

Dual Monitoring of Cracking and Healing in Self-healing Coatings using Microcapsules Loaded with Two Fluorescent Dyes

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Abstract

We report the development of an extrinsic self-healing coating system that shows no fluorescence from the intact coating, yellowish fluorescence in cracked regions, and greenish fluorescence in healed regions, thus allowing the separate monitoring of cracking and healing of coatings. This fluorescence monitoring self-healing system consisted of a top coating, an epoxy matrix resin containing mixed dye-loaded in single microcapsule. The dye-loaded microcapsules consisted of a poly(urea-formaldehyde) shell encapsulating a healing agent containing MAT-PDMS and styrene, a photo-initiator and a mixture of two dyes, one that fluoresces only in the solid state (DCM) and a second that fluoresces dramatically increased in the solid than solution state (4-TPAE). A mixture of the healing agent, photo-initiator and the two dyes was yellow due to fluorescence from DCM. On UV curing of this mixture, however, the color changed from yellow to green and the fluorescence intensity increased due to fluorescence from 4-TPAE in the solid state. When a self-healing coating embedded with microcapsules containing the DCM/4-TPAE dye mixture was scratched, the damaged region exhibited a yellowish color that changed to green after healing. Thus, the self-healing system reported here allows the separate monitoring of cracking and healing based on changes in fluorescence color.

Keywords:

Extrinsic self-healing; Self-healing detection; Aggregation-induced emission; Dye-Loaded microcapsule; Self-healing monitoring

1. Introduction

One of the roles of a coating is to protect the underlying substrate from external impacts, thereby protecting it from corrosion and other processes that may compromise its mechanical properties. Thus, coatings can extend the lifetimes of materials and, in various contexts, enhance public safety. The development of self-healing coatings, and techniques for monitoring such coatings in real time, has proved to be an effective means of extending the lifetime of materials. Recently, a technique was introduced for monitoring self-healing coatings based on changes in color or fluorescence at damaged locations on the coating surface.^[1-10] This technique is of great practical utility as it allows the condition of a coating to be assessed through visual inspection.

In a previous report, we studied self-healing coatings containing fluorescence dye-loaded microcapsules in which self-healing gave rise to aggregation induced emission (AIE) that could be used to detect the healing process (See Figure 1).^[1] Furthermore, we have studied the detection of cracks and healing separately by adding a fluorescence layer.^[8] However, the formation of an additional layer in the coating system has the disadvantage of making the process uncomfortable. To properly monitor a self-healing system, cracking and healing should be detected separately because it is important to maintain the role of the coating by monitoring on coating surface. This is especially the case for irreversible extrinsic self-healing materials using microcapsule.

Here, we introduce a self-healing system that shows different fluorescence color behavior after cracking and healing, allowing the two processes to be monitored separately. This dual monitoring capability is achieved by loading each microcapsule with two types of fluorescent dye: a normal ACQ (aggregation caused quenching) dye with yellowish fluorescence and an AIE dye with a highly contrasting greenish fluorescence. These two fluorescent dyes play

respond differently during cracking and healing of the self-healing coating. (see Figure 1) The normal ACQ fluorescent dye maintains its fluorescence intensity on going from the liquid to the solid phase,^[11,12] whereas the AIE dye exhibits dramatically increased fluorescence in the solid compared to the liquid phase^[3,13-16].(see Figure 2(a)) Thus, if the coating is in its original intact state, it will show no fluorescence. On cracking of the coating, however, the normal fluorescent dye begins to fluorescence but the AIE dye exhibits relatively little fluorescence. Then, as the coating solidifies during self-healing under UV irradiation, the AIE dye begins to fluoresce, causing the color to change (see Figure 2(b)).

2. Results and discussion

2.1. Fluorescence properties of the healing agent following photo-curing

To examine the change in fluorescence color of the dyes during self-healing, a sample comprised of a liquid photo-curable healing agent containing the normal dye, AIE dye, or both dyes was subjected to photo-curing under UV (wavelength, 365 nm) irradiation, and the photo-polymerization was monitored by rheometry (Figure 3). In the case of irradiation of the healing agent containing a photo-initiator, the storage modulus (G') began to increase after about 1200 s of UV light irradiation and the modulus increased to 10^8 Pa by 3600 s. In contrast, the healing agent without a photo-initiator showed no change in G' during UV irradiation, indicating that polymerization did not occur.

When the healing agent containing the photo-initiator and only the normal dye ((4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran, DCM) was irradiated with UV light, the fluorescence color and intensity were little changed after 1800 s (see Figure 3a). In the case of the healing agent containing photo-initiator and only the AIE dye (1,1,2,2,-

tetrakis(4-(diphenylamino)phenyl)ethane, 4-TPAE) (Figure 3b), the fluorescence color changed from violet (UV source color) to blue and the intensity dramatically increased after 3000 s, the time regime in which the modulus became high. Finally, when the healing agent containing photo-initiator and a mixture of the normal and AIE dyes was subjected to UV irradiation (Figure 3c), the fluorescence color changed from yellow to green and the intensity increased following photo-curing. These changes in fluorescence color and intensity during curing in the rheometer could also be observed with the naked eye (see Figure S1). These findings thus show that, when the healing agent containing both dyes undergoes photo-curing under UV light, the fluorescence emission changes from the yellow fluorescence of only the normal dye (DCM) in the liquid state to a green color due to fluorescence from both the normal and AIE dyes (4-TPAE) in the solid state. Collectively, the above results indicate that, if microcapsules containing both the normal and AIE dyes are included in a self-healing coating, cracking of the coating will give rise to yellow emission from the normal dye but as healing progresses the color will change to green as emission from the AIE dye begins. Thus, this system is capable of separate monitoring of cracking and healing based on changes in fluorescence color.

2.2. The self-healing coating system with dye loaded-microcapsules

Dye-loaded microcapsules containing the healing agent (MAT-PDMS and styrene), photo-initiator (BIE) and fluorescent dyes (DCM and 4-TPAE) with a poly(urea-formaldehyde) (UF) shell were prepared by *in-situ* polymerization in an oil-in-water emulsion (Figure 4a). The synthesized microcapsules were all spherical particles with a smooth outer surface (Figure 4b-d) and diameters of 20 to 260 μm with an average size of about 130 μm (Figure S2b). The FT-IR spectrum of the microcapsules (Figure S2a) contained several absorption bands that could

be attributed to the poly(urea-formaldehyde) shell, including features at 3730-3030 cm^{-1} corresponding to N-H and O-H stretching vibrations, at 1643 cm^{-1} corresponding to the C=O stretching vibration, and at 1564 cm^{-1} corresponding to the C-N stretching vibration. The FT-IR spectrum of the core material, which served as a healing agent, included C=O stretching and C=C stretching absorption bands at 1721 cm^{-1} and 1639 cm^{-1} , respectively. These results mean that the synthesized microcapsules were well formed, with the healing agent encapsulated by the UF shell.^[1,5]

To examine the change in fluorescence of the microcapsules during photo-curing, microcapsules containing the healing agent plus DCM, 4-TPAE, or both dyes were treated with 365 nm UV light for 1 h. As shown Figure 4a, the DCM-loaded microcapsule showed yellow fluorescence before irradiation and yellow fluorescence of similar intensity after irradiation (see Figure 4b-1 and 4b-2). By contrast, the 4-TPAE-loaded microcapsules showed no fluorescence before irradiation but strong blue fluorescence after irradiation (Figure 4c-1 and 4c-2). Lastly, microcapsules loaded with both dyes showed yellow fluorescence before irradiation but green fluorescence after irradiation (Figure 4d-1 and 4d-2). These results confirm the suitability of the dye-loaded microcapsules for crack and healing detection in self-healing coatings.

2.3. Dual monitoring of cracked and healed regions with fluorescent dye-loaded microcapsules

To test the suitability of the self-healing system for the separate detection of cracking and healing by monitoring fluorescence, self-healing coatings comprised of an epoxy matrix loaded with microcapsules containing a healing agent and a mixture of DCM and 4-TPAE dyes were

prepared (Figure S3). The coating surface was scratched with a razor and then irradiated with UV light. Optical microscope images of scratched surfaces of coatings containing microcapsules loaded with DCM, 4-TPAE, and a DCM/4-TPAE mixture are shown in Figure 5.

As expected, the scratched control coating without microcapsules showed no fluorescence before and after irradiation (Figure 5a). When DCM-loaded microcapsules were included in the coating, yellowish fluorescence was observed in both the cracked and healed states, with little difference in fluorescence color or intensity between the two states. In the case of the self-healing coating system with 4-TPAE dye-loaded microcapsules, however, no fluorescence was detected along the scratch, but blueish fluorescence emerged during healing (Figure 5c to 5c-1). Lastly, the scratched self-healing coating containing microcapsules with both the DCM and 4-TPAE dyes showed yellowish fluorescence along the scratch that changed to greenish fluorescence during healing. *These results showed that, when microcapsules containing both dyes were included in a self-healing coating, the contrasting fluorescence properties of the dyes can be exploited to distinguish scratched and healed regions.*

3. Conclusions

The present results demonstrate that cracking and healing in extrinsic self-healing coatings can be separately monitored by loading the microcapsules with two dyes, a normal fluorescent dye (DCM) that produces yellowish fluorescence in both the solid and liquid states and an AIE dye (4-TPAE) that shows no fluorescence in the liquid state but strong blueish fluorescence in the solid state. When a coating containing microcapsules loaded with this combination of dyes is scratched, the damaged area appears yellow due to fluorescence from the normal dye. Following irradiation, however, the healing agent in the microcapsules solidifies, causing blue

AIE fluorescence to occur in the healed regions. The self-healing coating system containing dye-loaded microcapsules reported here can thus be used for the dual monitoring of cracking and healing.

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4. References

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Figures and Tables

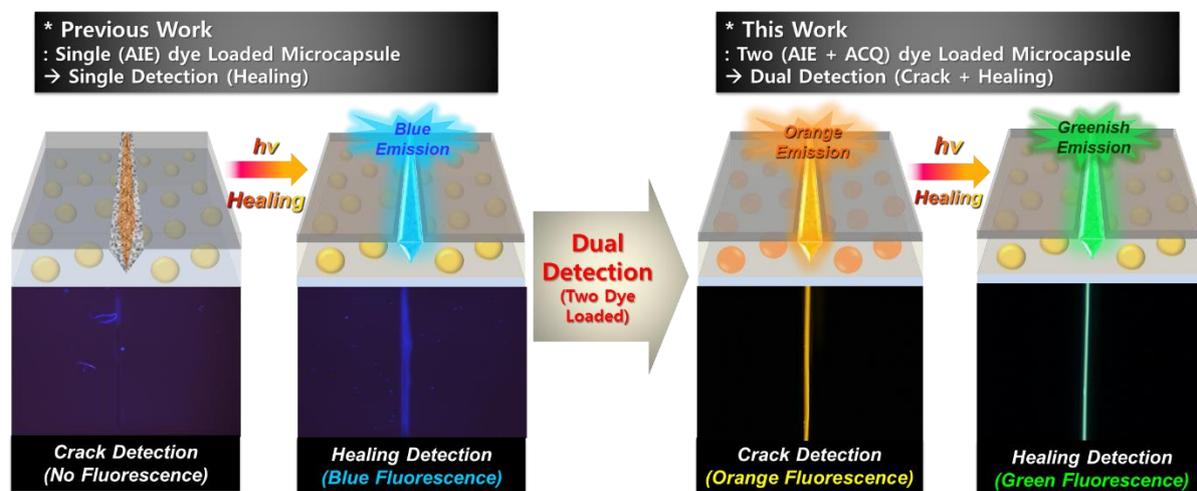


Figure 1. Schematic diagram of dual monitoring of cracking and healing using microcapsules loaded with two fluorescent dyes.

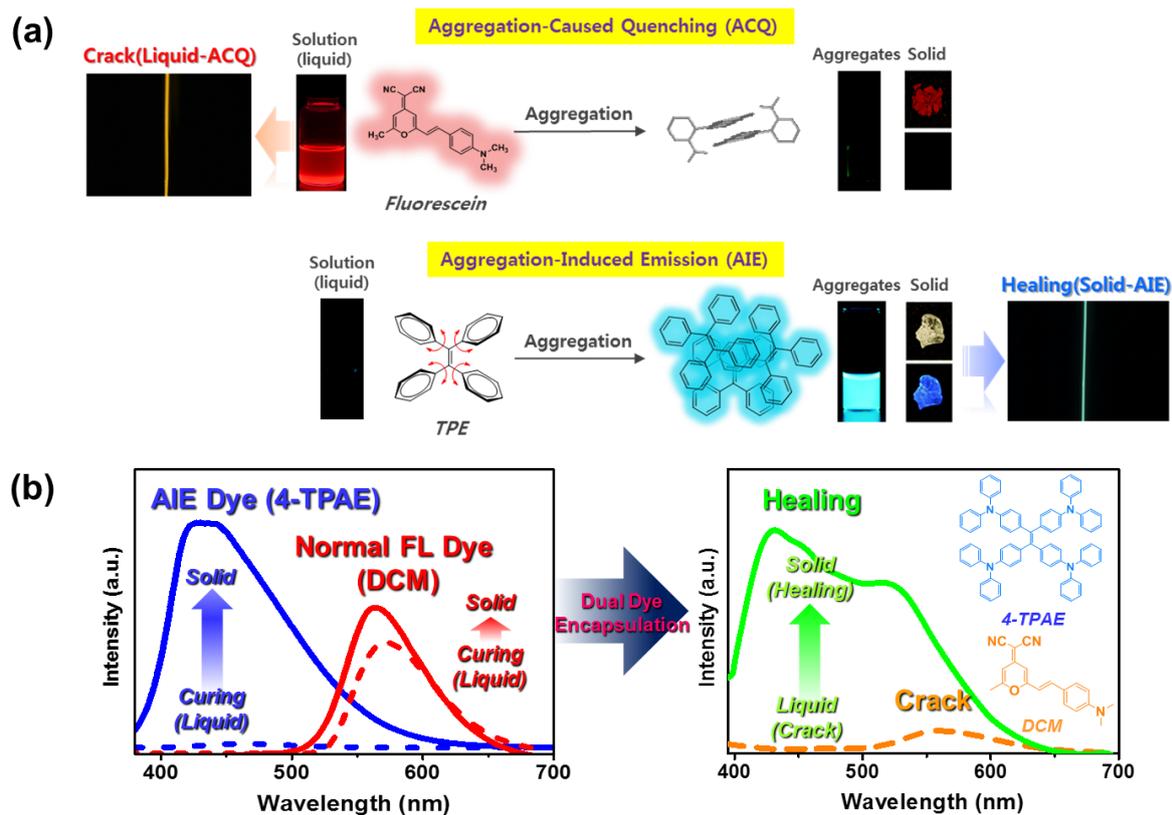


Figure 2. (a) Schematic of cracking (aggregation-caused quenching, ACQ) and healing (aggregated induced emission, AIE) detection using microcapsules loaded with dyes. (b) Fluorescence spectrum of the AIE dye (4-TPAE), normal dye (DCM) and 4-TPAE/DCM mixture before and after curing.

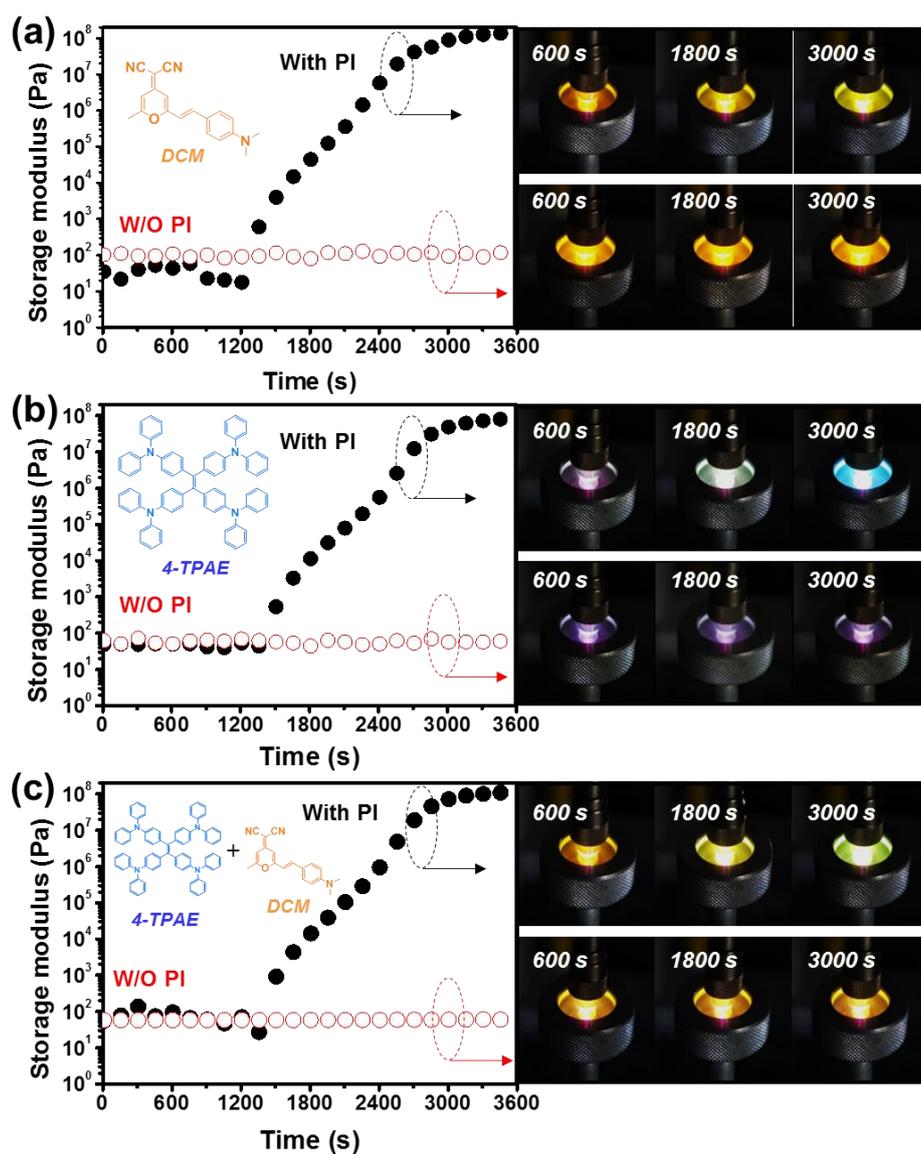


Figure 3. Photo-crosslinking of the healing agents was monitored using a rheology test under UV irradiation (black dots: healing agent with photo-initiator (PI); red dots: healing agent without photo-initiator). (a) DCM, (b) 4-TPAE, (c) DCM/4-TPAE mixture in healing agent.

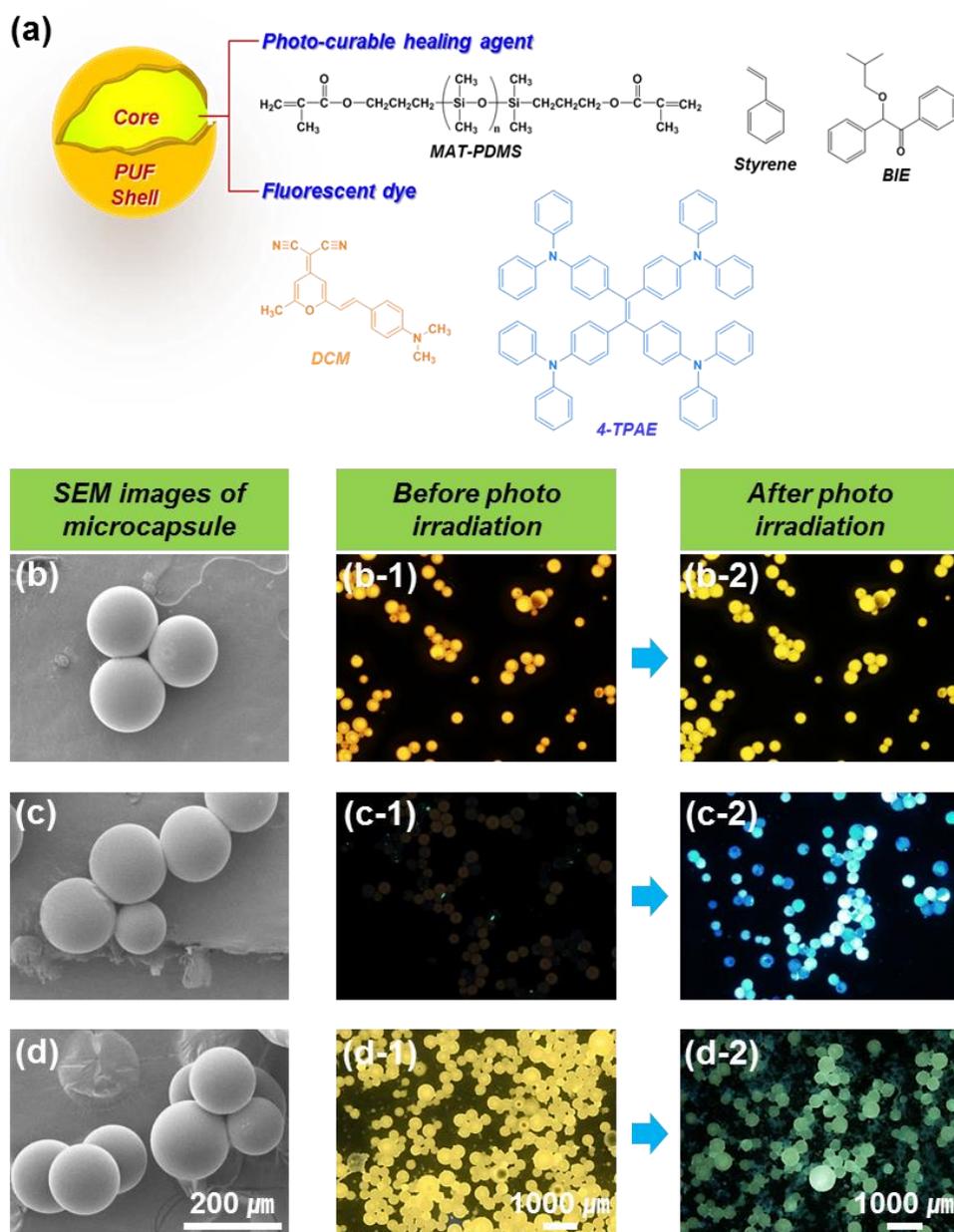


Figure 4. (a) Dye-loaded microcapsules and chemical structure of healing agents and fluorescence dyes, SEM and optical microscope images of microcapsules before and after photo-irradiation for (b-line) DCM-loaded, (c-line) 4-TPAE loaded, and (d-line) 4-TPAE/DCM mixture-loaded microcapsules.

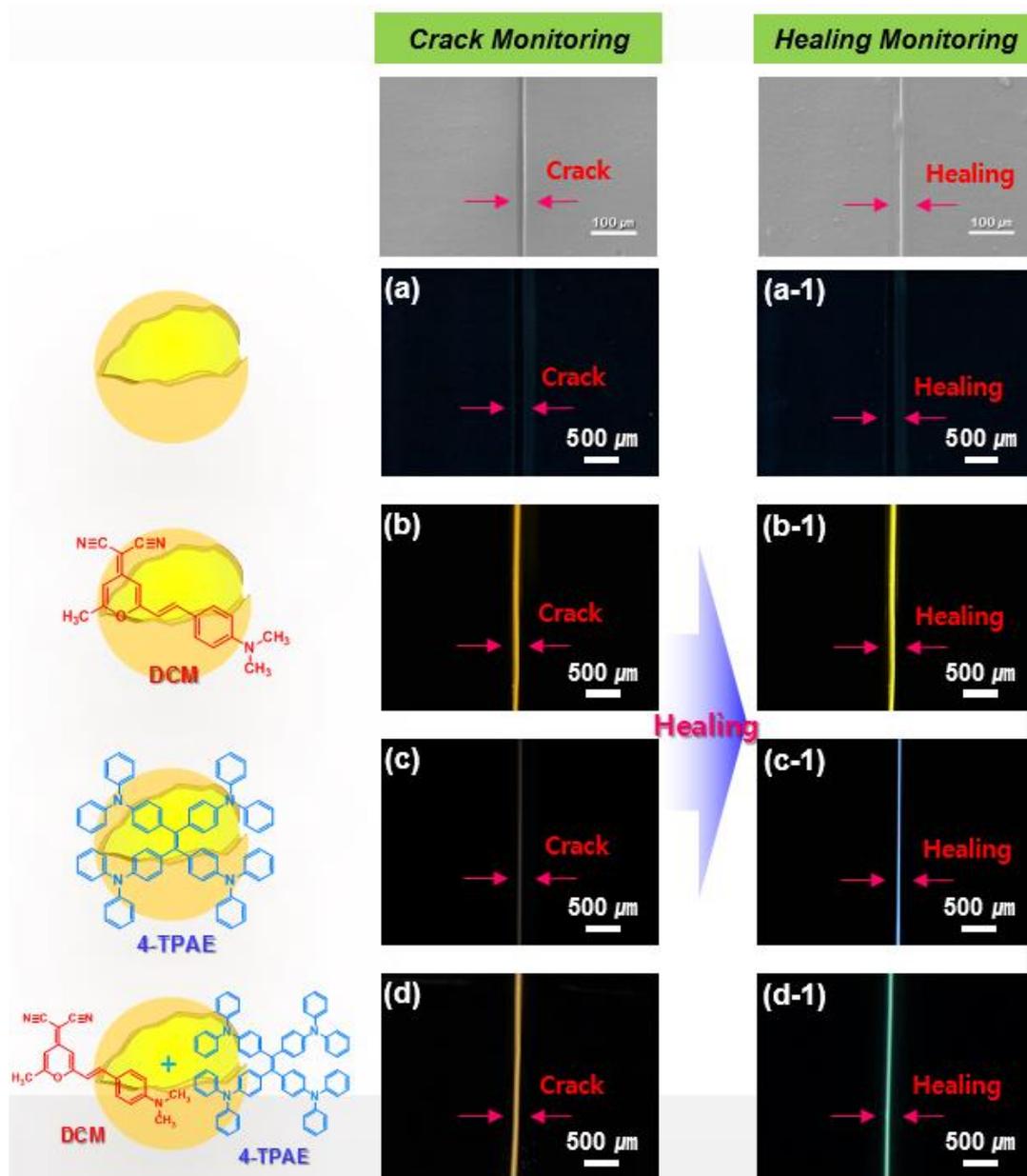


Figure 5. Photographs of scratched and healing regions of (a, a-1) a control coating without microcapsules and self-healing coatings with (b, b-1) DCM-loaded microcapsules, (c, c-1) 4-TPAE-loaded microcapsules, and (d, d-1) 4-TPAE/DCM mixture-loaded microcapsules.