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Conductive microcapsules for self-healing electric circuits

G. W. Lai,[a] S. J. Chang,[b] J. T. Lee,[c,d] H. Liu[a] and C. C. Li[a,]*

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Conductive microcapsules that are compatible with inorganic-based materials such as Ag conductive paste for casting electric circuits are prepared. These conductive microcapsules show high efficiency, more than 80% within 30 sec, for the restoration of the interrupted circuit that presented a cracking width about 150 μm.

Microcapsules have attracted attention in the field of novel and advanced materials due to their potential applications in high-tech industries.[1-13] The advantage of encapsulating specific materials in the core of a microcapsule is that the core materials can be quarantined to function only at the right time, i.e. they will remain stable inside the microcapsule until they are triggered. Due to wide variety of species available for the core materials, microcapsules have the potential to be employed in a wide industrial products, for instance, food and cosmetic additives,[14,15] drug delivering carriers for bio-material and medicine fields,[16,17] self-healing additives for microstructural and functional restorations[18-24] and so on. Among these applications, the self-healing function of microcapsules has attracted the most interest in recent decades. The research team of Scott R. White et al. was the first to reveal the potential for utilizing microcapsules as self-healing materials. From their report in 2001,[1] they successfully embedded the microcapsules of poly(urea-formaldehyde) (PUF) in resin which was cast on the surface of a certain substrate that needs to be protected or be able to restore itself as needed. Based on the healing mechanism, not only the structural fracture but other physical properties such as anti-corrosion or electrical conductivity can also be spontaneously restored.

Since the shell of most microcapsules is primarily polymeric which is mechanically soft and less compatible with lots of inorganic materials, the utilization of microcapsules is generally circuitous; the microcapsules are embedded in a polymeric film on the top of the target substrate that needs the self-healing function. This is especially true when the substrate is a metal- or ceramic-based material because of the very different surface tensions. This procedure makes the use of microcapsules complicated and limits their use in other applications. On the other hand, the triggering force may decay during transmission and only the microcapsules near the interface between the polymer and the target substrate have the opportunity to function, while those embedded far from the interface will become useless. To make the use of microcapsules more convenient and more efficient in the healing process, wastage of microcapsules should be reduced and they should be buried directly in the target substrate.

One of the most important self-healing applications of microcapsules is the ability of the electrical micro-lines of the printed circuit to restore themselves. It has been known that the surface tensions of polymer and metal are generally in a discriminated range of less than 100 mN m^{-1} and larger than 1000 mN m^{-1},[25,26] respectively. To improve the compatibility of polymeric microcapsules with the metallic matrix and to reduce the negative effect on the electrical conductivity caused by the addition of insulated microcapsules, surface modifying microcapsules are required. Nevertheless, attaining a continuous and good quality coating of metal, such as silver (Ag) nanoparticles, on the surface of microcapsules is a challenge and has not been found in the literature. In this investigation, a new and simple method for surface modifying PUF microcapsules with Ag nanoparticles based on the colloidal technique is proposed. On the other hand, for easier processing of the microcapsules with harder, inorganic-based Ag paste, eicosane was used as the core material in this preliminary study. Eicosane has a low melting point of 38 ^{o}C. It is solid at room temperature and can make microcapsules more robust, and also it can be easily melted by warming it slightly near its melting temperature when restoration is required.

Figure 1a shows the microstructures of eicosane-encapsulated poly(urea-formaldehyde) (PUF-C20). The microcapsules are spherical and the size is distributed from 1 to 10 μm. According to the analyses of the cross-sectional image and thermogravimetric

[a] Department of Materials & Mineral Resources Engineering, and Institute of Materials Science and Engineering, National Taipei University of Technology, Taipei 10608, Taiwan
[b] Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu 30011, Taiwan
[c] Department of Chemistry, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan
[d] Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 80708, Taiwan
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weight loss of the microcapsules, the shell thickness was found to be about 50-100 nm (Figure S1) and the content of the core material was roughly 70 wt%. To make the PUF-C20 microcapsules conductive, the microcapsules were coated with a homogeneous and continuous layer of Ag nanoparticles by the method of in-situ chemical reduction.[27] As shown in Figure 1b, a continuous coverage of Ag nanoparticles was obtained outside the shell of microcapsules. The size of the Ag nanoparticles on the surface of Ag-coated PUF-C20 (Ag@*m*PUF-C20) was about 50 nm, as seen from high resolution SEM image (Figure S2), and the thickness of the Ag-coated PUF shell was about 100-150 nm (Figure S3). It is believed that the coverage of Ag nanoparticles may also benefit the mechanical stability of the microcapsules. Figure 1c compares the dispersion of the two microcapsules, PUF-C20 and Ag@*m*PUF-C20, in water. While suspending in water, the white PUF-C20 microcapsules floated on top of the aqueous suspension as shown to the left of Figure 1c. This is attributed to the high content of eicosane in the microcapsule, whose density is lower than water. After surface modification with Ag nanoparticles, the color of microcapsules changed to black and settled while suspended in water. These results show that heavier Ag nanoparticles are successfully coated on microcapsules.

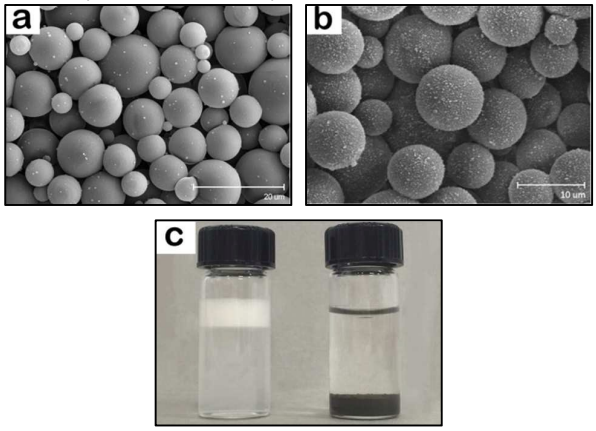

Figure 1 SEM images of (a) PUF-C20 and (b) Ag@*m*PUF-C20. (c) Aqueous suspensions of microcapsules of PUF-C20 (left) and Ag@*m*PUF-C20 (right).

To study the effect of embedding microcapsules on the electrical property of circuits, Figure 2a compares the currents of three circuits as a function of applied voltages (I-V curves). The electric resistances, based on calculations using the slope of the I-V curves, were 610 mΩ, 665 mΩ and 620 mΩ for the three circuits embedded without and with 20 vol% of PUF-C20 and Ag@*m*PUF-C20, respectively. The circuit with no embedding showed the least electric resistance. The circuit resistance increased by about 9.0% and only 1.6% when embedded with 20 vol% of PUF-C20 and Ag@*m*PUF-C20, respectively. The large decrease in the conductivity for the circuit embedded with PUF-C20 should be attributed to the insulating property of PUF-C20. Besides, it is believed that the poor dispersity of the PUF-C20 microcapsules in the Ag matrix may also play an important role on decreasing the conductivity. During the process of blending microcapsules into the Ag paste, it was found that the viscosity of the paste was significantly higher when blending with PUF-C20 than with Ag@*m*PUF-C20, showing that there were more aggregates of PUF-C20. For Ag@*m*PUF-C20, it had a metallic coating on its surface; therefore, it was more compatible with Ag paste and exhibited better dispersity, resulting in less negative effect on the conductivity.

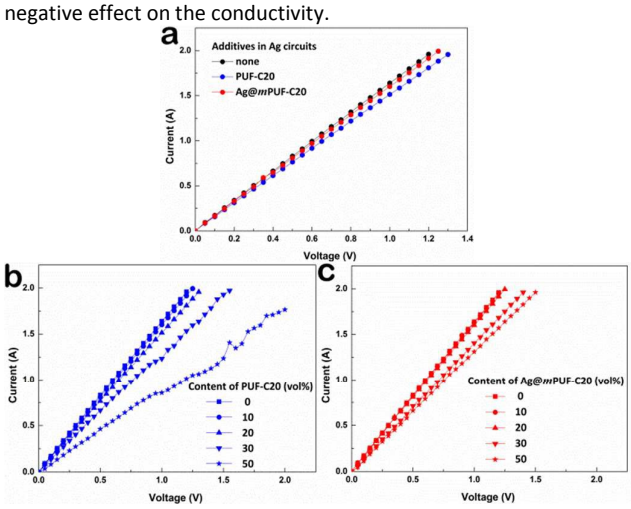

Figure 2 Response currents as a function of applied voltages (I-V curves) for various Ag-based circuits. (a) I-V curves of circuits embedded with different additive of none, 20 vol% of PUF-C20 and 20 vol% of Ag@*m*PUF-C20. I-V curves of circuits embedded with (b) PUF-C20 and (c) Ag@*m*PUF-C20 at various contents.

To study the effect of dispersity of microcapsules on the electrical property of circuits, the conductivities of circuits embedded with various contents of PUF-C20 and Ag@*m*PUF-C20 were measured and compared in Figure 2b and 2c, respectively. When embedded with PUF-C20 (Figure 2b) the circuit showed a more significant decrease in the electric current with an increase in the content of microcapsules. The ratios for the reduction of electrical conductivity were respectively 2.4%, 9.0%, 28.3% and 85.0% when the contents of microcapsules were 10 vol%, 20 vol%, 30 vol% and 50 vol%. Additionally, the I-V curves were unstable, deviating from linearity, especially when the content of PUF-C20 was higher than 20 vol%. This result suggested that the composition in the circuit matrix was not homogeneous and that severe aggregation was observed for PUF-C20. When the embedded microcapsules were Ag@*m*PUF-C20 (Figure 2c), the results changed. The ratios for the reduction of electrical conductivity were respectively 0.5%, 2.3%, 16.5% and 24.9% when the contents of microcapsules were 10 vol%, 20 vol%, 30 vol% and 50 vol%. All I-V curves remained stable and displayed good linearity even at a high content of 50 vol%, indicating the homogeneous distribution of microcapsules in the circuit. This suggests that it is important to consider dispersion when studying the application of microcapsules. This will be studied in more detail in further investigations.

To assess the healing efficiency of the microcapsules, the variation in the electric current was recorded after the circuit was scratched and showed that the scribed width was about 150 μm at the widest part and 30 μm at the narrowest part. In this study, the core material was eicosane with a melting point of 38 °C. A warming temperature of 38 °C was provided for 30 sec to trigger the restoration of microcapsules for the Ag circuit. Under the applied

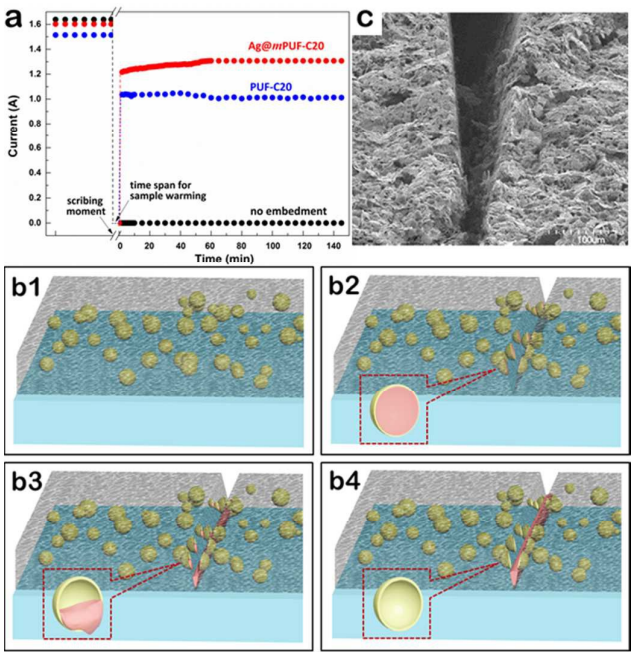

Figure 3 (a) Variation in current before and after being damaged, including the time period of warming at 38 °C for 30 sec (the interval between dashed lines, not to scale), for three circuits with and without embedded 20 vol% of PUF-C20 and Ag@mPUF-C20 under a constant applied voltage of 1 V. Schematic mechanism for restoration: (b1) direct embedding of microcapsules (green) in the Ag-based circuit matrix (grey) on a glass substrate (light blue); (b2) eicosane remains in the core after damage; (b3) melted eicosane released under 38 °C; (b4) damage recovered from both fillings of the Ag particles rearranged from the matrix and the re-solidified eicosane. (c) Cross-sectional SEM image of recovered zone near the interface between the Ag matrix and glass for the PUF-C20 embedded circuit.

constant voltage of 1 V as shown in Figure 3a, the currents of the three circuits failed to zero instantly while being interrupted. With 30 sec of warming, the response current for the control circuit with no embedded microcapsules was irrecoverable and remained at zero; nevertheless, the currents for the circuits embedded with 20 vol% microcapsules of PUF-C20 and Ag@*m*PUF-C20 showed a sudden recovery of 66% and 81%, respectively. Therefore, it is clear that the embedded microcapsules, as well as their core material, determined the availability for the restoration. Since PUF-C20 and Ag@*m*PUF-C20 have the same core material, they should exhibit the same healing mechanism, as illustrated in Figure 3b. Figure 3b1 shows the as-prepared microcapsules embedded directly in the Ag circuit. Microcapsules embedded directly in the matrix have not been reported in the literature, due to the unstable nature of the microcapsules, leaking of the core or the breaking of the microcapsules during processing, and the poor compatibility of the polymer-based microcapsules with the non-polymeric Ag matrix may be another challenge. In this experiment, the core eicosane was not released until heat was provided near 38 °C. Eicosane stayed in the core after the microcapsules broke, as shown in Figure 3b2. By warming at 38 °C, eicosane melted and started to fill into

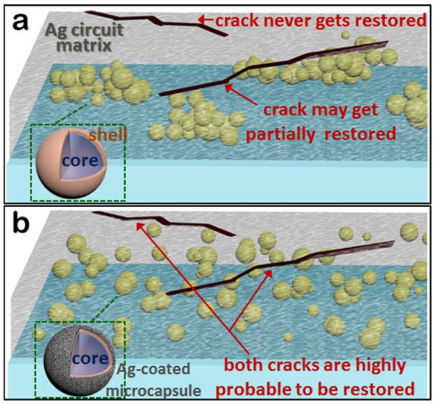

Figure 4 (a) Diagram of cracks may not be completely restored when microcapsules are poorly distributed. (b) This diagram shows the high probability for cracks being restored when microcapsules are well-dispersed.

the valley, and simultaneously in fluidic eicosane may rearrange the Ag particles from the matrix and carry them into the valley to connect the open circuit and restore conductivity (Figure 3b3–b4). This proposed mechanism for conductive restoration was evidenced by the observation of cross-sectional image of the recovered zone, as shown in Figure 3c. The settling of Ag particles at the bottom of the recovered zone is clearly visible. Besides, the recovered zone was also observed from the top-side view of the damaged circuit (Figure S5). Since restoration is dominated by the behavior of the core eicosane, it is extremely interesting to understand why the two microcapsules, PUF-C20 and Ag@*m*PUF-C20 which possess the same core material, exhibited such different electrical restoration efficiencies (Figure 3a). According to the results in Figure 2, the dispersity of microcapsules played an essential role in affecting the electrical property of circuits. It is possible that the poorer efficiency of PUF-C20 also correlated to its poorer dispersity in the Ag matrix (Figure S6).

Figure 4a shows a conductive matrix containing aggregated microcapsules. When the microcapsules are aggregated, they will leave some areas with insufficient or no embedded microcapsules. As a result, the microcapsule-deficient area will not be completely restored when cracks occur. Besides the reduced efficiency of restoration for electrical conductivity, the detrimental effect of the aggregated microcapsules to the mechanical property of circuits can be further anticipated. For circuits with well dispersed microcapsules, as shown in Figure 4b, the area available for restoration will not be limited. When the dispersion is uniform, the healing efficiency only depends on the amount of core functional material available. This amount is larger that can be attained by increasing the loading or the size of microcapsules and is expected to result in better restoration efficiency.

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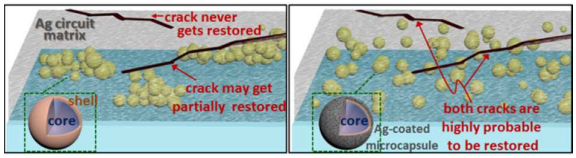
Graphical and textual abstract



Well dispersed conductive microcapsules can be processed directly with inorganic-based Ag paste and perform high restoration efficiency for as-cast electrical circuits.