Solid–Liquid Self-Adaptive Polymeric Composite

Pei Dong,†,‡ Alin Cristian Chipara,†,‡ Phillip Loya,† Yingchao Yang,† Liehui Ge,† Sidong Lei,† Bo Li,‡ Gustavo Brunetto,‡ Leonardo D. Machado,‡ Liang Hong,† Qizhong Wang,† Bilan Yang,† Hua Guo,† Emilie Ringe,† Douglas S. Galvao,‡ Robert Vajtai,§ Mircea Chipara,† Ming Tang,† Jun Lou,*,† and Pulickel M. Ajayan*,‡

†Department of Materials Science and NanoEngineering, Rice University, 6100 Main Street, Houston, Texas 77005, United States
‡Applied Physics Department, State University of Campinas, Campinas-SP 13083-959, Brazil
§Department of Physics and Geology, University of Texas—Pan American, 1201 West University Drive, Edinburg, Texas 78539, United States

Supporting Information

ABSTRACT: A solid–liquid self-adaptive composite (SAC) is synthesized using a simple mixing–evaporation protocol, with poly(dimethylsiloxane) (PDMS) and poly(vinylidene fluoride) (PVDF) as active constituents. SAC exists as a porous solid containing a near equivalent distribution of the solid (PVDF)–liquid (PDMS) phases, with the liquid encapsulated and stabilized within a continuous solid network percolating throughout the structure. The pores, liquid, and solid phases form a complex hierarchical structure, which offers both mechanical robustness and a significant structural adaptability under external forces. SAC exhibits attractive self-healing properties during tension, and demonstrates reversible self-stiffening properties under compression with a maximum of 7-fold increase seen in the storage modulus. In a comparison to existing self-healing and self-stiffening materials, SAC offers distinct advantages in the ease of fabrication, high achievable storage modulus, and reversibility. Such materials could provide a new class of adaptive materials system with multifunctionality, tunability, and scale-up potentials.

KEYWORDS: hierarchical structure, self-adaptive, self-healing, self-stiffening, solid–liquid composite

1. INTRODUCTION

Many natural materials have adaptive capabilities to actively respond to the applied external loads, i.e., Polypterus senegalus.¹ When this “living fossil” fish is challenged by external force, its reinforcing composite can protect itself from a biting attack, due to its unique deformation mechanisms. In general, the “adaptiveness” of the inner structures allows structural and corresponding property changes under external driving forces, and these changes can often recover to their original states when the stimulation is removed. Design of artificial self-adaptive material should focus on not only changing properties of the materials, but also designing new morphologies and phase distribution schemes to increase adaptability of the inner structure.² Creating a solid–liquid material could be an attractive new direction to realize the ability to reorganize and adapt the inner structure to the external load, leading to exciting self-adaptive behaviors including self-healing and reversible self-stiffening.

As an important class of self-healing materials, the recently reported microencapsulated,³ microvascular,⁴ and vascular⁵ material has attracted much attention owing to its solid–liquid phase distributions.⁵ Generally, the liquid phase is encapsulated by a solid shell in these materials. After load-induced microcrack formation and its penetration into the solid shell, the trapped liquid flows out to fill the cracks. Such structures offer the material the ability to autonomously heal the cracks⁶ and restore properties such as mechanical strength and electrical conductivity.⁷ Unfortunately, this kind of self-healing is not repeatable, due to limited fluidity that arises from the fact that the liquid resides inside the solid shell instead of percolating throughout the whole solid matrix. Additionally, the complicated fabrication process⁶ presents a large challenge for practical utilization in many potential applications.

With biological processes as inspiration, such as bone remodeling,⁸ muscle development,⁹ and blood vessel structure evolution,¹⁰ several artificial self-stiffening material systems have
recently been developed,\textsuperscript{12,13} despite the design complexities in such systems. The increase of the storage modulus, a size-independent parameter, is used to characterize the self-stiffening behavior.\textsuperscript{14} Previously, Carey et al. reported 12% self-stiffening by using the carbon nanotubes/PDMS soft composite under DMA testing at a 5% strain amplitude and at a frequency of 5 Hz.\textsuperscript{12} The storage modulus was less than 17 MPa at 100 °C. Although no storage modulus data was presented, Agrawal et al. also reported a 90% increase of stiffness (defined as the force/displacement ratio) in liquid crystal elastomers, when subjected to an amplitude of 5% strain and a frequency of 5 Hz.\textsuperscript{15} However, these all-solid systems have limited ability to accommodate structural changes and lack crucial reversibility.

In retrospect, it would seem that, to make a highly adaptive material, the best option would be to create a reconfigurable internal structure. This could be achieved if one were to create a solid–liquid continuum framework at the appropriate scales so that the liquid could deform and dynamically respond within the deformable skin. To prepare such a composite, it would be possible to choose one solid polymer and a viscous liquid polymer as constituents. Inherent porosity (with trapped air) could also enable this structure to dynamically access morphologically varying configurations with limited swelling or other local mechanical damage such as internal fracture. Guided by this design principle, poly(vinylidene fluoride) (PVDF) was chosen as the solid skeleton for the designed composite in the current study, due to its good thermal and mechanical properties.\textsuperscript{16–18} Polydimethylsiloxane (PDMS), a viscous liquid, was used as the soft liquid phase. To maintain the liquid phase of the PDMS, no curing agent was used during the fabrication process. Tetrahydrofuran (THF) was used to fully dissolve PVDF and disperse PDMS. Previously, a solvent evaporation method was used as a facile method to encapsulate the self-healing agents.\textsuperscript{19} Here, the probe sonication and magnetic stirring were used simultaneously to ensure complete mixing of all the components. The drying process not only removes the solvent and forms a porous structure, but also causes the PVDF and PDMS to demix into an interpenetrating solid skeleton and liquid phase. This creates a highly complex interencapsulated structure, which provides structural integrity although nearly 50 wt % of the composite is liquid. By controlling the synthesis temperature, it is possible to retain most of the liquid PDMS phase while evaporating the majority of the THF solvent. The distributed solid phase PVDF, encapsulating the liquid phase PDMS, provides the material with solid mechanical robustness while maintaining viscous adaptability, allowing for exciting self-healing and self-stiffening behaviors in a reversible fashion upon external stimulations.

2. EXPERIMENTAL SECTION

SAC Preparation. PVDF (Alfa Aesar, MDL: MFCD00084470, melt viscosity (230°C, 100/s) 23 500–29 500 poise) and hydroxy terminated PDMS (Sigma-Aldrich, viscosity of 18 000–22 000 cSt) with the same weight were added to the THF solvent in order. The weight percentage of PVDF and PDMS in THF is lower than 10%. These two components were mixed using probe sonication (VCX 750, Sonics & Materials, Inc.) and magnetic stirring simultaneously for around 3 h. The mixture was sonicated until at least 50% of the solvent was evaporated and was further evaporated in a vacuum oven overnight at 95 °C. Then, the material was taken out and cooled to room temperature. Soft, intermediate, and hard SAC materials were prepared by changing the probe sonication temperature, which directly leads to different evaporation speeds. The soft SAC was sonicated at 95% amplitude without heating the probe. Intermediate and hard SAC were prepared with a probe temperature of 65 and 85 °C, respectively, at 98% amplitude.

Morphology Characterization. The optical image of the sample was captured using a Canon T3i digital camera. The SEM images were taken by FEI Quanta 400 ESEM, FEI Helios Nanolab 660, and Zeiss Auriga Crossbeam. The FIB procedure was performed using FEI Helios Nanolab 660 and Zeiss Auriga Crossbeam. Movie S1 was recorded using FEI Helios Nanolab 660. The EDS mapping was prepared using Quantax EDS from Bruker.

Mechanical Characterization. For in situ probing, a probe with ~10 μm diameter tip attached to a nanomanipulator (Zyvex S-100) was used to manipulate a bead inside a FEI Quanta 400 ESEM. The FEI Quanta 400 ESEM recorded Movies S2 and S3. For the in situ tensile testing, a Gatan microtensile tester with a 2N load cell was used to perform the tensile test inside a FEI Quanta 400 ESEM. A prenotched rectangular sample was clamped on sample stages before repeated loading cycles. The notch length is ca. 50% of the sample dimension along the longitudinal notch direction. In the tensile test, the sample was then loaded at a displacement rate of 0.5 mm/min. The FEI Quanta 400 ESEM recorded Movie S4. For the DMA testing, the samples were hand-cut with a razor blade. The mechanical properties of this material were tested and analyzed using a TA Instruments DMA Q800. Tests were carried out under a constant frequency of 5 Hz with an amplitude of 30 μm (fixed displacement) by up to 400 000 cycles. The DMA tests were conducted at the room temperature.

3. RESULT AND DISCUSSION

The as-fabricated PVDF–PDMS self-adaptive composite (SAC), shown in Figure 1a, contains both solid and liquid phases and possesses an interesting hierarchical microstructure (Figure 1) as discussed below. The scanning electron microscope (SEM) image of SAC in Figure 1b shows its porous structure as expected from the evaporation process, with many bead-like structures stacking each other (one such bead is highlighted by the red dashed circle). Figure 1c is the high magnification SEM image of the shell of the bead. An algorithm was used to analyze many SEM images, and from a sample of 240 beads an average diameter of 45.2 μm was found, with a standard deviation of 21.9 μm. (See Supporting Information Figures S1, S2, S3 and Table S1). The measured density of the porous SAC (Figure 1a) is ~0.61 g/cm³.

The schematic image of the SAC is shown in Figure 1e. The silver color represents the shell of the beads, while the red color shows the viscous phase outside. At the next (second) level in this hierarchical structure, two types of microstructures are observed in the interior of the beads (highlighted by the blue color in Figure 1e), shown in Figure 1df, and Supporting Information Movie S1. Figure 1d shows the cross section of a bead cut by the focused ion beam (FIB), exhibiting a spinodal decomposition-like morphology presumably resulting from the demixing of immiscible components in the PVDF–PDMS polymer blends. A second type of bead’s internal structure, shown in Figure 1f, consists of many spheres with diameter in the range 100–200 nm dispersed in a matrix. Energy dispersive X-ray spectroscopy (EDS) mapping (Figure 1hi) shows that silicon is absent in the spheres but rich in the matrix, and fluorine (F) is more concentrated in the spheres. This result suggests that the spheres are a PVDF-rich phase and the matrix is a PDMS-rich viscous phase as Si only exists in PDMS and F only in PVDF. Notably, Figure 1i shows that a significant amount of PVDF is dispersed in PDMS even though they are immiscible. It is likely that the high viscosity of PDMS kinetically prevents the complete crystallization of PVDF. Close
This is direct evidence of the SAC, made possible by the existence of the solid−liquid composite. (Figure 2a,b) The schematic image of the SAC. The silver color represents the shell of the beads, while the red color shows the viscous phase outside. The two types of the inner structures (blue) of the bead are shown in parts d and f. (g) Scanning transmission electron microscopy (STEM) image of the sphere with the surrounding dendrite structure, illustrating the crystallization of PVDF. (h and i) EDS mapping results of Si (red) and F (yellow) elements, respectively, in the sphere with the surrounding dendrite structure.

To examine the mechanical integrity and robustness of the SACs, a probe with ~10 μm diameter tip attached to a nanomanipulator (Zyvex S-100) was first used to manipulate a bead inside an SEM (FEI, Quanta 400). As shown in Figure 2a,b, the bead underwent pronounced rolling under the applied force. However, the relative motion of the bead and the rest of the sample did not cause them to separate. Instead, the bead merged with nearby beads upon rotating and exhibits considerable resistance to fracture shown in Supporting Information Movies S2 and S3. The spots on the bead where signs of rolling and merging are visible as highlighted with red arrows before and after in situ probe contact in Figure 2a,b. This is direct evidence of the flexibility of the structure of the SAC, made possible by the existence of the solid−liquid interface. Upon retrieval of the probe, an extending string of small liquid beads was drawn between the bead and probe, as shown in Figure 2c and its inset. This confirms that liquid phase is present on the bead surface or within the shell layer.

A simple fracture test under repeated loading was next conducted using a microtensile tester with a 2N load cell. Figure 2d shows the in situ SEM image of a prenotched (highlighted by the red dashed line) rectangular sample clamped on the sample stages before the repeated loading cycles. The notch length is ca. 50% of the sample dimension along the longitudinal notch direction. In the tensile test, the sample was then loaded at a displacement rate of 0.5 mm/min. The engineering strain is estimated to be ~3.6% at the peak load. Figure 2e shows the in situ SEM image of the crack propagation in the sample, marked by the red dash line, during loading. The crack grew to a total length of ca. 75% of the sample dimension at the end of the loading stage. Interestingly, the crack started to disappear during the unloading stage, as shown in Figure 2f. Movie S4 shows healing behaviors from the in situ tensile testing. Higher magnification SEM images of the sample region where a crack evolves before, during the loading stage. Higher magnification SEM images of the sample region where a crack evolves before, during the loading, and during unloading (f). (g−i) The higher magnification SEM images of a sample region with an evolving crack before loading (g), during loading (h), and during unloading (i). The schematic to illustrate the self-healing mechanism has been provided below (g−i). (j) The cyclic load−unload curve. The labels d, e, and f represent the moments when the previous SEM images were taken. The crack in parts d and e and healing behavior in parts f and i can be observed repeatedly during the cyclic load−unload processes. (k) The load−displacement curves between 1st and 2nd cycles and from different cycles (l).

Figure 1. Characterization of the hierarchical solid−liquid composite. (a) Image of solid−liquid SAC. (b) SEM image of the porous SAC. (c) High magnification SEM image of the shell of the bead. (d) SEM image of the inner structure of the bead, displaying spinodal structure, after being cut by the focused ion beam (FIB). (e) Schematic image of the SAC. The silver color represents the shell of the beads, while the red color shows the viscous phase outside. The two types of the inner structures (blue) of the bead are shown in parts d and f. (f) SEM image of another type of inner structure of the bead, showing distributed spheres with surrounding dendrite-like structures, after being cut by the FIB. The thick layer outside is the sputtered Pt for FIB cutting. (g) Scanning transmission electron microscopy (STEM) image of the sphere with the surrounding dendrite structure, illustrating the crystallization of PVDF. (h and i) EDS mapping results of Si (red) and F (yellow) elements, respectively, in the sphere with the surrounding dendrite structure.

Figure 2. Characterization of self-healing behaviors. (a−c) In situ SEM images of a bead during probing enabled by a nanomanipulator (a), after probing (b), and after removing the probe (c). (d−f) The in situ SEM images of the sample before loading (d), during loading (e), and during unloading (f). (g−i) The higher magnification SEM images of a sample region with an evolving crack before loading (g), during loading (h), and during unloading (i). The schematic to illustrate the self-healing mechanism has been provided below (g−i). (j) The cyclic load−unload curve. The labels d, e, and f represent the moments when the previous SEM images were taken. The crack in parts d and e and healing behavior in parts f and i can be observed repeatedly during the cyclic load−unload processes. (k) The load−displacement curves between 1st and 2nd cycles and from different cycles (l).
The schematic to illustrate the self-healing mechanism has been provided in Figure 2g–i as well. The silver sphere represents the PDMS-rich shell, and the red area shows the PDMS wrapping the whole system. Before loading, the two beads were stacked on each other. During the loading, the two beads were forced to separate. Either PDMS on the surface or coming from the interior of the beads provides a closure force due to capillary and viscoelastic interaction which causes the crack to heal upon unloading. To verify whether such crack-closure indeed presents self-healing in the material, the cyclic load–unload curve was plotted with load levels corresponding to images in Figure 3d–f clearly marked (Figure 2j). It is clear from this loading cycle curve that the force needed to advance the crack could always recover, suggesting the existence of self-healing behaviors. The load–displacement curves from different cycles are shown in Figure 2k,l. Despite some observable changes in the curves, they in general showed very good repeatability for up to 41 cycles with no significant load-bearing capability loss. We found that the crack propagates along the same pathway upon loading in the cycling test, indicating that the existence of self-healing behaviors in SAC material is largely size-independent. The maximum increase of SAC’s storage modulus is up to 683% with the maximum storage modulus achieving 412 MPa (Figure 3f,g). It is important to note that the morphology and mechanical properties of the SACs can be easily tuned by changing the synthesis parameters. In Figure 3, three different samples, of varying storage moduli (A, soft; B, intermediate; C, hard), are chosen to demonstrate the ubiquitous self-stiffening behaviors in SACs. The size of the resulted beads in their hierarchical structure is affected by the evaporation rate of THF: faster solvent evaporation rate causes the viscosity of PDMS/PVDF blend to increase more rapidly, which reduces the ability of droplets to coalesce and results in smaller bead sizes, as shown in Supporting Information Table S2. This gives us the ability to tune the storage modulus and self-stiffening behaviors of the materials (Figure 3). The SEM images of the as-fabricated SAC samples are shown in Figure 3a–c, respectively. The storage modulus evolution for the same sample in two separate tests is shown in Figure 3d–g. The storage modulus of sample A, shown in Figure 3d, increased from 2.9 to 11.6 MPa after 400 000 cyclic loading. The sample was fully relaxed before another test. The inserted image in Figure 3d shows the starting points of the storage moduli for pristine and relaxed sample A, which are quite similar. Similar self-stiffening behaviors were also observed in these two separate tests, demonstrating good repeatability. Figure 3g is the histogram of the storage modulus at the beginning and ending point of A, B, and C, before and after relaxation. Remarkably, the stiffened SAC samples are able to recover a large part of their structural compliance after loading and relaxation. Figure 3d shows that the storage modulus of A returned from 11.6 MPa at the end of the DMA test to 3.3 MPa after relaxation, which compared well to the original modulus of 2.9 MPa. Similar relaxation in storage modulus is also shown in B and C, Figure 3e,f. These results clearly show that the self-stiffening phenomenon observed in SAC material is largely reversible.

The self-healing and self-stiffening behaviors possessed by SAC are direct consequences of its internal porous structure that incorporates solid, liquid phases in a continuous fashion. Our choice of the system components, i.e., a solvent (THF), a viscous liquid (PDMS), and a semicrystalline polymer (PVDF), contribute synergistically to the formation of this intriguing microstructure. THF helps disperse two immiscible components (PVDF and PDMS) into a liquid solution. Upon gradual removal of THF, the following processes are thought to occur in the composite: (1) Creation of porous structure by evaporation of THF: because of the high viscosity of PDMS, the void space in the solution left behind by vaporized THF cannot be completely filled during synthesis, which produces open pores in the composite. In response to the presence of internal pores, the viscous PDMS/PVDF mixture undergoes...
localized morphology changes and forms liquid beads to reduce local surface energy. (2) Demixing of PDMS/PVDF solution via spinodal decomposition. Removal of THF decreases the mutual solubility of PDMS and PVDF in the solution and should eventually cause them to demix. Immiscible polymer blends often demix in the liquid phase through a spontaneous process known as “spinodal decomposition”. The intertwined PDMS-rich and PVDF-rich domains observed inside the beads (Figure 1d) strongly resemble demixed liquid morphology after spinodal decomposition. Similar spinodal structure is also seen in porous PVDF membranes (e.g., Figure 3 of ref 23 by Li and Katsouras et al.) prepared by an analogous vapor-induced phase separation method involving PVDF, an immiscible component, and a solvent. Because THF is removed more rapidly from the surface region than from the interior of the liquid through evaporation, demixing is expected to occur earlier and faster near the surface than in the bulk liquid. With continuous evaporation of THF and increased immiscibility between PVDF and PDMS, the PVDF-rich domains in the surface shell grow by displacing PDMS liquid out of the surface layer, which eventually results in a largely solid shell. Upon further cooling, PVDF in the mixture crystalizes; the spinodal decomposition morphology could be either preserved by rapid crystallization, or replaced by dendritic PVDF morphology when the crystallization rate is slower, which allows for morphological changes through diffusion of PVDF and PDMS at the crystal growth front. More detailed characterization of the thermodynamic stability, phase separation, and crystallization kinetics of the PVDF/PDMS/THF ternary system will be carried out in the future to further improve the control of the SAC microstructure.

A key step in the structural evolution of SAC during synthesis is the formation of a continuous solid PVDF shell on the bead surface, which both encapsulates PDMS liquid and stabilizes the pore space. This surface layer provides structural robustness to the composite, but its thinness also gives the bead structure significant deformability and flexibility that is instrumental to SAC’s self-adaptiveness. As discussed above, we postulate that the solid shell structure originates from a surface-mode spinodal decomposition, followed by subsequent crystallization and growth of PVDF domains. The self-stiffening behavior of SAC can be attributed to the reduction of porosity as shown in Supporting Information Figure S5 and the increased interaction among PVDF/PDMS beads under loading. Densification of the porous composite structure upon compression contributes to an increase in nominal storage modulus, which is likely to be irreversible. Nevertheless, the majority of the stiffening is likely to originate from the viscoelastic interaction between the beads in the composite. When two neighboring beads are compressed against each other, their PVDF shells can have large elastic deformation like two hollow rubber balls thanks to the small thickness. As a result, the contact area and force between the beads are increased, which contributes to the enhancement in the stiffness of the sample. After the applied force is removed, the deformed shells can recover their original shapes, making self-stiffening a reversible process. However, because of the inclusion of the highly viscous PDMS inside the beads, the deformation of a bead as a whole exhibits viscoelastic characteristics. This explains why SAC displays a gradual rather than instantaneous change in storage modulus over many cycles in DMA tests. In addition, insignificant self-stiffening was found in samples tested at ≤135 °C (below the glass transition temperature of PDMS as ~125 °C), which also demonstrates the essential role of a viscous liquid phase in the self-stiffening phenomenon.

4. CONCLUSIONS

In conclusion, a new type of composite, SAC, with a unique combination of liquid and solid phases, was synthesized by a mixing–evaporation process, which forms a hierarchical microstructure made of beads encapsulating liquid PDMS within thin shells of solid PVDF. The material processes the self-healing capability during the tensile test, due to the presence of the liquid phase that can allow a liquid-like joining behavior of the crack surfaces. This material also undergoes significant reversible self-stiffening under compression, with a maximum increase of storage modulus up to 683%, which is much larger than that reported for solid composites and other materials. Both self-healing and self-stiffening behaviors of SAC represent the adaptive nature of the material due to the intermixed solid–liquid microstructure, which can be tuned by processing to get controllable mechanical behavior. In a comparison to that of traditional microencapsulated materials, the processing of SAC is simple, tunable, and scalable. Most importantly, by studying the mechanism, such solid–liquid hybrid systems represent a new direction in the design of dynamic and adaptive materials which could have a large number of exciting applications, e.g., biocompatible materials for tissue engineering, and lightweight defect tolerant structural materials, etc.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b10667.

Automated diameter measurement algorithm, the diameter distribution of the spheres before and after DMA testing, XRD results, the normalized height of the SAC sample before and after DMA and after relaxation (PDF) Movie S1 demonstrating two types of microstructures inside the sphere, including both the spinodal (Figure 1D) and sphere domain structures (Figure 1F), made from SEM images (AVI) Movie S2 demonstrating the rotating motion of the bead during probing enabled by a nanomanipulator inside an SEM (AVI) Movie S3 demonstrating the merging motion of the bead during probing enabled by a nanomanipulator inside an SEM (AVI) Movie S4 demonstrating the self-healing behavior during the tensile test enabled by a microtester inside an SEM (AVI) Movie S5 demonstrating the healing behavior by compressing the two pieces of the SAC into one piece (AVI)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: jlou@rice.edu.
*E-mail: ajayan@rice.edu.

Author Contributions
P.D. and A.C.C. carried out the material synthesis and characterization, and the experimental data analysis. P.L. carried out the probing experiment. Y.Y. helped perform the in situ
tensile test. L.D.M. carried out simulation of the diameters of the sphere. L.H. drew the schematic image. Q.W. and B.Y. helped synthesize the material. M.T. explains the formation of the material in theory. J.L. and P.M.A. initiated the project. All authors participated in discussions. P.D., Y.Y., L.G., S. L., B. L., M.T., J.L., and P.M.A. contributed to writing the manuscript.

**Author Contributions**

P.D. and A.C.C. contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors would like to gratefully acknowledge the Air Force Office of Scientific Research (Grant FA9550-13-1-0084) for funding this research, and the program director Dr. Joycelyn Harrison for her guidance. L.H. and M.T. acknowledge support from DOE Project DE-SC0014435. The authors also thank FEI and Zeiss Company for providing SEM and EDS images after FIB cutting.

**REFERENCES**


