

Powderization of Gallium–Indium Eutectic Alloy with Small Molecular Surfactants for Simple Preparation of Liquid Metal–Polymer Composites

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Abstract

Gallium-based liquid metals are promising materials for fabricating polymer composites with electrical and thermal conductivities because of their intrinsic deformability, accompanied by metallic properties. However, their high surface tension often prevents the easy preparation of uniformly dispersed composites. Herein, we propose the “powderization” method of the eutectic gallium–indium alloy by using a small-molecular dispersant, such as 1-dodecanethiol, affording powdery samples that are able to be treated like a solid-state powder. Mechanical shear forces can induce the recovery of the liquid metal bulk through the coalescence of the microparticles in the powdery samples. It is also demonstrated that several types of polymer composites based on these powdered liquid metals are prepared simply by manual mixing and exhibit stimulus-responsive electrical conductivity and microwave heating.

Introduction

Combination of polymers with inorganic fillers to create composites has been a versatile strategy for developing functional materials because it easily sophisticates material properties, such as mechanical,¹ thermal,^{2,3} and optical,⁴ properties. In particular, research on flexible conductive materials that take advantage of the flexibility of polymer materials by using conductive fillers has attracted a great deal of attention because of their potential versatility in wearable electronics and soft robotics.^{5,6} As for conductive fillers, a variety of inorganic materials such as metal particles, metal foils, carbon nanotubes, and graphene have been well researched.⁶⁻⁸ However, most of the conductive fillers tend to rigidify their composites and often lack mechanical properties such as stretchability and elasticity, resulting in the loss of the flexibility of the polymer matrix and hindering their applications.

To overcome this problem caused by the addition of conductive fillers to flexible matrices, liquid metals have been attracting attention as an alternative to such rigid fillers.⁹⁻¹³ Liquid metals are unique materials that are in a liquid state near room temperature while exhibiting metal-derived properties such as high electrical and thermal conductivity. Therefore, it is presumable that they could intrinsically accommodate the essential requirements of stretchable electronics. Among them, eutectic gallium-indium

alloy (EGaIn) has been widely utilized as a useful liquid metal filler because of its low melting point (15.5 °C), high electrical conductivity ($3.5 \times 10^6 \text{ S m}^{-1}$), negligible toxicity, and bio-compatibility.¹⁴⁻¹⁶ By using such gallium-based liquid metals, conductive composite materials have been developed with various functions such as pressure-induced conductivity,^{17,18} self-healing conductivity,^{18,19} high- κ dielectric,²⁰ and mechanical advantages like mechanically robust,²¹ and tunable rigidity.²²

However, one problem in preparing liquid metal-polymer composites is their low affinity for substrate materials.^{16,23} The large surface tension often makes it difficult to mix them uniformly in matrices. While these composites are typically created by mixing bulk liquid metals with polymer precursors or solutions using methods such as manual mixing, magnetic stirring, direct syringe injection, or ultrasonication,¹⁶ achieving uniform dispersion of liquid metal particles requires specific conditions based on the type of polymer matrix used, such as a prolonged mixing time and a highly viscous precursor. When liquid metals are dispersed in a polymer matrix through simple manual mixing, a sufficiently high viscosity of the polymer precursor or solution is necessary, as the liquid metal particles should sediment in mixtures with a viscosity that is too low.^[24] Additionally, controlling the size of liquid metal domains within the composites has been challenging.

In this context, one of the possible ways for solving those problems is “powderization” of the liquid metal. In this method, the bulk liquid metals are broken down to microparticles that are stabilized with dispersants and their oxide layers. Powderization makes it easier to handle liquid metals, resulting in the expansion of applications in materials. It has been reported that stable liquid metal-based “powder” (LMP) can be obtained by using polymer dispersants such as surface initiated polymerization²⁴ or block copolymers.^{25,26} However, the organic component in the previously reported LMP were typically more than 50 wt%, leading to the loss of the electrical conductivity of the liquid metals^{24,27} and undesired changes in properties of composites due to the dispersing agents. Although it was also reported that ultrasonication to EGaIn in water followed by freeze drying afforded solid-like EGaIn,²⁸ simple sonication in water typically often lead to an unstable suspension.²⁹ On the other hand, there are many reports about the preparation of micro- and nanoparticles in the form of suspension by applying ultrasonication in the presence of small molecular surfactants, like thioles,^{30–32} carboxylic acids,^{33,34} catechols,³⁵ amines,²⁹ phosphonic acids,³⁶ and phosphorothioates.³⁷ However, a powderization method has not been established using such small molecules. Therefore, there is still ample opportunity to develop a straightforward method for preparing uniformly dispersed liquid metal composites with significant electrical conductivity.

Herein, we demonstrate that small molecule-based dispersing agents are applicable for preparing LMP. We discovered that the LMP with 1-dodecanethiol is stable enough to be handled with a spatula. The content of its organic component in the LMP was about 0.25 wt%, which was much lower than that of the previous polymer-based LMP. As a result, the small molecule-based LMPs showed a stimulus-responsive property, *i.e.*, they returned from the powdery state to the liquid form upon applying mechanical forces. It is demonstrated that the prepared LMPs can be easily applied to fabricate electrically conductive composites with stimulus responsiveness and composite materials that are able to be heated by microwave irradiation.

Preparation of EGaIn microparticles (LMP)

The powderization method of EGaIn is illustrated as Figure 1a. Initially, to find appropriate dispersants for the powderization, EGaIn dispersions in ethanol were prepared by ultrasonication in the presence of various dispersants, such as trimethylolethane (**TME**), oleic acid (**OIAc**), 1-dodecanethiol (**DT**), oleylamine (**OIAm**), octylphosphonic acid (**OPA**), dodecylphosphonic acid (**DDPA**), octadecylphosphonic acid (**ODPA**), trioctylphosphine (**TOP**), and poly(acrylic acid) (**PAA**). Freshly prepared EGaIn was added to an ethanol solution of each dispersant and sonicated with a bath sonicator, resulting in the corresponding dispersion (**Disp-X**, X = dispersant; Figure 1b). As a control, the dispersion without any additional dispersant (**Disp-EtOH**) was also prepared the same method since it was reported that an EGaIn dispersant was also obtained in pure EtOH.³⁸ Next, the microparticles were collected as a powdery sample by the following two ways: (i) Centrifugation followed by decantation and drying under vacuum; (ii) washing with ethanol, solvent replacement with benzene, and then lyophilization under vacuum. Methods (i) and (ii) afforded block-like (**Block-X**, Figure 1c) and powdery samples (**LMP-X**, Figure 1d), respectively. Importantly, **Block-DT**, **Block-DDPA**, **Block-EtOH**, and **LMP-DT** were prepared in this study as the noticeable

amount of EGaIn bulk remained in the dispersions rather than **Disp-DT**, **Disp-DDPA**,
and **Disp-EtOH**.

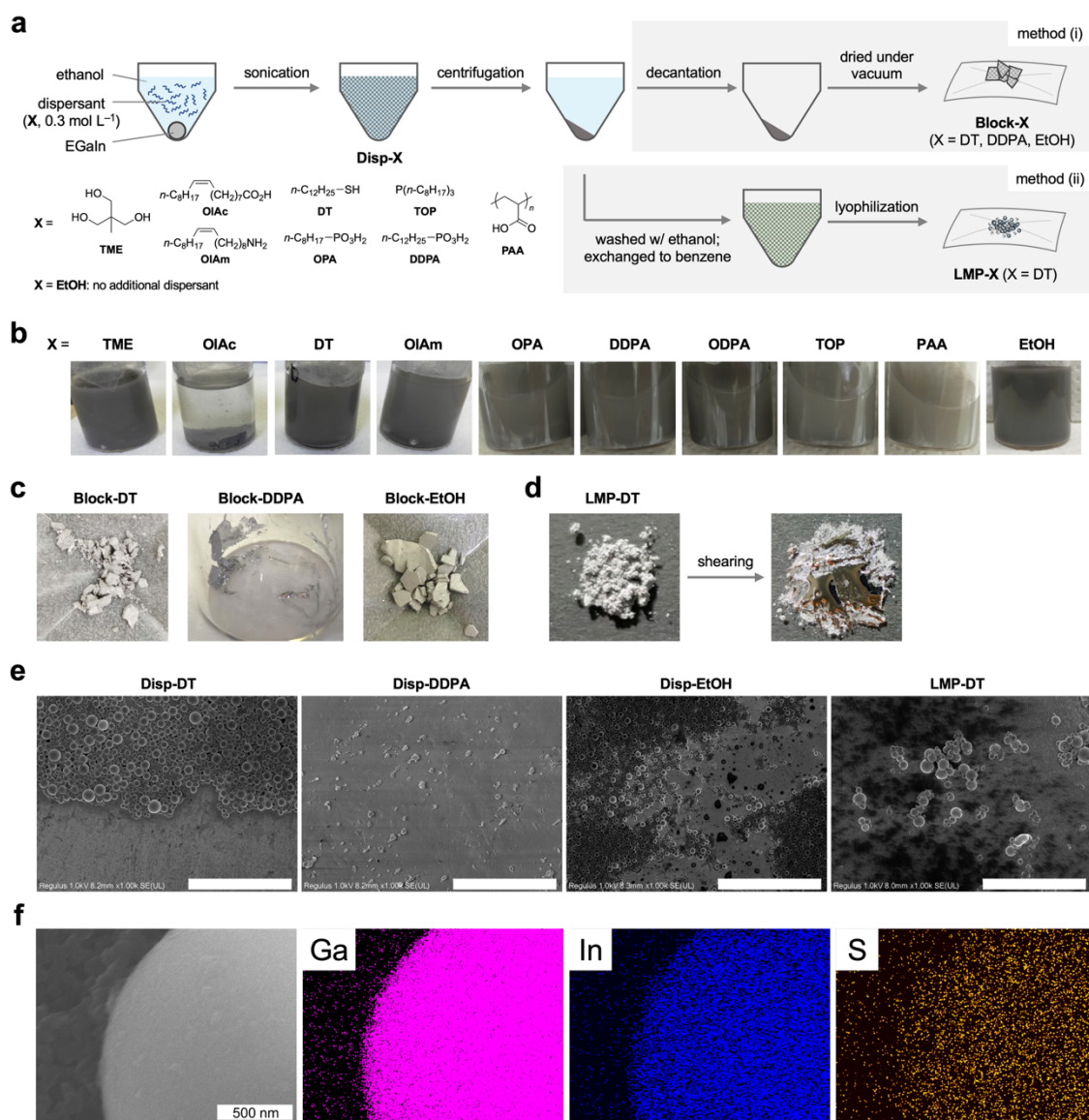


Figure 1. (a) Schematic illustration of powderization method of EGaIn. (b) Photographic images of dispersions with different dispersants. (c) Photographic images of **Block-DT**, **Block-DDPA**, **Block-EtOH**, and (d) **LMP-DT** before and after applying forces with a stainless spatula. (e) FE-SEM images of **Disp-DT**, **Disp-DDPA**, **Disp-EtOH**, and **LMP-DT**. Scale bar: 50.0 μ m. (f) EDX images of **LMP-DT**. Scale bar: 500 nm.

All dispersions looked gray but showed differences in the amount of remaining EGaIn in bulk (Figure 1b). **Disp-DT** and **Disp-DDPA** hardly exhibited apparent residual EGaIn bulk. On the other hand, in the other dispersions, a part of EGaIn remained as a bulk droplet even after the sonication time was extended for more than 1 h (Figure 1b). It is worth noting that a homogeneous dispersion of EGaIn was also obtained without a dispersant (**Disp-EtOH**). It was already reported that carbonized species (graphitic carbon layers) produced during sonication could serve as a stabilizer of EGaIn particles.³⁸ Therefore, we concluded that **Disp-DT**, **Disp-DDPA**, and **Disp-EtOH** were optimal for further investigation. The morphology and particle size of the microparticles in the dispersions prepared with and without dispersants were evaluated by field-emission scanning electron microscopy (FE-SEM, Figure 1e). Spherical microparticles with diameters ranging from 0.1 to 10 μm were observed from **Disp-DT** and **Disp-EtOH**, while relatively irregular shaped microparticles were produced from **Disp-DDPA**. From the SEM analysis, the average particle diameters of **Disp-DT**, **Disp-EtOH**, and **Disp-DDPA** were estimated to be 2.5 ± 1.1 , 0.84 ± 0.54 , and 2.0 ± 1.7 μm (mean $\pm$ standard deviation), respectively (Figure S3). In addition, the particle diameter of **Disp-DT** was also estimated to be 2.0 μm from laser diffraction analysis (Figure S4).

The properties of the solid-like block samples (**Block-DT**, **Block-DDPA**, and **Block-EtOH**) were tested qualitatively. All block samples were not lustrous and not electrically conductive, while metallic luster and electric conductivity was recovered by scraping, scratching, or pressing by a spatula. The mechanical stress should induce coalescence of the microparticles with the rupture of the oxide shell, resulting in recovering the EGaIn bulk. Such mechanical sintering of EGaIn-based materials has been reported previously.³⁹ Interestingly, their sensitivity to mechanical stimulus depended on the dispersants in the order of **Block-DDPA** > **Block-EtOH** > **Block-DT**. **Block-DDPA** was extremely sensitive to external stimulus and was difficult to handle with keeping it non-lustrous because a part of the block turned to a liquid when scraped with a spatula. The mechanical sensitivity of **Block-EtOH** was lower than that of **Block-DDPA**, while some of its similarly returned to a liquid form. In contrast, as **Block-DT** was relatively less sensitive, it was able to be treated like a solid-like substance. On the other hand, shear forces still induced the transition of **Block-DT** from the solid-like state to a liquid form like the others. These dispersant-dependent sensitivity to stimulus might originate from the difference in the shape of the primary particles. Their FE-SEM images revealed that the primary microparticles of **Block-DDPA** had a spiky shape, while those of the others were much spherical (Figure 1e). Therefore, it is implied that the primary microparticles of **Block-**

DDPA could be subjected to stronger forces than those of the other blocks when external force is applying. The lower roundness of the primary particles of **Block-DDPA** might stem from the thicker oxide film (Figure S5), which could prevent them from forming spherical structures.

The properties of **LMP-DT** were investigated. Instead of the direct drying employed in method (i), we applied lyophilization in method (ii) which is one of the robust methods for obtaining segregated microparticles as a powdery solid.^{40,41} The particles were washed three times with pure ethanol to remove excess **DT** that was not contributing to the stabilization of the microparticles. Subsequently, the solvent replacement with benzene was carried out for lyophilization. The resulting substance was able to be handled like a powdery solid with a flowability using a stainless spatula, as well as **Block-DT** (Figure 1d, Supplementary Movie 1). To the best of our knowledge, this is the first time that powdered EGaIn has been prepared with a small-molecule dispersant rather than polymeric dispersants. It should be emphasized that thermogravimetry analysis suggested that the amount of the organic component in **LMP-DT** was about 0.25 wt% (Figure S6), which was significantly smaller than that of the previously reported powdered EGaIn based on polymeric surfactants.^{24,25,27} Such a lower content of the organic component should be responsible for the easy recovery of the bulk EGaIn by small mechanical forces

(only the weight of a spatula, Supplementary Movie 1). FE-SEM images (Figure 1e) showed that the primary particles of **LMP-DT** were dispersed very well (primary particle size: $1.9 \pm 1.5 \mu\text{m}$), suggesting that weak interactions between the particles. Most importantly, **LMP-DT** required relatively stronger forces to turn to a liquid-like state than **Block-DT**, enabling us to handle it more easily. The more separated primary particles of **LMP-DT** might be key to its higher durability than **Block-DT** (SEM images of **Block-DT**: Figure S2). The elemental distribution in **LMP-DT** was studied using energy-dispersive X-ray (EDX) spectroscopy mapping attached with the FE-SEM (Figure 1f). The signal of sulfur derived from DT was co-localized with those of gallium and indium, suggesting that the dispersants worked as surface modifiers as previously reported.^{30,42} The thiol molecules could interact with the surface metal species because it is known that the S–Ga bond is formed during the surface modification of gallium with 4-mercaptopyridine by using ultrasonication.⁴³

It is worth mentioning that the powdered EGaIn materials prepared in this study were stable under ambient conditions on the order of months. In addition, the powdered samples were able to be transformed into the bulk EGaIn state even after they were immersed in water and subsequently dried under vacuum.

Application to Electrically Conductive Composites

Block-DT was applied to the preparation of LM–polydimethylsiloxane (PDMS) composite materials bearing electrical conductivity. Composites **Block-DT/PDMS-x** ($x = 20$ and 80), consisting of 20 and 80 wt% of **Block-DT**, respectively, were prepared (Figure 2a). Initially, **Block-DT** was re-dispersed in chloroform by bath sonication. Then, the solution was uniformly cast onto a PTFE petri dish. After vacuum drying, PDMS precursor and a curing agent were added and stirred using a spatula. Finally, the mixture was heated at $225\text{ }^{\circ}\text{C}$ for 30 minutes on a heating plate to make a composite. In addition, as-prepared bulk EGaIn was also used for making **EGaIn/PDMS-20** and **-80** instead **Block-DT**.

The cross-sectional images of **Block-DT** and **EGaIn/PDMS-80** showed that the EGaIn particles were dispersed more uniformly for the former sample (Figure 2b). In **EGaIn/PDMS-80**, there were apparently two layers, *i.e.*, EGaIn-rich opaque one and PDMS-rich transparent one. When EGaIn is mixed directly in a PDMS precursor, the EGaIn particles should be large and settle to the bottom of the dish during the curing process. Meanwhile, the microparticles of EGaIn in **Block-DT/PDMS** should be small enough to be kept dispersed until the crosslink is completed.

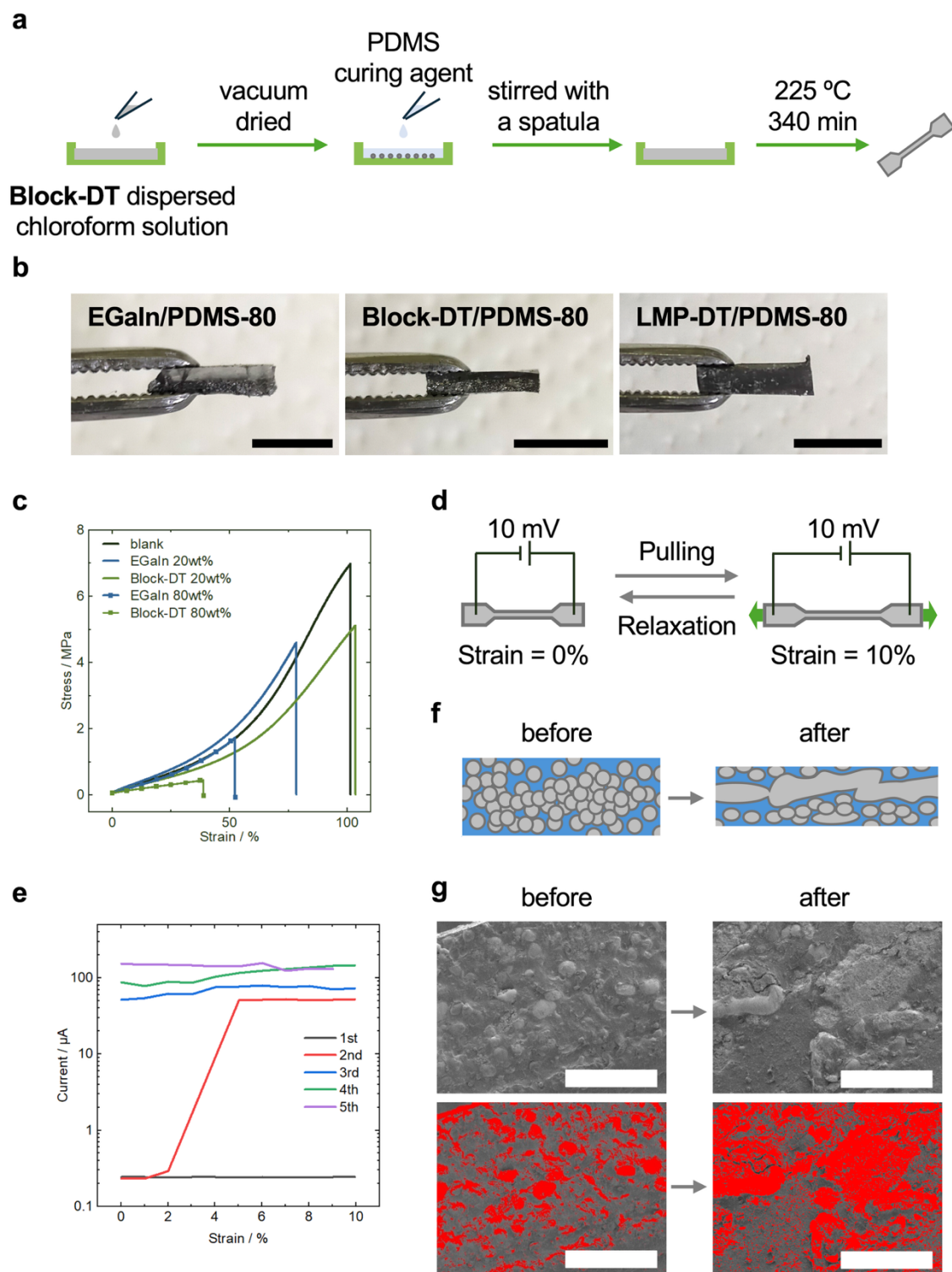


Figure 2. (a) Schematic illustration of the preparation method of **Block-DT/PDMS** composite. (b) Photographic images of the cross-section of **EGaIn/PDMS-80**, **Block-**

DT/PDMS-80, and **LMP-DT/PDMS-80**. Scale bar: 5 mm. (c) Stress–strain curves of **EGaIn/PDMS** and **Block-DT/PDMS**. (d) Schematic illustration of the measurement method of **Block-DT/PDMS** composite. (e) Electrical conductivity–strain dependence of 80 wt% Block-DT/PDMS composite. (f) Schematic illustration of the appearance of the conductive pass. (g) FE-SEM images of cross section perpendicular to the direction of elongation and image with LM-regions highlighted in red. Scale bar: 500 μm .

Mechanical properties were investigated through a tensile test (Figure 2c). The Young's modulus and breaking stress of **Block-DT/PDMS** were smaller than those of pure PDMS (Table 1). Surprisingly, the breaking strain of **Block-DT/PDMS-20** was comparable to that of PDMS, suggesting the relatively homogeneous dispersion of the particles. The drastic decrease in the breaking stress and strain of **Block-DT/PDMS-80** could stem from the intrinsic softness of the EGaIn microparticles. It is worth mentioning that other conductive fillers, such as graphene and carbon nanotubes, usually stiffen the resulting composites.^{44–46} Therefore, the use of the LM particles should be advantageous for developing soft conductive materials. The bilayer structure of **EGaIn/PDMS** resulted in a dramatic decrease in breaking strain even at the 20 wt% of EGaIn probably because the unevenness at the boundary between the EGaIn- and PDMS-rich layers could easily form cracks.

Next, the electrical conductivity of **Block-DT/PDMS** was investigated. Importantly, the as-prepared specimens with different weight fractions of **Block-DT** hardly showed electrical conductivity. On the other hand, deformation forces, like stretching and bending, provided significant enhancement of electrical conductivity to **Block-DT/PDMS-80**. Consequently, its change in current was investigated during repeated stretching–releasing cycles under applying 10 mV of constant voltage (Figure 2d and e). Its initially measured

current (I_{OFF}) was below 1.0 μA , while the current abruptly increased at 5 % of strain during the second elongation cycle. Subsequently, the current was gradually enhanced as the cycle was repeated, reaching over 100 μA after 5 cycles. This change in electrical conductivity can be explained as shown in Figure 2f. In general, small particles of EGaIn coalesce to form a bulk liquid metal state when compression forces are applied, a process known as mechanical sintering. This occurs in both the powdered EGaIn state and in polymer composites.^{18,39} In our PDMS composites, however, the stretching–releasing cycles resulted in an increase in current despite the absence of external compression forces. On the other hand, when a polymer material is stretched, it experiences an internal compression force acting perpendicular to the direction of stretching (the Poisson effect). Since the Poisson’s ratio of PDMS is nearly 0.5 (approximately 0.4950⁴⁷ for Sylgard 184), the compression strain is about 5% when 10% tensile strain is applied to the composites, likely leading to the formation of conduction paths. During the first elongation, the particles in the composite coalesce with each other by the internal compression force, but still hardly form conduction paths. Subsequently, in the second and later cycles, larger domains should be generated and play a significant role in conduction paths composed of the EGaIn bulk. Indeed, FE-SEM images before and after elongation cycles suggested the formation of larger EGaIn domains (Figure 2g). It should be noted that a similar strain-

induced conductivity enhancement was observed in network polymers composed of liquid metal nanoparticles covered with a silanized oxide layer covalently bound to the network.⁴⁸ In our system, on the other hand, the liquid metal particles were not covalently linked to the polymer network, indicating that the covalent bonds between the oxide layer of liquid metal particles and polymer networks are not necessarily needed for the strain-induced conductivity enhancement of liquid metal-polymer composites.

Finally, as a comparison, an 80 wt% PDMS composite was prepared using **LMP-DT**, and the same conductivity test was performed (Figure S7). In stark contrast to **Block-DT/PDMS-80**, **LMP-DT/PDMS-80** hardly showed the conductivity enhancement upon stretching, even when 30% strain was applied during the tenth cycle. Efficient coalescence of the microparticles during stretching might be hindered due to their more uniform dispersion (Figure 2b) stemming from the well-dispersed primary particles (Figure 1e). The more uniform dispersion of the microparticles within **LMP-DT/PDMS-80** led to its higher breaking stress (2.8 MPa) and breaking strain (83%) compared to those of **Block-DT/PDMS-80** and **EGaIn/PDMS-80**. On the other hand, the pressure applied to **LMP-DT/PDMS-80** induced conductivity enhancement, similar to **Block-DT/PDMS-80**.

Table 1. Mechanical and electric properties of composites

	Young's Modulus / MPa	Breaking Stress / MPa	Breaking Strain (%)
PDMS	2.6	7.0	101
Block-DT/PDMS-20	2.4	5.1	103
Block-DT/PDMS-80	1.4	0.4	39
EGaIn/PDMS-20	2.7	4.0	72
EGaIn/PDMS-80	2.2	1.7	52

Application to Microwave Heating

It is known that metal particles with an appropriate particle size can be heated by microwaves.^{49,50} In general, metals have only slight interactions with microwaves because of their high reflectivity of electromagnetic waves and quite small penetration depths (50–100 nm). One of the crucial properties of EGaIn is the relatively large penetration depth of microwave (approximately 5.5 μm at 2.45 GHz microwave, see Supporting Information), thanks to its moderate electrical resistivity. Therefore, it holds potential as a heating source in materials, although microwave heating of EGaIn-based materials has not been reported. Therefore, the microwave heating of liquid metal/polymer composites was investigated. Since the microparticles in **Block-DT** were highly aggregated and partly formed larger coalesced domains in the composites, sparks were generated from their surface when microwave was irradiated. Therefore, microwave heating was examined here using **LMP-DT**, which showed a smaller degree of agglomeration. Initially, the PDMS composite materials containing 10 wt%, 50 wt%, and 80 wt% of **LMP-DT** were prepared by the same operation as above. Microwaves (1000 W) were irradiated to the composites for 3 minutes using a microwave oven, and the temperature was measured using an infrared camera. According to Figure 3, the **LMP-DT/PDMS** composites were heated more efficiently than PDMS alone. The nearly linear dependence between the **LMP-DT** fraction and

temperature implies that the **LMP-DT** particles should serve as a microwave absorber. Furthermore, with a prolonged irradiation time, the temperature of the composite increased almost monotonically, reaching 103 °C after 9 minutes of irradiation (Figure S8). Of course, the bare PDMS sample was also heated after 9 minutes of irradiation, but the resulting temperature was 57 °C, quite below that of the composite. These results suggest that **LMP-DT** might be a viable heat source for microwave heating.

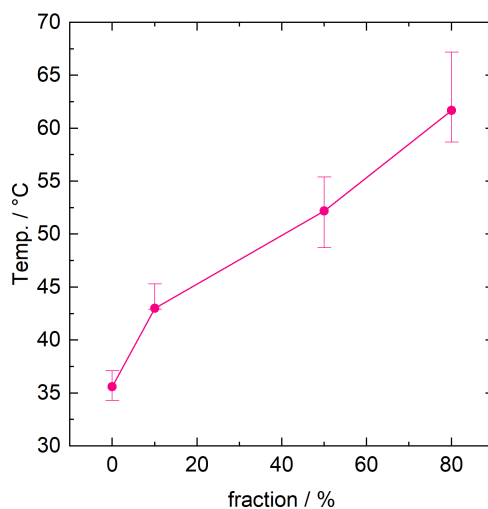


Figure 3. Temperature achieved through microwave heating (1000 W, 3 min) of **LMP-DT/PDMS** composites with different LMP-DT fractions and bare PDMS (fraction = 0%).

Furthermore, a composite of **LMP-DT** and a shape memory polymer (**LMP-DT/SMP**), where the microwave irradiation induced its deformation. **LMP-DT/SMP** was prepared by employing a liquid-crystal elastomer-based epoxy resin as a shape memory polymer⁵¹ (Figure 4a). A stoichiometric amount of diglycidyl ether and sebacic acid were mixed in the presence of **LMP-DT** (20 wt%) in a PTFE Petri dish and subsequently heated at 180 °C using a heating plate. After it was manually stirred using a spatula, a catalytic amount of triazobicyclodecene was added and vigorously stirred. After it started to harden, it was poured on a PTFE substrate and cooled down to room temperature. The as-prepared **LMP-DT/SMP** resin was heated with a heating gun until it became soft, then the material

was deformed by applying a compression force between two PTFE plates until it returned to room temperature. To test the shape restoration of **LMP-DT/SMP** using microwave, microwave was applied to the deformed sample for 3 min, resulting in the recovery of the initial shape (Figure 4b). A thermography camera image (Figure 4c) clearly showed that the temperature of the sample reached more than 140 °C, which is higher than the isotropic transition temperature of the resin (~ 100 °C) and lower than the topology-freezing transition temperature (~ 160 °C).

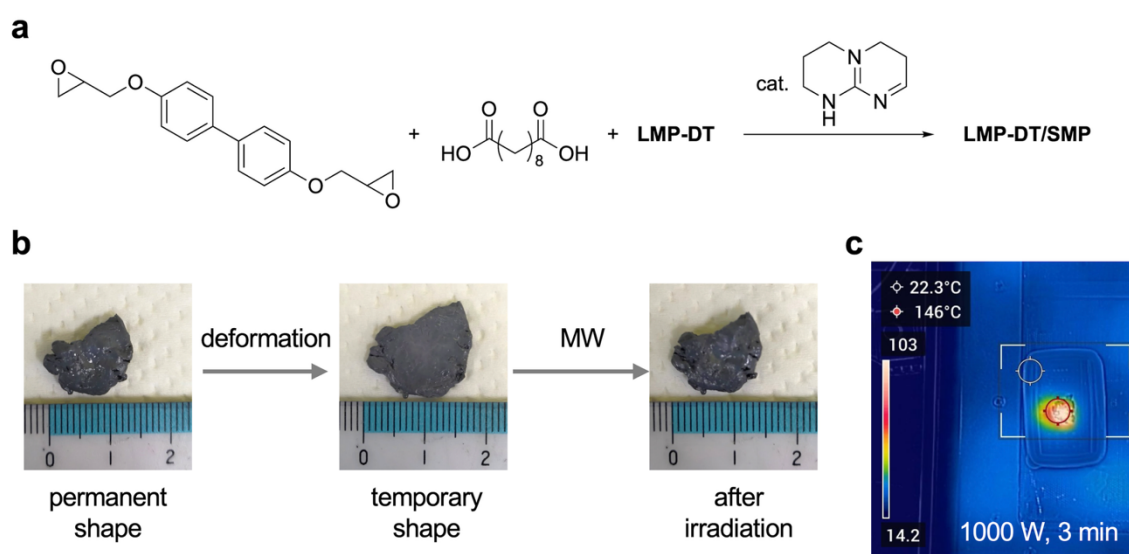


Figure 4. (a) Preparation of **LMP-DT/SMP**. (b) Photographic images of the composite in the permanent (initial), temporary, and after-irradiation shapes. (c) Thermographic image of **LMP-DT/SMP** just after microwave heating.

Conclusion

The powderization of EGaIn was successfully achieved by drying liquid-metal microparticle dispersions prepared through ultrasonication of EGaIn mixed with small-molecular dispersants in ethanol. It was confirmed that lyophilization of the dispersion in benzene is an effective technique for producing the most easily handled powdery liquid metal, **LMP-DT**. The powdered liquid metals were used to prepare composite materials with PDMS and a shape-memory polymer by simple hand mixing. The PDMS composites showed the stress-responsive electrical conductivity and were conductive under tensile stress. Therefore, the proposed fabrication method for composites based on the powdered EGaIn holds potential for applications in stretchable electronics. Furthermore, the microwave irradiation of the shape-memory polymer composite induced heating throughout the entire material, resulting in a shape change. The easy-to-handle powdered liquid metals could provide robust ways for producing key components for soft robotics, stretchable devices, and thermal management systems. In addition, further studies on the interactions between microwaves and EGaIn could open a new avenue for applications of liquid metals to microwave-induced chemical reactions,⁵⁰ pyrolysis of polymer materials,⁴⁹ and so on.

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