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Full Length Article

Robust polyurea/poly(urea–formaldehyde) hybrid microcapsules decorated with Al_2O_3 nano-shell for improved self-healing performance

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ABSTRACT

Polyurea/poly(urea–formaldehyde)/Al_2O_3 hybrid microcapsules with a dense Al_2O_3 nano-layer containing 4,4′-methylenebis cyclohexyl isocyanate (HMDI) have been successfully fabricated via combaning Atomic layer deposition (ALD) process and interfacial/in-situ polymerization process. This dense Al_2O_3 nano-layer can be controllable deposited in the form of a single atom film through continuous self-limiting reactions of $Al(CH_3)_3$ and H_2O on the surface of the PU/PUF microcapsules at a temperature range of 120–180 °C. The formed hybrid microcapsules showed a monodispersed diameter of ~60 μm with a controlled and nano-sized Al_2O_3 shell.

Moreover, the deposited Al_2O_3 nano-shell significantly increased the thermal stability and mechanical property of hybrid microcapsules, which could maintain their integrity under harsh conditions. In addition, by embedding hybrid microcapsules into an epoxy matrix, an excellent anticorrosion performance in scratched coatings via self-healing functionality was obtained. Therefore, the formed hybrid microcapsules with enhanced thermal stability and mechanical property via ALD process could promote their practical application in self-healing composites.

1. Introduction

Self-healing composites based on microcapsules have been widely used as self-healing coatings [1], phase change materials [2], anti-corrosion coatings [3], and self-lubricating materials [4]. The encapsulated self-healing agent would be released from the ruptured microcapsules inside the coating, and transformed into solid materials via polymerization reaction during their flowing into the microcrack, and repair the microcrack in the coating. However, the shell walls of microcapsules are commonly composed of polymer materials, usually result in a relatively low self-healing efficiency and hinder their further application in self-healing composites [5–7]. These vulnerable microcapsules are usually unstable or even ruptured in harsh surrounding environments, which may result in the devastation of composites and economy hazards. For example, a high temperature may need during the preparation process of mixing and molding, and a high stress may occur during the storage process of collision and extrusion [8–10]. Therefore, the mechanical strength of microcapsules must be optimized to maintain integrity without any cracking during the preparation and storage process of microcapsules.

To fabricate robust microcapsules, microcapsules with a multi-layer shell or a hybrid organic/inorganic shell have been fabricated [11–18], such as polyurea/poly(urea–formaldehyde) (PU/PUF) double shelled microcapsules with elastic modulus of 3.7 GPa [19], and Ni meal/Epoxy resin shelled microcapsules with shell strength of 120 MPa [20]. Especially, construction of inorganic materials onto the organic shells can not only increase the shell mechanical strength, but also endow the microcapsules much more functions, such as superior thermal stability, barrier property and stimuli responsive. For example, Liu et al. fabricated a hybrid nano/microcapsule shelled with polyurethane and silica nanoparticles via interfacial polymerization based on Pickering emulsion templates, and the resultant hybrid nano/microcapsules exhibited an improved solvent resistance, thermal stability and mechanical property [21]. Su et al. reported a hydrolysis process of Titanium(IV) bis (ammonium lactato) dihydroxide as the precursor for the formation of hybrid Alginate/TiO_2 microcapsules, and the formed TiO_2 layer reinforced the chemical stability and mechanical properties of the microcapsules [22]. He *et al.* prepared a pH responsive Ca-alginate/

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protamine/silica hybrid capsules by combining co-extrusion minifludics, adsorption and biosilicification, and the trans-membrane permeability of shell can be changed by adjusting the ambient pH value [23]. Although, introducing inorganic shell into the organic shell can effectively improve the mechanical properties of the microcapsules, their synthesis strategies usually involve complicated operation steps like layer-by-layer deposition or etching. The receipts of the synthesis solution and the reaction conditions must be carefully controlled, such as suitable pH during biosilicification process or hydrolysis process. Moreover, most of hybrid microcapsules show un-controllable microstructure of hybrid shell, such as shell thickness and uniformity, which restrict their practical application of hybrid microcapsules [24–27]. Therefore, it is highly necessary to develop a facile technique to fabricate hybrid microcapsules with controllable and rigid shell structures.

Herein, a monodisperse hybrid microcapsules (ALD-treated hybrid microcapsules) with a PU/PUF organic micro-layer shell and a dense Al_2O_3 nano-layer shell have been successfully fabricated via combining atomic layer deposition (ALD) process and interfacial/in-situ polymerization process. By using ALD technology, a tight and dense Al_2O_3 nano-layer can be controllable deposited in the form of a single atom film through continuous self-limiting reactions on the surface of the PU/PUF microcapsules at a temperature range of 120–180 °C. This dense Al_2O_3 nano-layer endows the ALD-treated hybrid microcapsules with enhanced mechanical and thermal stability when compared to that of pure PU/PUF microcapsule with a double organic layer. Moreover, the ALD-treated hybrid microcapsules embedded in epoxy resin as an anti-corrosion coating show a well self-healing performance.

2. Experimental section

2.1. Materials

4,4′-Diphenylmethane diisocyanate prepolymer (Suprasec2644) was obtained from Huntsman Chemical Trading Co., Ltd (Shanghai, China). 4,4′-methylenebis cyclohexyl isocyanate (HMDI) and Tetraethylenepentamine (TEPA) were purchased from Sigma-Aldrich. Gum arabic, urea, chloroform, polycarbonate, formaldehyde solution (37 wt%), resorcinol (99.0% purity), poly(ethylene maleic anhydride) copolymer (Mw = 100,000–500,000 g mol^{-1}), hydrochloric acid (HCl, 0.1 M), Ammonium chloride (99.5% purity), sodium hydroxide (NaOH), sodium chloride (NaCl) and Epolam 5015 were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd, China. $Al(CH_3)_3$ was purchased from Nanjing ai mou yuan Scientific equipment Co. Ltd, China. All the chemicals in this study were used as received without further purification.

2.2. Preparation of microcapsules

2.2.1. Preparation of PU/PUF microcapsules

The PU/PUF microcapsules were fabricated in three steps. Firstly, an oil solution containing Suprasec 2644 (1 g) and HMDI (9 g) were quickly added into an aqueous solution of gum arabic (2 wt%, 70 mL) at 35 °C and an agitation rate of 900 rpm for 15 min to form oil-in-water emulsions. Secondly, TEPA aqueous solution (13 wt%, 23 g) was slowly added into the above solution, and then the interfacial polymerization of Suprasec 2644 was initialed to form PU microcapsules at 65 °C for 1 h. Thirdly, the formed PU microcapsules were added into a mixed solution containing resorcinol (3 g) and polyethylene maleic anhydride copolymer (1 wt%, 120 mL) at an agitation rate of 500 rpm for 30 min, and then mixed with a PUF pre-polymer solution, followed by heating to 55 °C at an agitation rate of 300 rpm for another 2 h. The PUF pre-polymer solution was prepared by mixing 5 g of urea and 12.66 g of formaldehyde at 70 °C and pH = 8 for 1 h. Finally, the PU/PUF microcapsules were obtained after rinsed with DI water 3–4 times and air-dried for 6 h.

2.2.2. Preparation of ALD-treated hybrid microcapsules

The PU/PUF microcapsules were transformed into ALD-treated hybrid microcapsules via ALD process. Namely, the PU/PUF shell microcapsules (0.25 g) were placed in a reaction container of an atomic layer deposition device. And then, $Al(CH_3)_3$ as the Al precursor and DI water as the oxygen precursor were alternately entrained in the N_2 carrier flow at 1.0 Torr using gas switching valves, respectively. The pulse durations for $Al(CH_3)_3$ pulse-N_2 purge-H_2O pulse-N_2 purge were 0.02–8–0.02–8 s. After the deposition was completed, the reactor was returned to atmospheric pressure and the ALD-treated hybrid microcapsules were obtained. The Al_2O_3 nano-layer with different film thickness was obtained for different deposited cycles (20 cycles and 80 cycles). The fabricated hybrid microcapsules deposited at three temperature of 120 °C, 150 °C, and 180 °C were labeled as ALD-treated-120/150/180 hybrid microcapsules.

2.3. Characterization methods

2.3.1. Morphological characterization

Surface morphology of PU/PUF microcapsules and ALD-treated hybrid microcapsules were characterized via a scanning electron microscope (SEM) running at 20 kV. X-ray photoelectron spectroscopy (XPS) was applied to analyze the chemical structure of the PU/PUF microcapsules and ALD-treated hybrid microcapsules. The XPS analysis was carry out with Monochromatic Al-Ka X-rays, and reference line was set as C1s (284.5 eV). The inner structure and morphology, elemental composition and distribution of ALD-treated hybrid microcapsule were analyzed by field emission transmission electron microscope (TEM, Tecnai G2 F20 S-Twin TMP). Since the microcapsule particle size exceeded the maximum measurement range of TEM, sub-micron sized particle stacked on the surface of the ALD-treated-150 °C hybrid microcapsules were selected for analysis.

2.3.2. Thermal stability of microcapsules

Thermogravity analysis (TGA, Q500) was performed to analyze the thermal stability of the PU/PUF microcapsules and the ALD-treated hybrid microcapsules. The thermal stability of the microcapsules was characterized by analyzing the quality changes of the microcapsules. The thermogravity analysis was carried out under a N_2 atmosphere from room temperature to 600 °C at a heating rate of 10 °C/min.

2.3.3. Mechanical testing

Mechanical property of microcapsules was characterized via a hot-pressing treatment. Namely, 50 mL of chloroform and 10 g of polycarbonate was mixed at an agitation rate of 500 rpm, and then 1 g ALD-treated-150 microcapsules were added. Subsequently, the above mixed solution containing microcapsules was pasted onto the surface of aluminum foil (10 cm × 10 cm) using a knife coater, and then cured for 1 h, and the microcapsules-PC film was obtained. Using hot-pressing, the film was tested at 90 °C and 0.5 MPa for 1 min and 2 min. Finally, the tested film was characterized using optical microscope.

2.3.4. Preparation and characterization of self-healing anticorrosion coatings

Characterization of self-healing performance of the microcapsule composite was carried out via salt spray test. Epoxy resin film (Epolam 5015, AXSON) containing 30 wt% ALD-treated-150 hybrid microcapsules were fabricated with tetraethylenepentamine as curing agent under an ambient temperature. Namely, 1 g of epoxy resin and 9 g of tetraethylenepentamine were mixed at an agitation rate of 150 rpm for 5 min, and then 3 g of ALD-treated-150 microcapsules were added at the same stirring conditions. Subsequently, the above mixed solution containing microcapsules was pasted onto the surface of polished steel plate using a knife coater (450 μm in thickness), and then cured for 24 h at the room temperature, and the epoxy resin containing ALD-treeated-150 hybrid microcapsule coating was obtained. For salt spray test, salt

spray corrosion with corrosive liquid (50 g L^{-1} NaCl) at 35 °C for 48 h was performed according to the national standard for salt spray test (ISO 9227), and cross-scratch was manually made on the coating with a scalpel. For comparison, epoxy resin coating with PU/PUF microcapsules and without microcapsules was prepared and tested under the same conditions.

3. Results and discussion

The PU/PUF microcapsule was used as the template for the preparation of ALD-treated hybrid microcapsule via ALD process (Fig. 1). Firstly, the PU/PUF microcapsule was prepared via the interfacial and in-situ polymerization process: the mixture of Suprasec 2644 and HMDI was emulsified into a stable oil-in-water emulsion (Fig. 1a and a1), then a poly urea (PU) layer and a poly(urea–formaldehyde) (PUF) layer was orderly deposited onto the surface of emulsion via the reaction of Suprasec 2644-TEPA (Fig. 1b and b1) and urea–formaldehyde (Fig. 1c and c1). As shown in the SEM image (Fig. 2a), the formed PU/PUF microcapsule exhibited a high core content ratio of 70.09% and a good spherical shape with an average particle size about 60 μm. The encapsulation efficiency of HMDI in PU/PUF microcapsules was 67.3%. Moreover, the surface of PU/PUF microcapsule with many grooves was composed of closely packed sub-micron sized particles (Fig. 2e). Those particles were poly(urea–formaldehyde) polymer nanoparticles from the linear PUF pre-polymer via the condensation of methylol urea and the amino groups under alkaline conditions via a series of reactions at high temperatures [28].

Using these uniform PU/PUF microcapsules as templates, the ALD-treated hybrid microcapsules with a dense and controllable Al_2O_3 nano-layer can be prepared via ALD process for 80 cycles (Fig. 1d and d1). As shown in Fig. 2b, the surface of these formed ALD-treated hybrid microcapsules became smoother and denser because the deposition of Al_2O_3 onto the network of PU/PUF microcapsules. During the atomic layer deposition process, $Al(CH_3)_3$ was firstly adsorbed on the surface or grooves of the PU/PUF microcapsule, and subsequently reacted with the hydroxyl group of H_2O, so the Al_2O_3 nano-shell was formed. Moreover, the coated Al_2O_3 nano-layer provided microcapsules with robust structure for protecting their inner contents while maintaining their size and shape. The ALD-treated hybrid microcapsules deposited for 80 cycles exhibited no obvious change in spherical shape (Fig. 2b–d), while the PU/PUF microcapsules suffered from an obvious collapse of shell structure. Interesting, when increasing the ALD temperature from 120 °C to 180 °C, the surface became much smoother, indicating a much more uniform Al_2O_3 nanoparticles were deposited onto the surface of microcapsule as the temperature rises. However, ALD-treated-120/180 hybrid microcapsules tended to be collapse or aggregated (Fig. 2b and d), which may be resulted from the weak shell structure at a relatively low temperature and the penetration of inner content HMDI into outer surface at a relatively high temperature. And the core content ratio of ALD-treated hybrid microcapsules decreased with the deposited temperature from 120 °C to 180 °C, namely 69.32%, 51.01% and 23.30% for ALD-treated-120/150/180 hybrid microcapsules, respectively. Furthermore, the obtained ALD-treated-180 hybrid microcapsules turned from white into yellow, which may be caused by the formation of polyurea via the polymerization of the diffusion inner content (hexamethylene diisocyanate) with H_2O (Fig. S1). In addition, a ruptured ALD-treated-150 hybrid microcapsule clearly showed a uniform two layers structure with a shell thickness about 2 μm (Fig. S2). Therefore, ALD-treated-150 hybrid microcapsules show good encapsulated efficiency without any rupture and adhesion.

The thermal stability of ALD-treated hybrid microcapsule was evaluated through thermogravimetric analysis (TGA), and compared with the PU/PUF microcapsule (Fig. 3). The free HMDI began to evaporation at 160 °C and continued to loss until 260 °C, while after encapsulation, the inner content encapsulated in PU/PUF microcapsules and ALD-treated hybrid microcapsules began to loss at about 180 °C and 200 °C, respectively, indicating the encapsulated inner content shows a great thermal stability. Moreover, the DTGA plots PU/PUF microcapsule and ALD-treated-180 hybrid microcapsule exhibited three weight losses: the first two weight losses occurred at temperature region 180–330 °C and 330–420 °C were mainly due to the evaporation of inner content HMDI and the decomposition of PUF resin shell [29], the third weight loss from 420 °C to 520 °C reached ~98%, which can be assigned to the decomposition and carbonization of polyurea shell [30]. In contrast, due

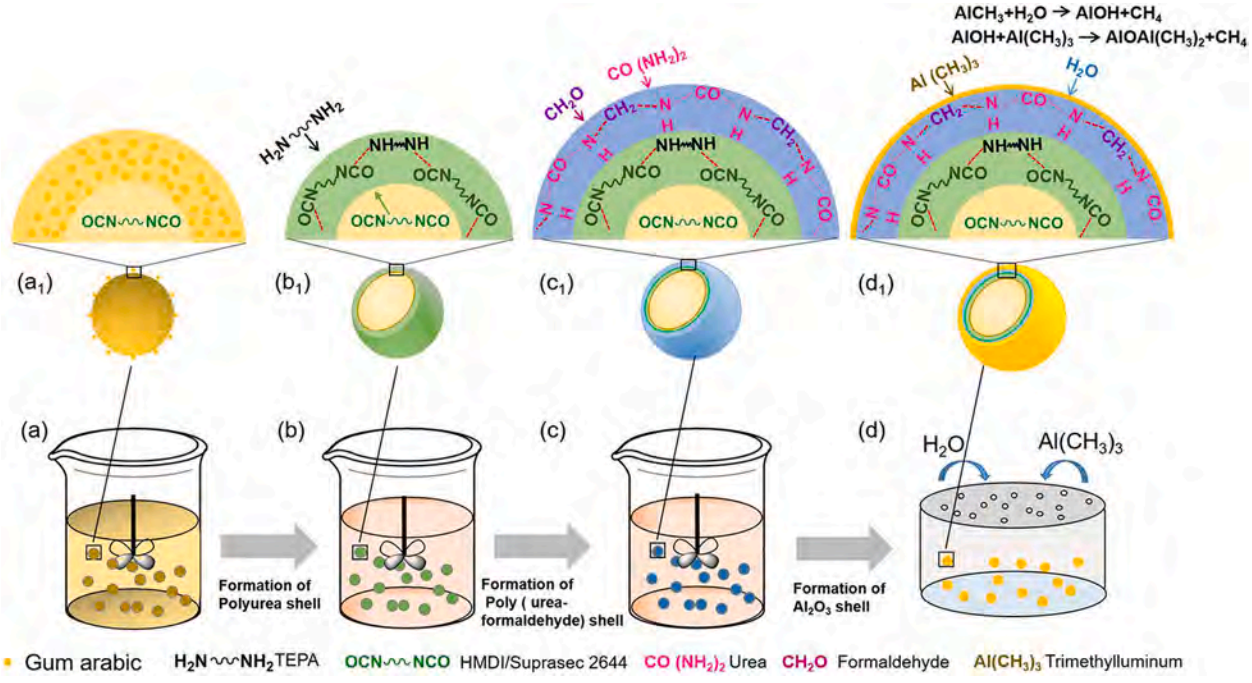

Fig. 1. Schematic illustration for the preparation of ALD-treated hybrid microcapsule: oil-in-water emulsions obtained via emulsification process (a, a1); the inner PU layer of microcapsule formed via interfacial polymerization of Suprasec2644 and TEPA (b, b1); the outer PUF layer of microcapsule obtained via in-situ polymerization of urea and formaldehyde (c, c1); Al_2O_3 nano-layer obtained after ALD treatment (d, d1).

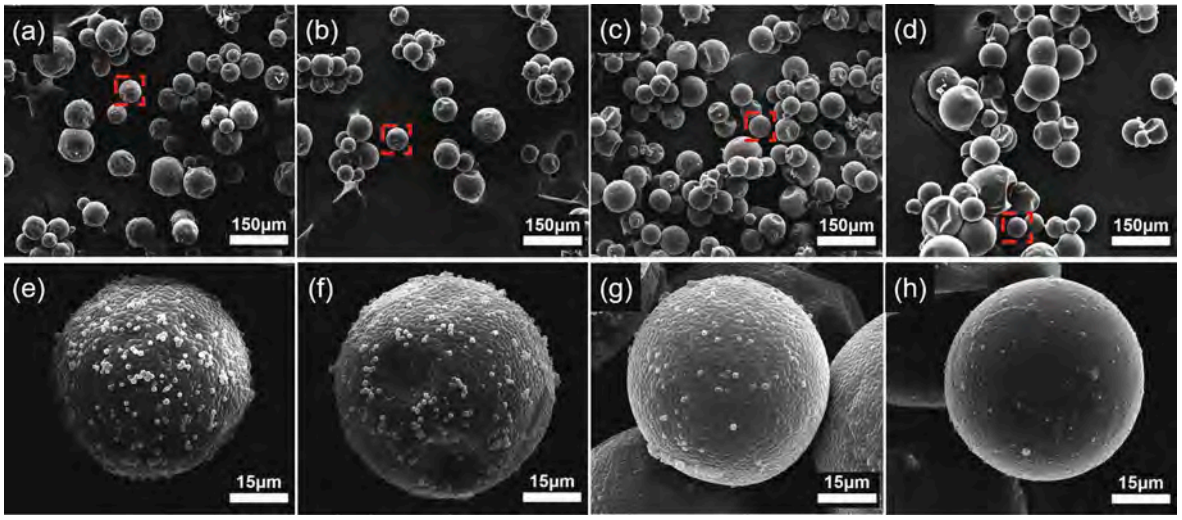

Fig. 2. The obtained microcapsules fabricated at different conditions: PU/PUF microcapsules (a, e), ALD-treated-120 hybrid microcapsules (b, f), ALD-treated-150 hybrid microcapsules (c, g), ALD-treated-180 hybrid microcapsules (d, h).

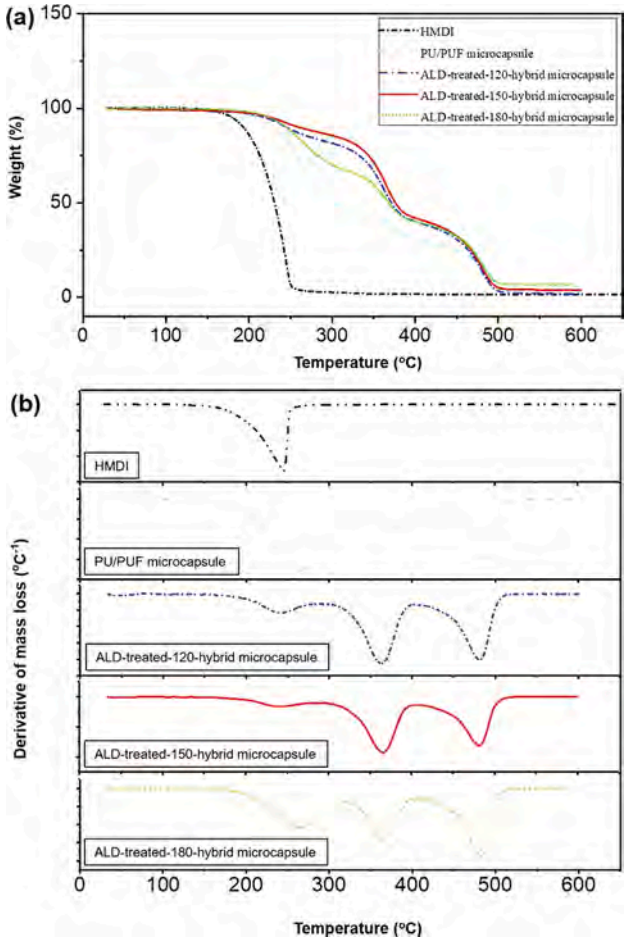

Fig. 3. TGA (a) and DTGA (b) plots of inner content HMDI, PU/PUF microcapsules, ALD-treated-120 hybrid microcapsules, ALD-treated-150 hybrid microcapsules, ALD-treated-180 hybrid microcapsules.

to the existence of dense Al_2O_3 nano-layer, the encapsulated HMDI in ALD-treated-120 and 150 hybrid microcapsules showed a better thermal stability, which began to decompose at a higher temperature of 200 °C and tended to be stable at 330 °C. It was obviously that ALD-treated-180 hybrid microcapsules was less thermally stable than those treated at 120 and 150 °C. The possible reasons may be as follows: during the transformation PU/PUF microcapsules into ALD-treated hybrid microcapsules via ALD process, the PU/PUF microcapsules were kept at 180 °C, 1.0 Torr for several minutes, while the inner content encapsulated in PU/PUF microcapsules began to loss at about 180 °C, which could result in the collapsing or decreased cross-linking density shell structure for the obtained ALD-treated-180 hybrid microcapsules. Moreover, the mass loss at the first stage of PU/PUF microcapsules was much larger than that of the second stage, while the mass loss at the first stage of ALD-treated hybrid microcapsules was much smaller than that of the second stage, which indicate that the improved thermal stability of encapsulated HMDI in ALD-treated hybrid microcapsules. In addition, the deposited Al_2O_3 on ALD-treated-120/150/180 hybrid microcapsules were 0.9%, 2.79% and 5.07%, respectively, which indicate the mass of deposited Al_2O_3 can be increased along with the deposited temperature. The above phenomenons prove that ALD-treated hybrid microcapsules have better thermal stability due to the higher melting point of the dense Al_2O_3 nano-layer. Therefore, ALD-treated-150 °C hybrid microcapsules with good thermal stability and encapsulation efficiency is further characterized.

To further investigate the distribution of Al_2O_3 nana-layer, the morphology of sub-micron sized particle stacked on the surface of the ALD-treated-150 °C hybrid microcapsule deposited for 80 cycles was characterized by TEM. As shown in Fig. 4a, two distinguish region can be observed and the thickness of the outer layer was about 25 nm. The elemental mappings of Al and O were dispersed in two region with a much stronger intensity in the outer layer (Fig. 4b and c), which was possibly resulted from Al_2O_3 nano-layer deposited on the outer surface of sub-micron sized particles. In contrast, the intensity of N and C were relatively lower in the outer layer (Fig. 4d and e), suggesting that the inner layer were mainly composed of PU/PUF polymer. In addition, the shell thickness of the deposited Al_2O_3 nano-layer can be easily controlled via change the deposited cycles, and a much thinner Al_2O_3 nano-layer of 14 nm can be obtained when deposited for 20 cycles (Fig. S3). On the basis of the above analyses, the deposited Al_2O_3 nano-layer with a controlled shell thickness was uniformly distributed on the surface of the ALD-treated hybrid microcapsules, which was beneficial to improve the mechanical property and protect their inner content.

The surface compositions of ALD-treated-150 hybrid microcapsules were further analyzed via the XPS spectrum ranging from 1350 to 0 eV and compared with that of PU/PUF microcapsules (Fig. 5). For PU/PUF microcapsules and ALD-treated-150 hybrid microcapsules, both of them

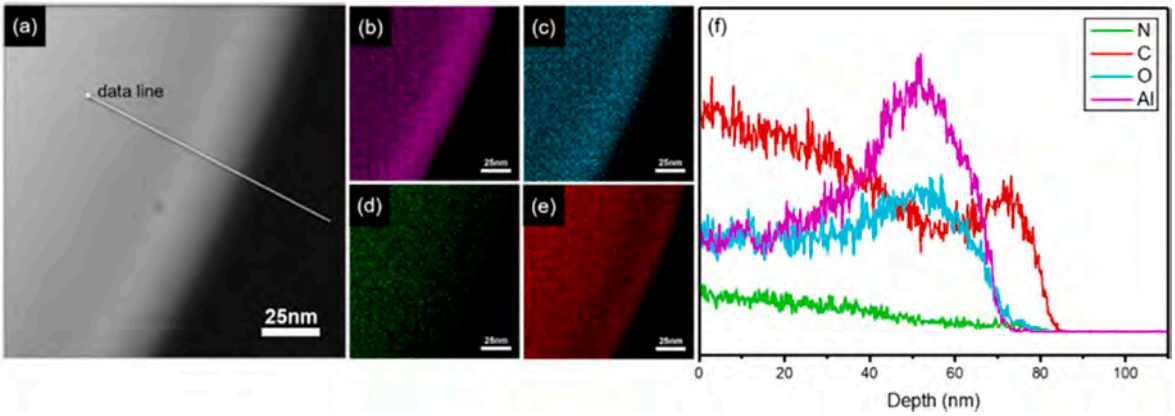

Fig. 4. TEM image of sub-micron polymer particles stacked on the ALD-treated-150 hybrid microcapsules (a) and its corresponding element mapping images (b-e): Al (b), O (c), N (d), C (e), and the corresponding EDX line profiles (f).

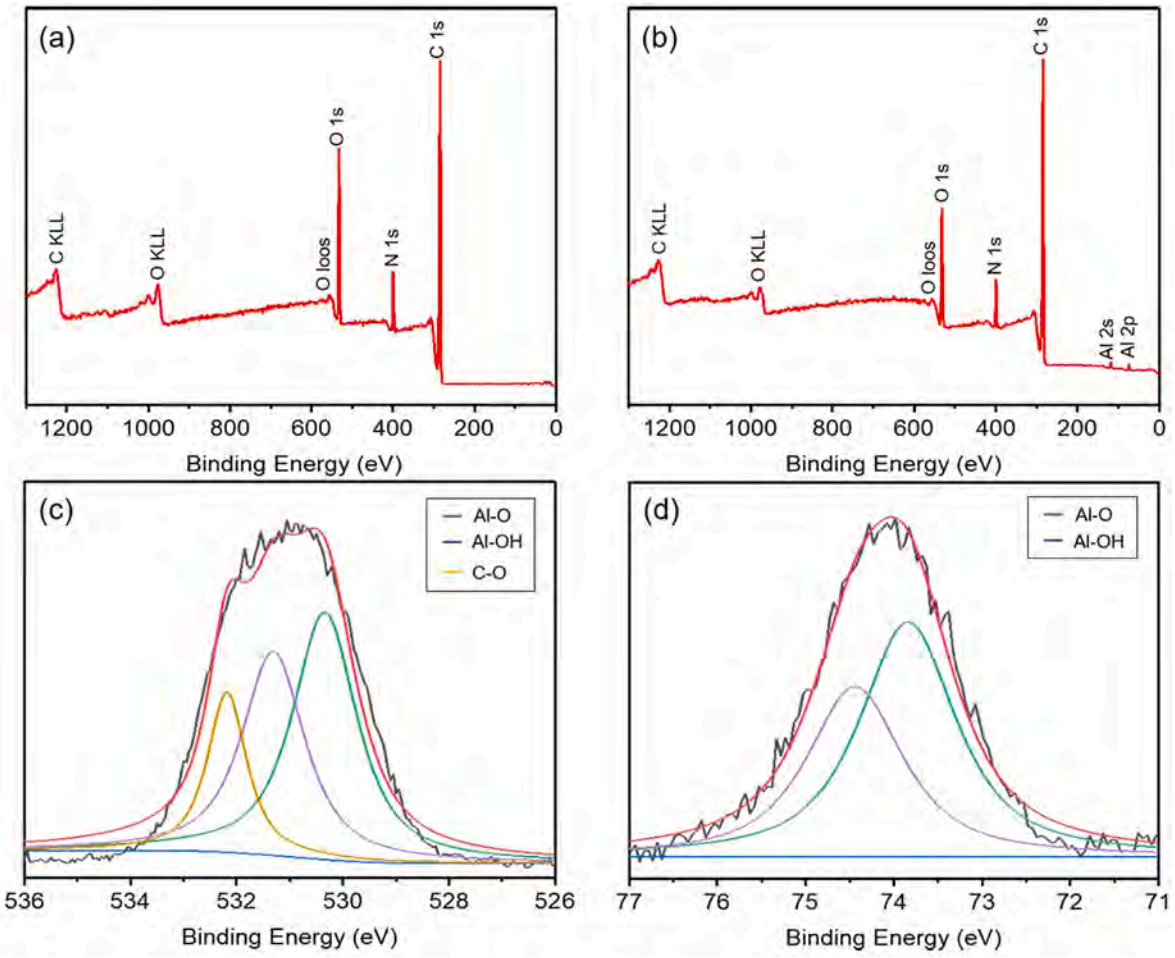

Fig. 5. Survey spectrum of PU/PUF microcapsules (a) and ALD-treated-150 hybrid microcapsules (b). O 1s (c) Al 2p (d) spectrum of ALD-treated-150 hybrid microcapsules.

showed the same peaks belong to electronic state O1s, N1s and C1s and Auger electrons C KLL and O KLL, while two additional peaks for Al 2p and Al 2s were appeared in ALD-treated-150 hybrid microcapsules (Fig. 5a and b), which could prove the successful deposition of Al_2O_3 nano-layer on PU/PUF shell. The intensity of the Al characteristic peak was relatively weak, this is because its low content of nano-sized Al_2O_3 shell. Moreover, the binding energy of the O1s and Al2p components were 531.1 eV and 73.9 eV (Fig. 5c and d), respectively, which agreed well with that of bulk Al_2O_3 [31].

The integrity of microcapsules is virtual important for their self-healing function to composite materials, any rupture before coating damaged would induce inner contents release and lose the function of self-healing. Therefore, ALD-treated-150 hybrid microcapsules embedded in the PC film were used as template to measure their mechanical properties via hot-pressing under a temperature of 90 °C and a high pressure of 0.5 MPa (Fig. 6a). Before hot-pressing, both PU/PUF

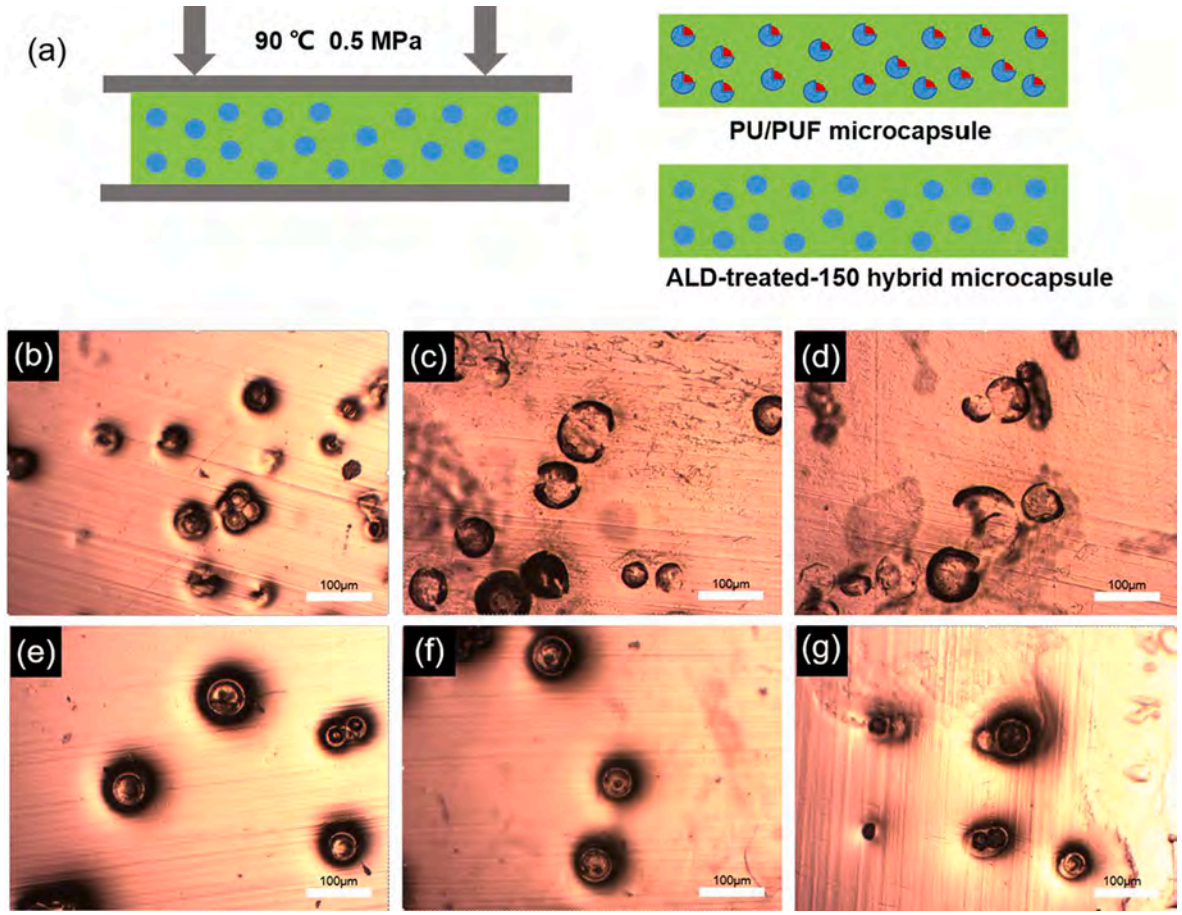

Fig. 6. Schematic illustration of mechanical properties of microcapsules embedded in the PC film via hot-press at 0.5 MPa and 90 °C (a), Optical micrograph of PU/PUF microcapsules-PC film (b–d) and ALD-treated-150 hybrid microcapsules-PC film (e–g) after hot-pressing for 0 min (b, e), 1 min (c, f) and 2 min (d, g).

microcapsules and ALD-treated-150 hybrid microcapsules showed spherical shape without any rupture (Fig. 6b and e). However, PU/PUF microcapsules were entirely ruptured after hot pressing for 1 min and 2 min (Fig. 6c and d). In contrast, all ALD-treated-150 hybrid microcapsules maintained their spherical shape without any rupture after hot-pressing for 1 min and 2 min (Fig. 6f and g). Thus, the mechanical property of the microcapsules was efficiently enhanced by the rigid Al_2O_3 nano-layer shell, which may avoid undesired escape of the encapsulated contents through the rupture shell.

Faced to the corrosion protection requirement of metal alloys used in offshore platform, the main issues that causing corrosion are high concentrations of salt and moisture. Therefore, to obtain a good and long anti-corrosion performance for offshore platform, an epoxy resin film containing 30 wt% microcapsules was pasted onto the surface of steel plate and its anti-corrosion performance was investigated via salt spray test. As a result, the pure epoxy resin coating after a clear cut was unable to protect the steel panel and serious corrosion was occurred after soaking in a salt spray corrosion environment (Fig. 7a and d) for 48 h. Such a poor anticorrosion performance was mainly resulted from the direct contact of salt and steel panel after the epoxy resin coating destroyed. In comparation with pure epoxy resin, a much better anti-corrosion performance of steel panel coated with the epoxy resin containing PU/PUF microcapsules can be obtained (Fig. 7b and e), which may resulted from the releasing of self-healing agent from the integrated PU/PUF microcapsules into the epoxy resin containing PU/PUF microcapsules. However, some corrosion traces along the cut can be observed on the surface of the steel panel after soaking in a salt spray corrosion environment. Those corrosion traces may be related to the early rupture of PU/PUF microcapsules, which may release their inner contents and loss their self-healing function before damage occur. While for the epoxy resin containing ALD-treated-150 hybrid microcapsule coating, an enhanced anticorrosion performance was observed (Fig. 7c and f), namely no obvious corrosion traces can be happened after the salt spray corrosion treatment for 48 h. This obtained anticorrosion performance was much better when compared with recent research by Song et al. [32], namely some corrosion traces were appeared after salt spray testing for 40 h on the surface of steel substrates coated with the polymer coating of 10 wt% PU/PUF microcapsules. This enhanced anticorrosion performance maybe related to the introduction of strengthened hybrid microcapsules and the release of HMDI. This released HMDI from the ruptured microcapsules can heal the crack automatically by reacting with surrounding moisture, sealing the crack rapidly, and retarding corrosion of the steel panel (Fig. 7g). The above results clearly demonstrate that the efficient corrosion protection of self-healing coating containing ALD-treated −150 hybrid microcapsules over the steel panel.

4. Conclusions

In summary, ALD-treated hybrid microcapsules with highly mechanical strength and thermal stability for improved self-healing performance under harsh conditions have been developed via combining ALD technology and interfacial/in-situ polymerization technology. This deposited Al_2O_3 nano-shell was highly controllable, uniform and rigid. The optimized ALD-treated-150 hybrid microcapsule showed a robust mechanical stability under a 90 °C and 0.5 MPa condition, and the pyrolysis temperature of inner content HMDI was significantly improved from 180 °C to 200 °C. In addition, the epoxy resin containing the formed hybrid microcapsules showed an excellent corrosion protection

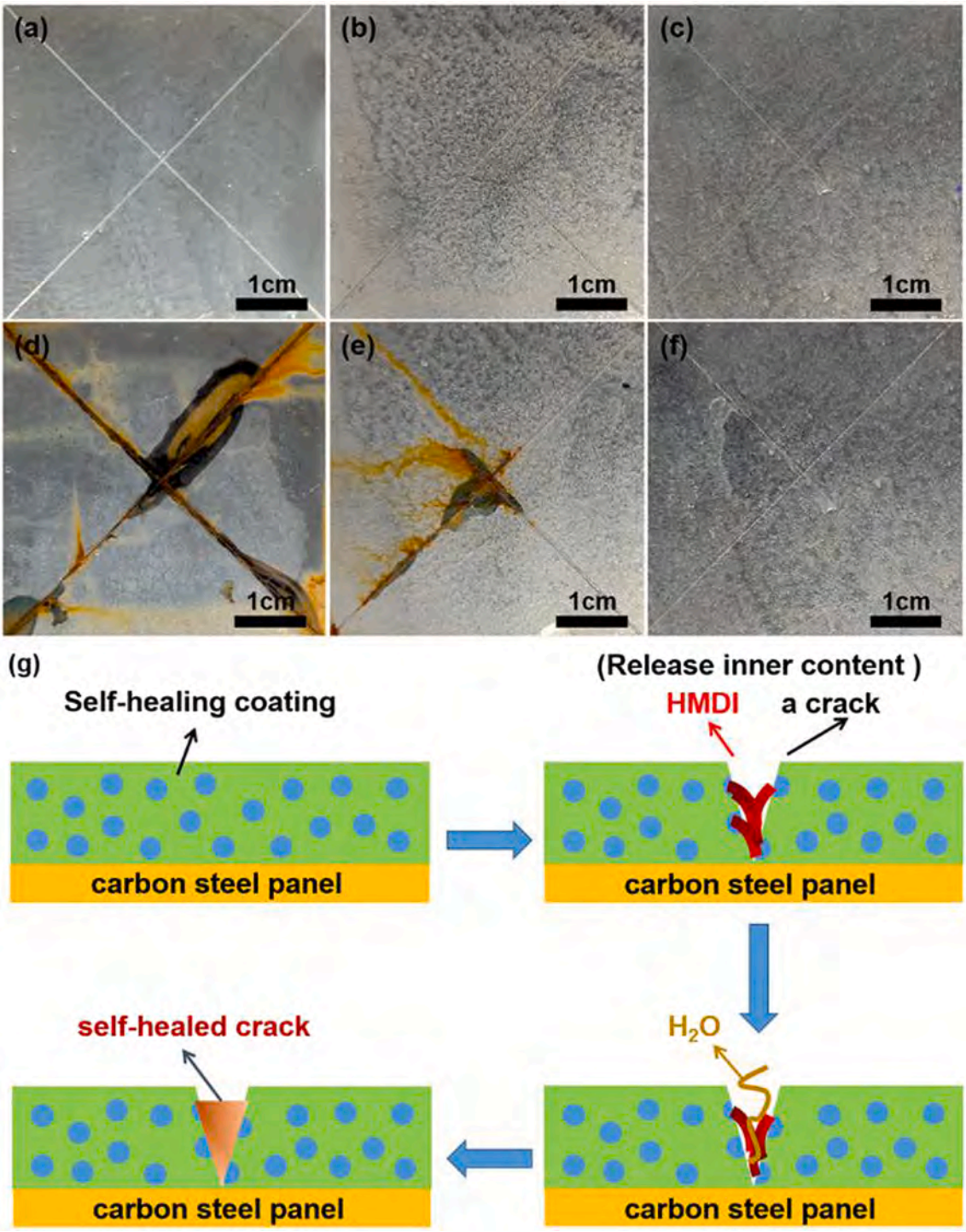

Fig. 7. Corrosion protection of steel panels coated with: pure epoxy resin coating (a, d), self-healing epoxy coating containing 30 wt% PU/PUF microcapsules (b, e) and ALD-treated-150 hybrid microcapsules (c, f). Optical images before (a–c) and after (d–f) salt spray test. Schematic illustration of anticorrosion process via self-healing process in the form of hybrid microcapsules (g).

under an accelerated corrosion process via salt spray corrosion treatment for 48 h. Therefore, this work may open a new opportunity to design a promising microcapsule based self-healing coatings with excellent self-healing performance via a facile synthetic route.

CRediT authorship contribution statement

Fang Wu: Investigation, Data curation. **Junfeng Li:** Writing - original draft. **Heng Quan:** Investigation, Data curation. **Jiang Han:** Visualization, Investigation. **Xiaoxuan Liu:** Formal analysis. **Xiaokun Zhang:** Methodology. **Jinglei Yang:** Supervision, Writing - review & editing. **Yong Xiang:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Optical image of PU/PUF microcapsules and ALD-treated-180 hybrid microcapsule, SEM image of ALD-treated-150 hybrid microcapsule and its broken shell structure, TEM image of sub-micron polymer particles stacked on the ALD-treated-150 hybrid microcapsule deposited for 20 cycles and its corresponding element mapping images. Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2020.148561.

References

[1] S. Chen, T. Han, Y. Zhao, W. Luo, J. Yang, A facile strategy to prepare smart coatings with autonomous self-healing and self-reporting functions, ACS Appl. Mater. Interfaces 12 (2019) 4870–4877.
[2] Z. Sun, L. Zhao, H. Wan, H. Liu, D. Wu, X. Wang, Construction of polyaniline/carbon nanotubes-functionalized phase-change microcapsules for thermal management application of supercapacitors, Chem. Eng. J. 396 (2020) 125317.
[3] C.N. Njoku, W. Bai, I.O. Arukalam, L. Yang, B. Hou, D.I. Njoku, Y. Li, Epoxy-based smart coating with self-repairing polyurea-formaldehyde microcapsules for anticorrosion protection of aluminum alloy AA2024, J. Coat. Technol. Res. 17 (2020) 797–813.
[4] D.W. Sun, Y.B. Chong, K. Chen, J.L. Yang, Chemically and thermally stable isocyanate microcapsules having good self-healing and self-lubricating performances, Chem. Eng. J. 346 (2018) 289–297.
[5] M. Behzadnasab, S.M. Mirabedini, M. Esfandeh, R.R. Farnood, Evaluation of corrosion performance of a self-healing epoxy-based coating containing linseed oil-filled microcapsules via electrochemical impedance spectroscopy, Prog. Org. Coat. 105 (2017) 212–224.
[6] Y. Zhu, K. Cao, M. Chen, L. Wu, Synthesis of UV-responsive self-healing microcapsules and their potential application in aerospace coatings, ACS Appl. Mater. Interfaces 11 (2019) 33314–33322.
[7] H.Y. Li, Y.X. Cui, H.Y. Wang, Y.J. Zhu, B.H. Wang, Preparation and application of polysulfone microcapsules containing tung oil in self-healing and self-lubricating epoxy coating, Colloids Surf. A Physicochem. Eng. Asp. 518 (2017) 181–187.
[8] M.M. Caruso, B.J. Blaiszik, H.H. Jin, S.R. Schelkopf, D.S. Stradley, N.R. Sottos, S. R. White, J.S. Moore, Robust, double-walled microcapsules for self-healing polymeric materials, ACS Appl. Mater. Interfaces 2 (2010) 1195–1199.
[9] W.C. Guo, Y. Jia, K.S. Tian, Z.P. Xu, J. Jiao, R.F. Li, Y.H. Wu, L. Cao, H.Y. Wang, UV-triggered self-healing of a single robust SiO_2 microcapsule based on cationic polymerization for potential application in aerospace coatings, ACS Appl. Mater. Interfaces 8 (2016) 21046–21054.
[10] V.D. Cao, S. Pilehvar, C. Salas-Bringas, A.M. Szczotok, L. Valentini, M. Carmona, J. F. Rodriguez, A.L. Kjøniksen, Influence of microcapsule size and shell polarity on thermal and mechanical properties of thermoregulating geopolymer concrete for passive building applications, Energy Convers. Manag. 164 (2018) 198–209.
[11] H.Y. Li, S. Li, F.B. Li, Z.K. Li, H.Y. Wang, Fabrication of SiO_2 wrapped polystryene microcapsules by pickering polymerization for self-lubricating coatings, J. Colloid Interf. Sci. 528 (2018) 92–99.
[12] F. Wu, W. Wang, L. Liu, X.J. Ju, R. Xie, Z. Liu, L.Y. Chu, Monodisperse hybrid microcapsules with an ultrathin shell of submicron thickness for rapid enzyme reactions, J. Mater. Chem. B 3 (2015) 796–803.
[13] P. Iqbal, T. Lu, Z. Zhang, Y. Li, Preparation of multilayer microcapsules encapsulating aqueous lithium bromide and their mechanical stability, Ind. Eng. Chem. Res. 58 (2019) 6364–6374.
[14] H. Li, Y. Ma, Z. Li, Y. Cui, H. Wang, Synthesis of novel multilayer composite microcapsules and their application in self-lubricating polymer composites, Compos. Sci. Technol. 164 (2018) 120–128.
[15] Y. Liu, L. Li, M. Guo, Z. Zhou, G.X. Chen, Q. Li, Improving dielectric and mechanical properties of $CaCu_3Ti_4O_{12}$ nanowire/epoxy composites through a surface-polymerized hyperbranched macromolecule, ACS Appl. Electron. Mater. 1 (2019) 346–353.
[16] S.M. Wu, L. Yuan, A.J. Gu, Y. Zhang, G.Z. Liang, Synthesis and characterization of novel epoxy resins-filled microcapsules with organic/inorganic hybrid shell for the self-healing of high performance resins, Adv. Polym. Technol. 27 (2016) 1544–1556.
[17] K.L. Chen, J.L. Zhou, X.G. Che, R.Y. Zhao, Q. Gao, One-stpe synthesis of core shell cellulose-silica/n-octadecane microcapsules and their application in waterborne self-healing multiple protective fabric coatings, J. Colloid Interf. Sci. 566 (2020) 401–410.
[18] M. Ge, J.T. Miao, L. Yuan, Q. Guan, G. Liang, A. Gu, Building and origin of bio-based bismaleimide resins with good processability, high thermal, and mechanical properties, J. Appl. Polym. Sci. 135 (2017) 45947.
[19] M.W. Keller, N.R. Sottos, Mechanical properties of microcapsules used in a self-healing polymer, Exp. Mech. 46 (2006) 725–733.
[20] D. Sun, H. Zhang, X. Zhang, J. Yang, Robust metallic microcapsules: a direct path to new multifunctional materials, ACS Appl. Mater. Interfaces 11 (2019) 9621–9628.
[21] X. Zhou, W. Li, L. Zhu, H. Ye, H. Liu, Polymer-silica hybrid self-healing nano/microcapsules with enhanced thermal and mechanical stability, RSC Adv. 9 (2019) 1782–1791.
[22] G. Leroux, M. Neumann, C.F. Meunier, A. Fattaccioli, C. Michiels, T. Arnould, L. Wang, B.L. Su, Hybrid alginate@TiO_2 porous microcapsules as a reservoir of animal cells for cell therapy, ACS Appl. Mater. Interfaces 10 (2018) 37865–37877.
[23] F. He, L. Mei, X.J. Ju, R. Xie, W. Wang, Z. Liu, F. Wu, L.Y. Chu, pH-responsive controlled release characteristics of solutes with different molecular weights diffusing across membranes of Ca-alginate/protamine/silica hybrid capsules, J. Membr. Sci. 474 (2015) 233–243.
[24] K. Li, H. Li, Y. Cui, Z. Li, J. Ji, Y. Feng, S. Chen, M. Zhang, H. Wang, Dual-functional coatings with self-lubricating and self-healing properties by combining poly (urea–formaldehyde)/SiO_2 hybrid microcapsules containing linseed oil, Ind. Eng. Chem. Res. 58 (2019) 22032–22039.
[25] W. Liu, Y. Zhao, C. Zeng, C. Wang, C.A. Serra, L. Zhang, Microfluidic preparation of yolk/shell ZIF-8/alginate hybrid microcapsules from Pickering emulsion, Chem. Eng. J. 307 (2017) 408–417.
[26] F.J. Rossier-Miranda, K. Schroën, R. Boom, Microcapsule production by an hybrid colloidosome-layer-by-layer technique, Food Hydrocoll. 27 (2012) 119–125.
[27] E.D. Bartzoka, H. Lange, G. Poce, C. Crestini, Stimuli-responsive tannin-FeIII hybrid microcapsules demonstrated by the active release of an anti-tuberculosis agent, ChemSusChem 11 (2018) 3975–3991.
[28] Y. Li, G.Q. Wang, Z.H. Guo, P.Q. Wang, A.M. Wang, Preparation of microcapsules coating and the study of their bionic anti-fouling performance, Materials 13 (2020) 1669–1684.
[29] S. Parsaee, S.M. Mirabedine, R. Farnood, F. Alizadegan, Development of self-healing coatings based on urea-formaldehyde/polyurethane microcapsules containing epoxy resin, J. Appl. Polym. Sci. 137 (2020) 46993–47007.
[30] D.W. Sun, J.L. An, G. Wu, J.L. Yang, Double-layered microcapsules with excellent thermal and non-polar solvent resistance for self-healing coatings, J. Mater. Chem. A 3 (2015) 4435–12502.
[31] P. Borylo, K. Lukaszkowicz, M. Szindler, J. Kubacki, K. Balin, M. Basiaga, J. Szewczenko, Structure and properties of Al_2O_3 thin films deposited by ALD process, Vacuum 131 (2016) 319–326.
[32] Y. Song, K.F. Chen, J.J. Wang, Y. Liu, T. Qi, G.L. Li, Synthesis of polyurethane/poly (urea-formaldehyde) double-shelled microcapsules for self-healing antiorrosion coatings, Chin. J. Polym. Sci. 38 (2020) 45–52.