SELF-ASSEMBLED GRAPHENE OXIDE MICROCAPSULES REINFORCED WATERBORNE POLYURETHANE COMPOSITE COATINGS FOR SELF-HEALING PROPERTIES

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ABSTRACT

Self-healing microcapsules were filled with a glue-like chemical that can repair damage and recover the original functions of the materials. However, most microcapsules are currently prepared with thick polymeric shell, not only weakening the matrix material in which they're embedded, but also involving tedious synthesis and filtration process. In this work, graphene oxide (GO) was employed as the microcapsule shells. We developed a single self-assembly process for microcapsule preparation through Pickering emulsion method. Graphene oxide microcapsules (GOMCs) with nanometer-thick shells were realised through the liquid crystalline assembling of building blocks of GO sheets. The GOMC were embedded into waterborne polyurethane matrix to prepare a self-healing polymer composite coating on metal surfaces. The anticorrosion properties and self-healing effects were achieved.

1 INTRODUCTION

Polymeric coatings are applied on metal surfaces to prevent corrosion reactions. Thermal cycling, mechanical scratch and accumulation of corrosion products make the coatings vulnerable to cracks/microcracks, which is followed by acceleration of corrosion reactions. Inspired by the self-healing properties of living-organism, self-healing materials attracted great research attention. The self-healing materials realized by microcapsule technology were proposed in 2001 by S.R. White [1]. The material design of the microcapsules was of great importance for preparing the self-healing materials. The requirements for the microcapsule materials include: 1) the efficient response to the triggering condition, like internal microcracks initiation; 2) upon releasing, the healing agent can flow into the cracks and then solidify; 3) the microcapsule shells can protect the healing agent from premature or leakage; 4) the microcapsules can store enough amount of healing agent and disperse uniformly in the matrix materials. To fulfill the requirements, the shell materials should have good barrier properties, good compatibility with the surrounding matrix, as well as being thin and robust.

Polymeric shells were most extensively studied in literatures, including polyurea-formaldehyde, [2] polyurethane, [3] polyuria [4] and polystyrene. [5] Typically, the monomers were assembled at the interface of Pickering emulsion. After the in-situ polymerization, the polymeric shells were prepared and the core materials were encapsulated. [6] To allow the formation of a integrate and robust polymeric shells, the thickness of the shell usually ranged from sub-micron size [8] to tens of microns [9], which sacrificed the efficiency on storage and releasing of healing agent. The instantaneous response of the healing effect may be affected. Besides, the in-situ polymerization involves tedious synthesis and filtration process, using a lot of organic solvents, which was not environmental-friendly.

Here, we proposed the graphene oxide (GO) as the microcapsule shells. The unique structure of GO made it amphiphilic, flexible and impermeable to small molecules. The amphiphilic properties were originated from the hydrophilic properties of carboxyl and hydroxyl groups and the hydrophobic basal plane, [10] which enabled the self-assembly of GO at oil/water interfaces and stabilized

Pickering emulsions. Once assembled at the interface, GO are also deformable by weak forces such as the surface tension at liquid/liquid interface. Compared to other amphipathic spherical particles, GO are two-dimensional layers with large surface area, which is favorable for producing an integral shells and wrap-up the healing agent.

In this paper, we fabricated graphene oxide microcapsules (GOMCs) and embedded them in waterborne polyurethane (PU) matrix to prepare the self-healing composite coatings. Linseed oil, as a catalyst-free polymerizable material, was employed as the core material in GOMCs. Upon the breakage of the GOMCs, linseed oil will fill the cracks and undergo polymerization process by reaction with oxygen.

2 EXPERIMENTS

2.1 Fabrication of GOMCs in Pickering emulsions

GO was prepared by the modified Hummers method from graphite intercalated compound (Asbury Graphite Mills, USA). An aqueous solution of GO (3.7 mg/ml, 5 ml) was mixed with linseed oil (0.37 g) by high shear mixing at 800 rpm for 4 min to prepare Pickering emulsions. PH value of the mixture was adjusted at 3.5~4.5.

2.2 Preparation of GOMCs/PU coatings

The Pickering emulsions was mixed with waterborne PU (NeoRez R-9679, DSM, the solid content is 37%) by magnetic stirring for 2 h. The solid content of the coating was maintained at 25%. HDG sheets (80 mm × 20 mm × 0.5 mm, supplied by Baosteel Ltd. (Shanghai)) were cleaned by alkaline degreaser and flushed by tap water before blowing-dry. The liquid composite coatings were applied on the steel surfaces with a bar coater and then the coated steel sheets were baked in an oven at 110 C° for 30 min. Control samples were coated by neat PU at the same conditions.

2.3 Characterization

A polarized light optical microscopy (POM, Zeiss Axio Imager A2m) was employed to characterize the Pickering emulsions, as well as the wet composite coatings. Scanning electron microscope (SEM, Quanta FEG450 FEI Co., Ltd, USA) was utilized to observe the morphology of GOMCs, the dispersion of GOMCs in waterborne PU, the self-healing effects of the composite coatings. The morphology of GO shell was studied by transmission electron microscope (TEM, Tecnai G2 F30), operating at an accelerating voltage of 300 kV. For TEM sample preparation, the microcapsules were supported by a copper mesh with porous carbon film, which was heated from 25 oC to 400 oC at a rate of 2 oC/min, followed by an isothermal treatment at 400 oC for 1 h within an argon atmosphere. Solution phase small/wide angel X-ray scattering (SWAXS) experiments were performed by SAXSess mc2. The generator was operated at 50 kV. The microstructure of GOMCs/PU composites was investigated by an X-ray diffractometer (XRD, D8-Advanced diffractometer system from Bruker with Cu Kα radiation). Digital Microscope (Leica DVM6) was used to evaluate the 3D morphological change upon the healing process.

The salt spray test was carried out on coated HDG plates (40 mm × 80 mm) with a 5% NaCl solution at 100% relative humidity at 35 oC according to ASTM B117-03.

The scratch was introduced manually with a scalpel blade, ensuring to reach the metallic substrate. The samples were placed under ambient condition waiting for self-healing.

3 RESULTS AND DISCUSSION

3.1 Formation of GOMCs through the self-assembly of GO

Graphene oxide (GO) is a unique two-dimensional surfactant due to its amphiphilicity [10]. It can adhere to the water/oil interfaces spontaneously and lower the interfacial energy, stabilizing the Pickering emulsion. As schematically described in Figure 1, the GO sheets assembled spontaneously at the water/linseed oil interface during the high shear mixing of the GO aqueous dispersion and the linseed oil. The Figure 2a showed the Pickering emulsion which can keep stable for over one month at ambient condition. The distinct shining halos were observed around the droplets in the Pickering emulsion under polarized optical microscope (Figure 2b). The bright rings were generated by the

birefringence and the anisotropic structure of the shell, which revealed the liquid crystal feature. The average diameter of the GOMCs was measured to be around 8um.

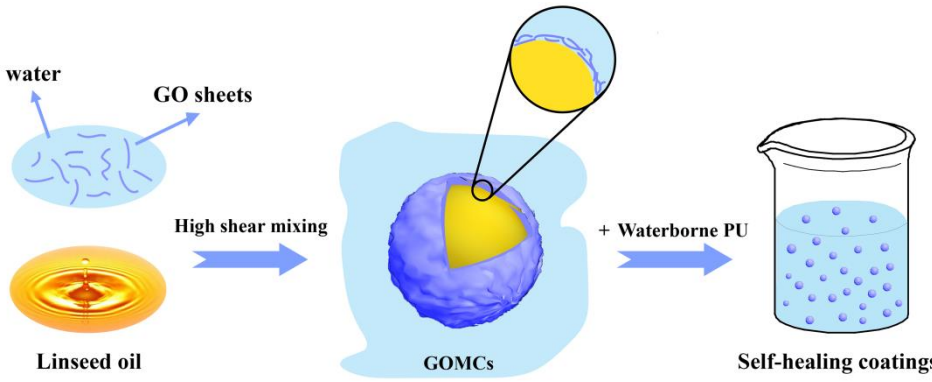

Figure 1. Schematics of GOMCs formation in Pickering emulsion and the preparation of GOMCs/PU coatings.

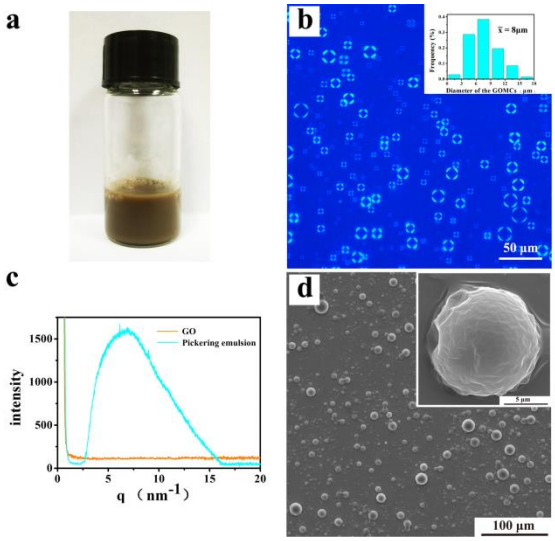

Figure 2. (a) Pickering emulsion placed for one month; (b) POM image of GOMCs in Pickering emulsion; inset: size distribution of GOMCs in Pickering emulsion; (c) SWAXS patterns for the Pickering emulsion and GO aqueous dispersion; and (d) SEM morphologies of GOMCs with different magnifications.

Solution phase small/wide angel X-ray scattering (SWAXS) patterns were shown in Figure 2c. The SWAXS spectrum of GO solution did not show any peaks due to the random orientation of GO sheets in the diluted solution. The GO-stabilized Pickering emulsion featured a broad peak at the scattering vector of 6.5 nm^{-1}, corresponding to an interlayer space of 0.97 nm, confirmed the liquid crystal structure of GO shell. The SEM micrographs of GOMCs were shown in Figure 2d with higher magnification inseted. The spherical shaped GOMCs were scattered on a silicon substrate. With higher magnification, the wrinkles of GO was clearly shown on the surfaces of GOMCs, which evidenced the shell of the microcapsules was composed of GO sheets.

3.2 Factors on the stability of the Pickering emulsion

The mass ratio between GO and linseed oil was a critical factor for the formation of GOMCs. Lack of the GO will result in the insufficient encapsulation and the leakage of linseed oil. Figure 3 (a) presented the POM images of the Pickering emulsion with the GO/linseed oil mass ratio of 1%, 3%,

5%, 7%. When the GO/linseed oil mass ratio was 1% and 3%, the size of GOMCs varied significantly and some of the bright rings did not show the liquid crystal feature, which was corresponding to an unstable emulsion, as shown in the inset of Figure 3(e). When GO/linseed oil mass ratio was 5% and 7%, the Pickering emulsions can keep stable for over six month at ambient condition (Figure 2e, inset) and the GOMCs are uniform in sizes. We measure the size of the bright rings and take the average value of the 1000 rings as presented in Figure 3(e). The average size of the linseed oil droplets was decreased with increasing the amount of GO and reached an plateau when the GO GO/linseed oil mass ratio was over 5%. The SEM micrographs of GOMCs prepared at GO/linseed oil mass ratio of 5% and 7% were shown in Figure 3f-g with higher magnification inseted. The spherical shaped GOMCs were scattered on a silicon substrate. With higher magnification, it is clear that the surface of GOMCs is wrinkling, which evidenced the shell of the microcapsules was composed of GO sheets. The clear morphology of the shell indicated that linseed oil was well wrapped-up, without sticking to the outer surface of the microcapsules.

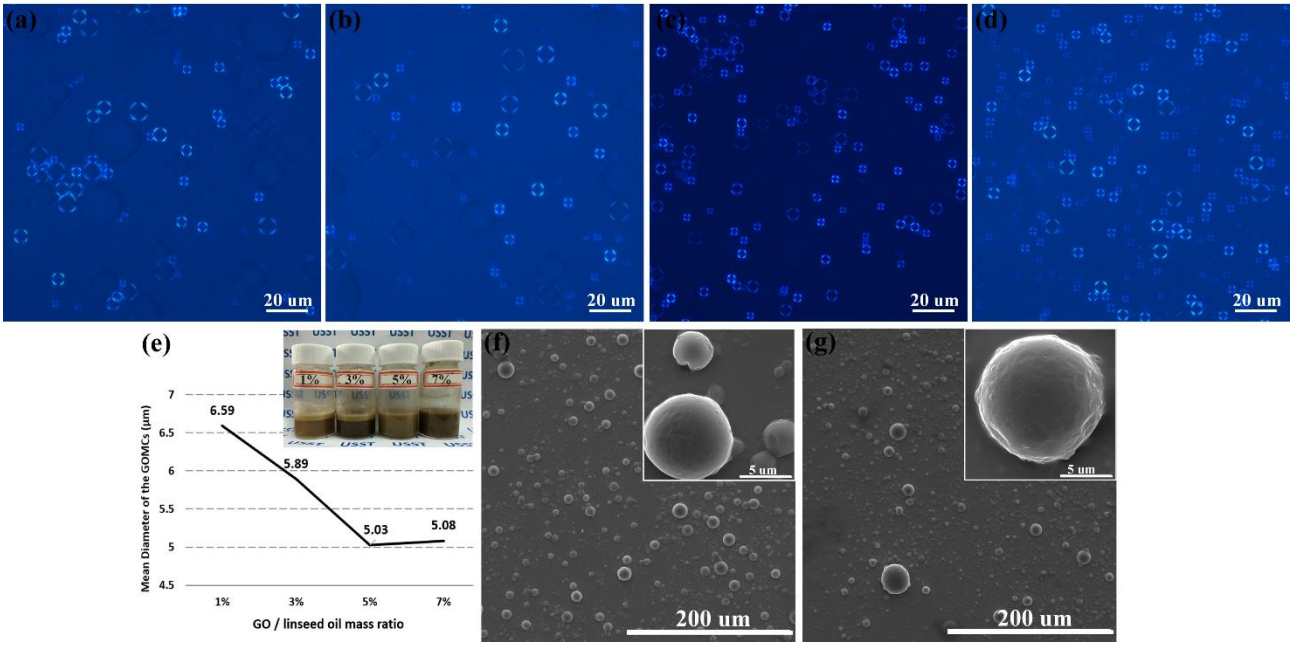

Figure.3 POM images of GOMCs in Pickering emulsions preparation at different GO/linseed oil mass ratio: (a) 1%, (b) 3%, (c) 5%, (d) 7%. (e) average GOMCs diameter as a function of GO/linseed oil mass ratio. Inset: digital image of the Pickering emulsions placed for six months. SEM morphologies of GOMCs with different magnifications preparation at different GO/linseed oil mass ratio: (f) 5%, (g) 7%. (oil/water ratio: 0.08, shear duration:4min)

Being a two-dimensional surfactant to stabilize the Pickering emulsions, GO's hydrophilic mainly originated from the carboxyl group on the edges. Therefore, the hydrophilic of GO sheets can be change by varying the pH value of GO aqueous solution. As the increase of the pH value, the GO sheets with abundant carboxyl groups became increasingly charged through ionization, which would result in a higher hydrophilicity. The zeta potential value increased with the pH as shown in Figure 4(a). The Pickering emulsion was stable when the pH value equalled to 3, as shown in Figure 4(b). As the increasing of the pH value, GO sheets changed from amphiphilic to hydrophilic, so that they escaped from the oil/water interface and dissolved in the water. Figure 4(b) showed a phase separation between water and oil. The bottom layer was water phase, which exhibited darker colour because of the dispersing of the GO. The size of the bright rings in POM images showed increased size with increasing the pH value, which was agreed with the instability of the emulsion.

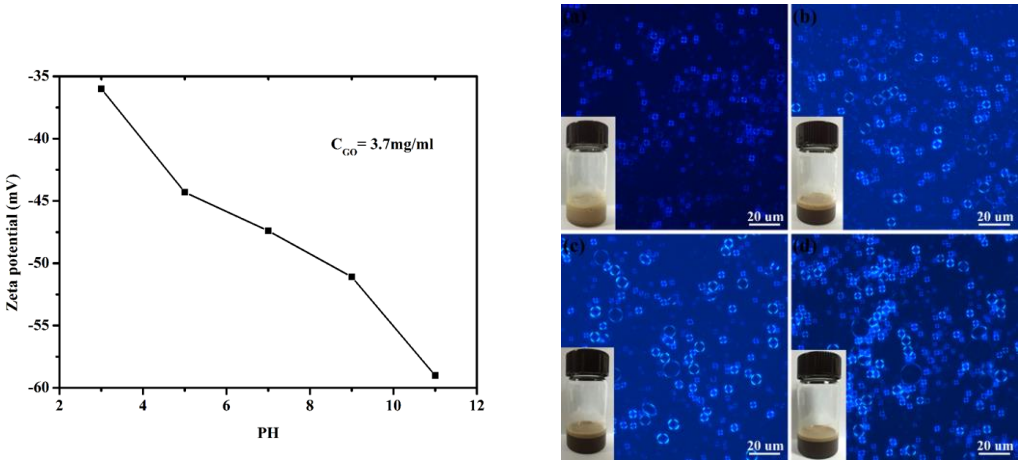

Figure.4 (a) Zeta potentials of GO aqueous solution at different pH values; (b) POM images and photographs 24 h after preparation of GOMCs in Pickering emulsions at different pH value of 3, 5, 7 and 9.

3.3 The self-healing and anticorrosion properties of GOMCs/PU coatings.

The 3D optical microscope images in Figure 5 presented the healing effect of the GOMCs/PU coatings in a different scale. As scratched coating showed a crack with depth of around 25μm, roughly equal to the thickness of the coatings, which meant the scratch had reached the surface of the metal substrate. After 15 d healing, the scratch was completely filled and the integrity of the coating was recovered.

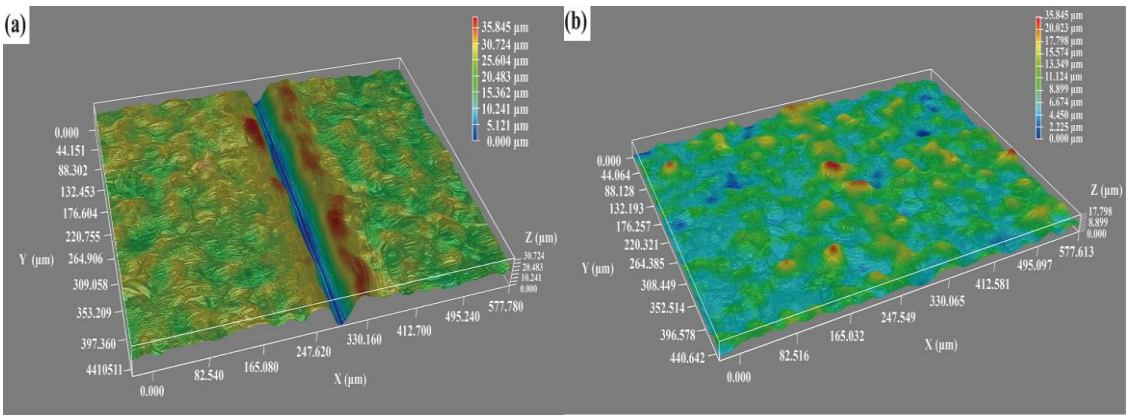

Figure.5 3D digital microscope images of the GOMCs/PU coatings (a) before and (b) after 15d of healing.

The anticorrosion properties of neat PU coatings and GOMCs/PU composite coatings were characterized by SST on HDG substrates. As demonstrated in Figure 6(a-b), the HDG plate coated with GOMCs/PU coatings showed no visual evidence of corrosion even after 116 h SST, while some white corrosion products were observed on the neat PU coated HDG plate. The GOMCs/PU composite coatings exhibited better anticorrosion properties than neat PU, which could be addressed by two reasons: 1) the barrier effect of the GO shell elongated the pathway of the corrosive medium. As the schematic drawing in Figure 6b, the diffusion of the small molecules, like H2O and O2, could be restrained by the physical barrier of GO shell; 2) the micro-cracks in the composite coatings was healed spontaneously, without being noticed, which retarded the corrosion process.

The neat PU and GOMCs/PU coatings were manually scratched with a scalpel blade respectively and placed 15 d under ambient condition for healing. After 43 h of SST, images of the coated HDG samples were taken as shown in Figure 6(c-d). White corrosion products accumulated along the X-

shaped scratch for the neat PU coated HDG plate. In contrast, no corrosion products can be seen on the HDG plate coated with the GOMCs/PU coatings. Even the X-shaped scratch became blurry due to the self-healing of the composite coating, which can be faintly seen with higher magnification as the inset in Figure 6d. As the schematics shown in Figure 6 (d), the GOMCs ruptured when the crack was introduced. The linseed oil encapsulated in the GOMCs was released and filled the cracks. After the oxidation/polymerization reaction, the linseed oil solidified and healed the cracks. The 15 d of healing duration allowed sufficient time for the oxidation reaction of the linseed oil.

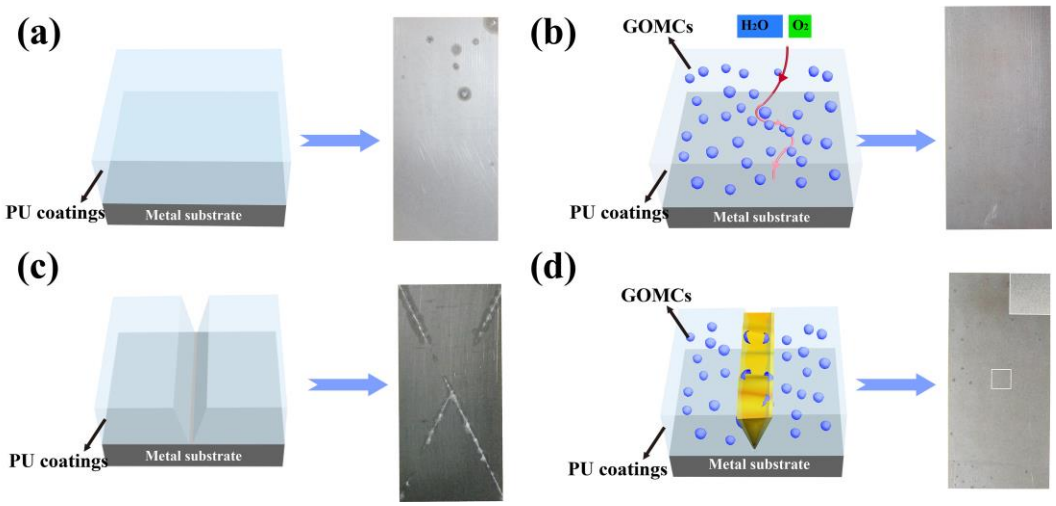

Figure.6 Schematic and images of (a) neat PU coating and (b) GOMCs/PU coatings, subjected to the salt spray test for 116 h. Schematic and images of (c) neat PU coating and (d) GOMCs/PU coatings after scratch and 15 d of healing, subjected to the salt spray test for 43 h. Inset: the enlarged view of the white block.

4 CONCLUSIONS

GOMCs were fabricated through the self-assembly of the GO sheets at oil/water interfaces in Pickering emulsions. The spherical-shaped GOMCs are composed of nanometer-sized GO shell with a liquid crystalline structure and linseed oil as healing agent. The GOMCs were embedded into waterborne PU matrix to prepare self-healing coatings. The self-healing properties of the GOMCs/PU coatings were proven by SEM and 3D optical microscope observations, as well as the SST results.
The GO shell prepared in this study can fulfill the requirement of microcontainers included the mechanical stability, the compatibility between the shell and the coating matrix, sufficient loading capacity, effective storage of healing agent, as well as the facile fabrication approach.

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