spoiling deformability. Figure 8(a) shows fluorescence spectra of a dye solution and droplets. Sample solution was prepared by dissolving rhodamine 6G and a surfactant in methanol. As the gray line shows, an ordinary solution in a glass vessel emitted fluorescence in the 550–600 nm wavelength range when it was excited with a pulsed green laser (532 nm wavelength, 5 ns duration). By contrast, droplets exhibited comb-like fluorescence peaks, as shown by the black lines. The peak wavelength λ_m is generally determined so that its multiple coincides with the optical length of the droplet periphery; i.e.,

$$m\lambda_m = \pi n d \quad (m=1, 2, 3, \dots), \quad (5)$$

where n and d denote the refractive index and diameter of the droplet, respectively. A cluster of these resonant peaks appears at a wavelength range that depends on the droplet diameter. As Fig. 8(b) shows, fluorescence peaks of a droplet (100 μm diameter) shifted from the 580 nm range to the 600 nm range when it expanded to 130 μm during a pressure process [17].

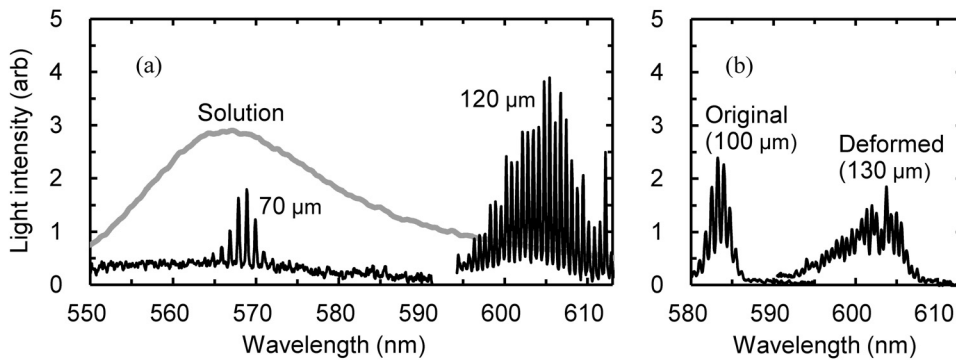


Figure 8: (a) Fluorescence spectra of a methanol solution and droplets (70 or 120 μm diameter) containing rhodamine 6G. (b) Spectral change by droplet deformation (100 $\rightarrow$ 130 μm) [17].

4 3-D DROPLET ARRAY

The inkjet method is useful to create a 2-D droplet array, as shown in Fig. 6(c). It is difficult, however, to create a 3-D array by using the inkjet method. We used an ultrasonic trapping method [18–20] to create a droplet-elastomer composite with a 3-D structure. Figure 9(a) illustrates an ultrasonic cell. Liquid (water) is contained in a glass cell whose ends are sealed with ultrasonic transducers. These transducers are driven by high-frequency electric signals and transmit ultrasonic waves of a frequency f (1–30 MHz). If the sound velocity is v , the ultrasonic wavelength Λ is

$$\Lambda = v/f. \quad (6)$$

In water ($v=1500$ m/s), for example, the ultrasonic wavelength is $500\text{ }\mu\text{m}$ at 3 MHz. If a multiple of the half wavelength coincides with the cavity length (cell length) L , i.e.,

$$L = k\Lambda/2 = kv/(2f) \quad (k=1, 2, 3, \dots), \quad (7)$$

a standing wave is generated between the transducers. Figure 9(b) shows temporal changes of the displacement and pressure distributions when the standing wave is generated. Water molecules ($\bullet$) vibrate right and left with a period $T(=1/f)$. The solid lines show the displacement of the water molecules. No vibration takes place at the nodes ($\uparrow$), while the amplitude becomes the largest at their midpoints (antinodes). By contrast, change of the pressure or the molecular density becomes the largest at the displacement nodes where molecules on the right and left move oppositely. Consequently, the displacement nodes become antinodes of pressure, as shown by the dotted lines. If particles are put into this standing wave, they vibrate with liquid molecules. At the same time, they shrink and expand owing to the pressure change. Bubbles (air particles) tend to aggregate at the displacement nodes, since vibration needs more energy than compression does. By contrast, solid particles require a large energy for compression, and hence, they aggregate at the pressure nodes. It is difficult to predict whether droplets act like solid particles or bubbles. In our experiment, droplets are usually trapped at the pressure nodes in PDMS oil.

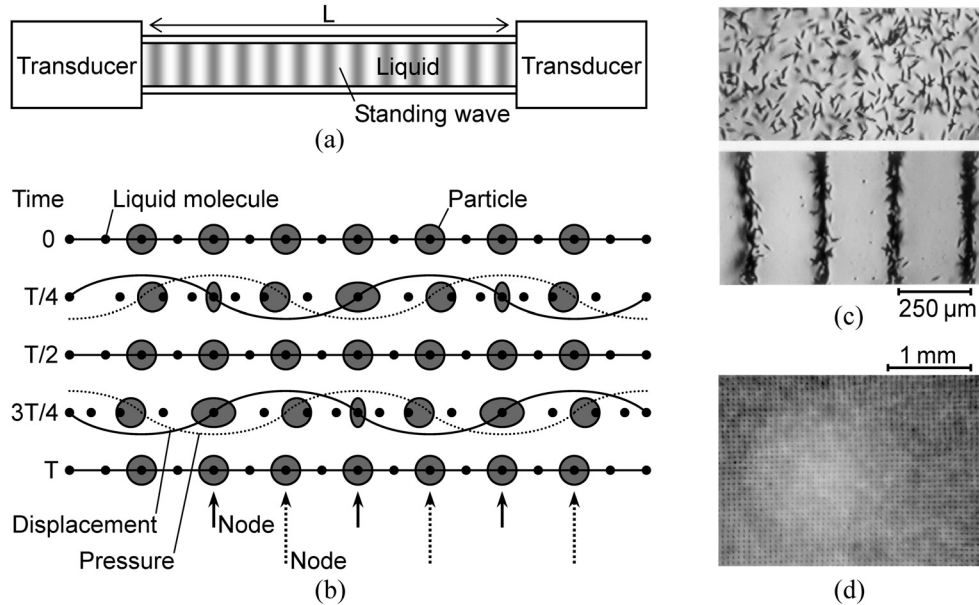


Figure 9: (a) Ultrasonic standing wave in liquid. (b) Vibration and deformation of particles in a standing wave. (c) Ultrasonic trapping of euglena that are swimming in water. (d) Composite of acrylic spheres ($10\text{ }\mu\text{m}$) and a PDMS rubber with a 2-D periodic structure [20–22].

Solid					Liquid		Solid/Liquid
Silicon	Silica glass	Iron	Ice	Polyethylene	Water	Ethanol	PDMS
8430	5970	5950	3200	1950	1500	1210	980

Table 1: Sound velocities (m/s) in various solids and liquids.

Figure 9(c) shows micrographs of euglena. As the upper photograph shows, they usually swim freely in water. When an ultrasonic standing wave of 3 MHz is generated, they are trapped at pressure nodes of 250 μm spacing, i.e., half wavelength $\Lambda/2$ [21, 22]. If ultrasonic standing waves are generated in both horizontal and vertical directions, particles are trapped at the intersections of the orthogonal nodal planes, creating a 2-D periodic arrangement. Anisotropic arrangement is attainable by changing the ultrasonic frequency depending on the direction. Various arrangement patterns (lattice structures) are also attainable by changing the direction of the ultrasonic waves. The particle arrangement, however, disappears when the ultrasonic wave transmission is stopped. One might think that particles can be fixed at trapped positions by freezing the liquid, but actually the arrangement is disturbed seriously during the solidification process, since the sound velocity changes notably by the phase transition; e.g. the velocity changes from 1500 to 3200 m/s when water freezes. PDMS is a suitable material from this viewpoint, since no sound velocity change occurs during the solidification process. In addition, the low sound velocity in PDMS is advantageous for creating a microstructure, since, as Eq. (6) shows, the particle spacing ($\Lambda/2$) becomes smaller as the sound velocity decreases. As Table 1 shows, sound velocities are generally larger in solids than liquids. PDMS rubbers exceptionally exhibit a smaller sound velocity than liquids. On the basis of these considerations, we fabricated a composite of acrylic spheres and a PDMS rubber [20]. A mixture of acrylic spheres (10 μm diameter), PDMS oil, and a curing agent was poured in a square cell. Two pairs of ultrasonic transducers that were attached to the cell sides generated two ultrasonic standing waves in the orthogonal directions. Ultrasonic frequencies for the two directions were adjusted independently at around 8 MHz so that the resonance conditions, i.e., Eq. (7), were satisfied. The ultrasonic wavelength at this frequency was $\Lambda=120$ μm . Consequently, the spheres were arranged periodically, constructing a lattice structure of 60 μm spacing. The ultrasonic wave transmission was continued for several hours until the PDMS solidified. Figure 9(d) shows a composite of acrylic spheres and the PDMS rubber that was fabricated in this manner.

When constructing this 2-D array, ultrasonic waves were transmitted in the horizontal plane and the trapping process was observed from the top. For constructing a 3-D array, all cell surfaces have to be enclosed by transducers, and hence, the inside of the cell is not observable. Microscopic observation from two orthogonal directions is indispensable to confirm 3-D arrangement. We therefore designed a novel ultrasonic apparatus. Figure 10(a) shows a piezo-electric transducer that was used in this experiment. This transducer consisted of a lead titanate zirconate (PZT) film and a high-frequency coupler (an electric circuit) for cable connection. The entire device was enclosed in a plastic box, and an ultrasonic wave was transmitted from its front surface (6 $\times$ 19 mm²). As Fig. 10(b) shows, three transducers were attached to three surfaces of a cubic cell (6 $\times$ 6 $\times$ 6 mm³). Two glass plates were attached to the front and top surfaces of the cell. A standing wave was generated between a transducer and the opposite glass plate, since the glass plate reflected ultrasonic waves. The remaining side of the cell was covered with a glass prism. This prism reflected an ultrasonic wave as well as deflected a light beam upward. Consequently, the inside of the cell was observable from both the top and side by using a microscope, as shown in Fig. 10(c).

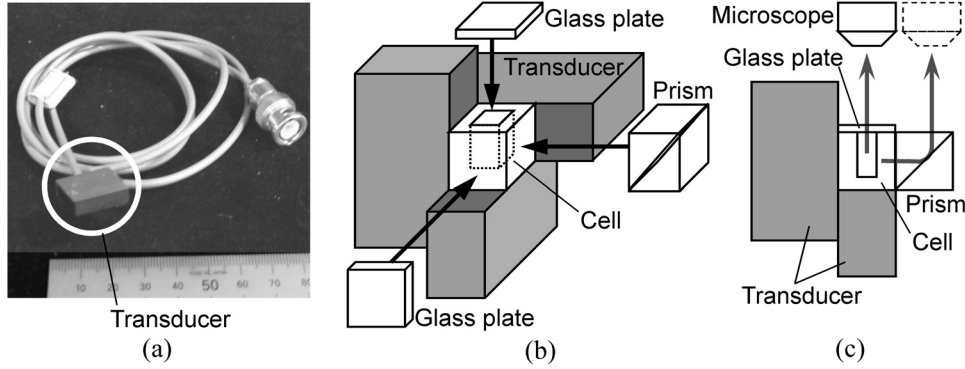


Figure 10: (a) Ultrasonic transducer with a vibration plane (front) of $6 \times 19 \text{ mm}^2$. (b) Apparatus for constructing a 3-D droplet array. (c) Droplet observation during the trapping process.

A sample cell for containing PDMS oil was made of PDMS rubber to avoid reflection of ultrasonic waves at the oil-rubber boundary. Otherwise, if a glass cell was used, both the inside and outside of the glass wall reflected ultrasonic waves, causing a disturbance of the standing-wave oscillation. A cavity of 2-mm square and 4-mm depth was created in this sample cell (outer dimension: 6-mm cube) by molding a PDMS rubber.

For fabricating a droplet-PDMS composite with a 3-D lattice structure, a mixing ratio of a solution and PDMS oil has to be determined suitably. A volume of a single droplet, V , is related to the droplet diameter d as

$$V = \pi d^3 / 6. \quad (8)$$

As Fig. 11(a) shows, the droplet volume increases rapidly as the diameter increases. If droplets are arranged with a spacing s , as shown by the inset in Fig. 11(b), each droplet occupies a volume of s^3 . The droplet concentration in the composite, q , is therefore

$$q = V/s^3 = (\pi/6)(d/s)^3. \quad (9)$$

With reference to Eq. (6), the spacing s is determined by the ultrasonic frequency as

$$s = \Lambda/2 = v/(2f). \quad (10)$$

From Eqs. (9) and (10), one has a relation

$$d = (6q/\pi)^{1/3} s = [3q/(4\pi)]^{1/3} (v/f). \quad (11)$$

Figure 11(b) shows the spacing and diameter that were calculated for droplet concentrations of 0.5, 1, and 5 vol%.

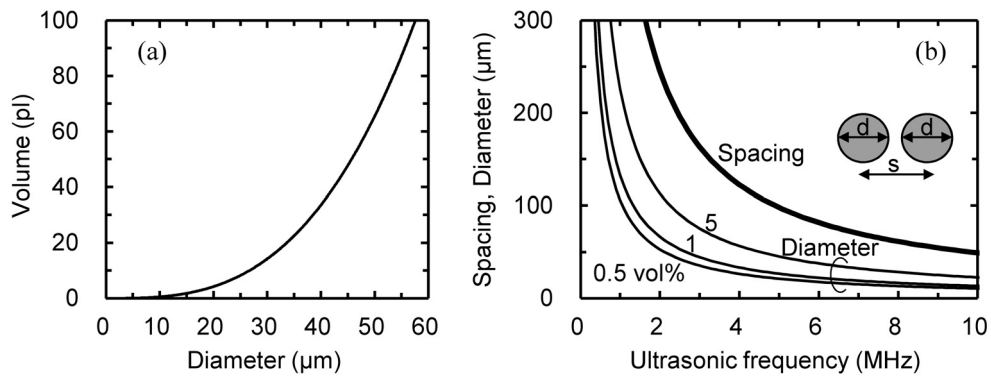


Figure 11: (a) Relation of the droplet diameter and volume. (b) Droplet spacing and diameter as functions of the ultrasonic frequency. Droplet concentration was assumed to be 0.5–5 vol%.

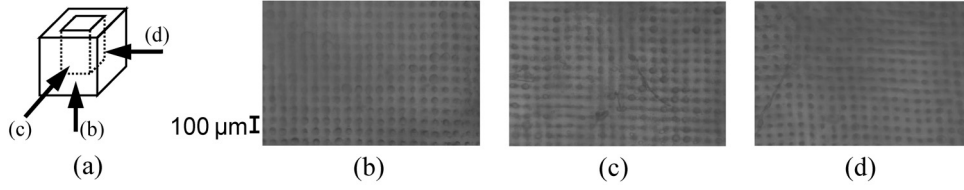


Figure 12: (a) Observation direction of the sample. (b)–(d) Micrigraphs of the droplet array.

On the basis of the theoretical prediction above, we fabricated a droplet-PDMS composite. The droplet concentration was set at $q=5$ vol% and the ultrasonic frequency was tuned at around 8 MHz, aiming at a droplet diameter of 20 μm and a period of 60 μm . As mentioned earlier (Fig. 5), a mixture of methanol and the surfactant (Tween 20) created stabile droplets. A preliminary experiment revealed that methanol tended to evaporate during the mixing and trapping processes if the methanol ratio was high in the mixture. The mixing ratio of methanol and the surfactant was therefore adjusted to 20:80 (in vol%). The mixture was colored with rhodamine 6G ($\sim 10^{-3}$ mol/l) for visualization. PDMS oil and a curing agent was put into a glass vessel, and then the mixed solution (methanol with the surfactant) was added at a concentration of $q=5$ vol%. After this oil-solution mixture was stirred well, it was poured into the sample cell shown in Fig. 10. As we observed the droplets through a microscope, we adjusted the ultrasonic frequency at around 8 MHz so that droplets were arranged periodically. The ultrasonic oscillation was continued for about 2 h until the solution became viscous enough. After stopping the oscillation, the sample was preserved for about 6 h to complete solidification.

The fabricated sample was taken out of the ultrasonic apparatus and observed from three directions, as shown in Fig. 12(a). Figure 12(b) shows a micrograph that was taken from the bottom. Droplets of 20–30 μm diameter were arranged at 60 μm period. As the microscope stage was raised gradually, i.e., as the focal plane was lowered, droplet lattices were observed every 60 μm movement. Figures 12(c) and 12(d) show micrographs that were taken from the sample side. These photographs confirmed formation of the 3-D droplet arrangement.

5 DISCUSSION

The ultrasonic trapping method was used for creating a 3-D droplet array in the current experiment. Although this method is advantageous for arranging a large number of droplets simultaneously, it can create only a uniform pattern. The inkjet method is more useful for creating a desired pattern, e.g., a cubic or rhombic lattice with a defect. Since a PDMS rubber can be cured layer by layer, a 3-D array may be constructed by lamination of a 2-D droplet array.

According to Eq. (10), the lattice period becomes smaller than 1 μm if the ultrasonic frequency is raised to 500 MHz. It is difficult, however, to generate a standing wave at such a high frequency, since the resonance (standing-wave excitation) is affected by a slight deviation of the cavity length or a thermal fluctuation of the sound velocity. A high-frequency transducer is also difficult to produce. Until now, our experiment was successful only in the frequency range below 30 MHz.

As Fig. 8 shows, a droplet exhibits fluorescence peaks that are caused by a resonance of circulating light. In addition to the resonance inside the droplet, the droplet array possibly causes a resonance between adjacent droplets. Both of these resonances are controllable by deforming the PDMS matrix. However, experiments on these phenomena are difficult to conduct with the current sample, since multiple droplets affect the measurement in a

complicated manner. We are currently considering a measurement method and devising a suitable sample structure for studying the interaction of these resonances.

6 CONCLUSION

Excellent functions of liquids can be utilized more effectively by constructing liquid-solid composites that improve disadvantages of liquids such as handling difficulty and instability. PDMS rubber is a useful host material that macroscopically act as a solid but microscopically function like a liquid. A toluene-PDMS composite exhibits a self-healable function owing to a high molecular diffusivity. A dye-doped droplet that is enclosed in a PDMS rubber acts as a micro-cavity laser. A 3-D droplet array can be constructed in a PDMS rubber by using an ultrasonic trapping technique.

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