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Pickering emulsion-based fabrication of epoxy and amine microcapsules for dual core self-healing coating

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ABSTRACT

Facile and efficient encapsulation of epoxy and tetraethylenepentamine (TEPA) in polyurea (PU) microcapsules are accomplished with Pickering emulsion templates by one-step, interfacial polymerization. The formation of microcapsule is deftly achieved by lightly shaking Pickering emulsions. The whole process is time andenergy saving hardly with any waste and residual. Epoxy microcapsules keep the spherical shape with core content of more than 90 wt%. Amine microcapsules shrink a little for evaporation of water and the conserved TEPA after air-dried is 82.1 wt%. The shell walls of two microcapsules are about 1 μm. With the protection of PU shells, both microcapsules exhibit excellent thermal resistance. Furthermore, self-healing function of epoxy and amine microcapsules is measured by incorporating microcapsules into epoxy coating, and tested by brine-submersion corrosion-accelerating experiment. The dual core self-healing coatings demonstrate excellent self-repairing performance with the crack of embedded microcapsules and reaction between epoxy and amine. The core materials can outflow from microcapsules and form isolations for metal substrate from corrosion hazard, therefore, make for good self-repairing and preserving function of the self-healing coating.

1. Introduction

Self-healing materials, as the important part of smart and bio-inspired materials, can automatically respond to external stimuli, repair the damage, and maintain the function and property. They have great potential in many applications, including automobile, aviation and aerospace industry [1–6]. Since the first generation healing system reported by White et al. [1], microcapsule-based self-healing composites or coatings have been intensively reported for efficient repairing performance. Upon damage occurs in materials, the embedded microcapsules are able to crack, and release repairing active chemicals and recover the defect [7–16]. Braun et al. firstly reported self-healing polymer coatings based on polydimethylsiloxane (PDMS)/dimethyldineodecanoate tin (DMDNT) catalyst system [17]. Sottos and Moore et al. conducted a series of research on dual part, and multi-component healing system [18–23]. Yang et al. made major investigations on encapsulation of liquid diisocyanate [24–28]. More recently, Zhang et al. reported a multilayer microcapsule consisted of isolated glycidyl methacrylate and catalyst, which also promoted the development of capsule-based self-healing materials [29].

Among all capsule-based healing system to date, epoxy-amine system is supposed to be one of the most reliable systems [30]. Epoxy is a major substrate applied for self-healing materials. It is desirable and compatible when the repairing chemistry of system is based on epoxy [31]. However, although several attempts have been carried out [32–35], there are still challenging and urgent requires for facile and efficient encapsulations of epoxy and especially, its hardener, with high core content and thermal stability [36,37].

To achieve the breakthrough on these issues, we developed a time and energy saving, one-step approach to prepare microcapsules based on oil-in-water (O/W) and water-in-oil (W/O) Pickering emulsions in this work. Pickering emulsion, different from traditional emulsion, is stabilized by adsorption of solid particles on the oil-water interface, which can endow emulsion with remarkable stability and resistance towards demulsification [38,39]. Meanwhile, the barrier constructed by solid particles in Pickering emulsion can preserve the core materials that required for

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encapsulation, and serve as the framework to form a strengthened shell wall of microcapsules [40]. These advantages give Pickering emulsion considerable superiority in the encapsulation of active liquid with high polarity [41], such as the aliphatic amine, a typical hardener of epoxy.

As the flow diagrams shown in Fig. 1, polyurea (PU) shell microcapsules loaded with epoxy and amine were synthesized by interfacial polymerization of diisocyanate and amine based on O/W and W/O Pickering emulsion templates respectively. Hydrophilic SiO_2 nanoparticles and hydrophobic nanoclays, served as solid stabilizers in emulsion, could be implanted into PU shells to strengthen Pickering emulsion and microcapsule. The emulsification process was accomplished by mixing of oil and water phase and following with high-speed shearing. Then, with protection of Pickering emulsions, epoxy and tetraethylenepentamine (TEPA) were facilely and sufficiently encapsulated in microcapsules after addition of reactive chemicals without any other equipment or manipulation (Fig. S1). The synthesis process was considerably time and energy saving, producing hardly any waste and residual. In addition, dual core self-healing system was prepared by incorporating the obtained epoxy and amine microcapsules into epoxy coating, and applied to test the healing function of the obtained microcapsules. The embedded microcapsules cracked when scratch applied on self-healing coating, followed with the outflow of core materials in epoxy and TEPA microcapsules. The scratched region was then repaired by new materials formed by reaction of epoxy-amine chemistry, indicating the self-repairing performance of these functional microcapsules in coating.

2. Experimental

2.1. Materials

The hydrophilic silica nanoparticles (N20), served as O/W Pickering emulsion stabilizer, were donated from Wacker Chemie AG (Burghausen). The nanoclay (Nanocor 1.44P) used in W/O Pickering emulsion was purchased from Beijing Eastwest specialized chemical company. Polyvinyl alcohol (PVA AH-26, polymerization degree of 2600, alcoholysis degree of 97–98.8%, viscosity of 58–66 mPa s) was purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Polyisobutene (PIB) was supplied by Shangdong Xinya Chemical Industry Co., Ltd. Epoxy resin (E51 CYD-128) and tetraethylenepentamine (TEPA) were bought from Sinopec Corp and TianJin FuChen Chemical Reagents Co., Ltd. Isophorone diisocyanate (IPDI) was supplied by Aladdin Industrial Corporation. Xylene, acetone and ethanol were received from Shanghai Richjoint Chemical Reagents Co., Ltd. Deionized (DI) water in all experiments was purified with Millipore (MA, USA) purification equipment by deionization and filtration to a resistivity above 18.0 MΩ cm.

2.2. Preparation of Pickering emulsions

For O/W Pickering emulsions, 30 mg silica nanoparticles (N20) was dispersed in 6 mL DI water with 1 wt% PVA by ultrasonic concussing at 40 KHz for 1 min. Epoxy resin of 3 g was added to the water phase. The mixture was emulsified with different shear rates from 3000 rpm to 12000 rpm by IKA disperser to form a stable O/W

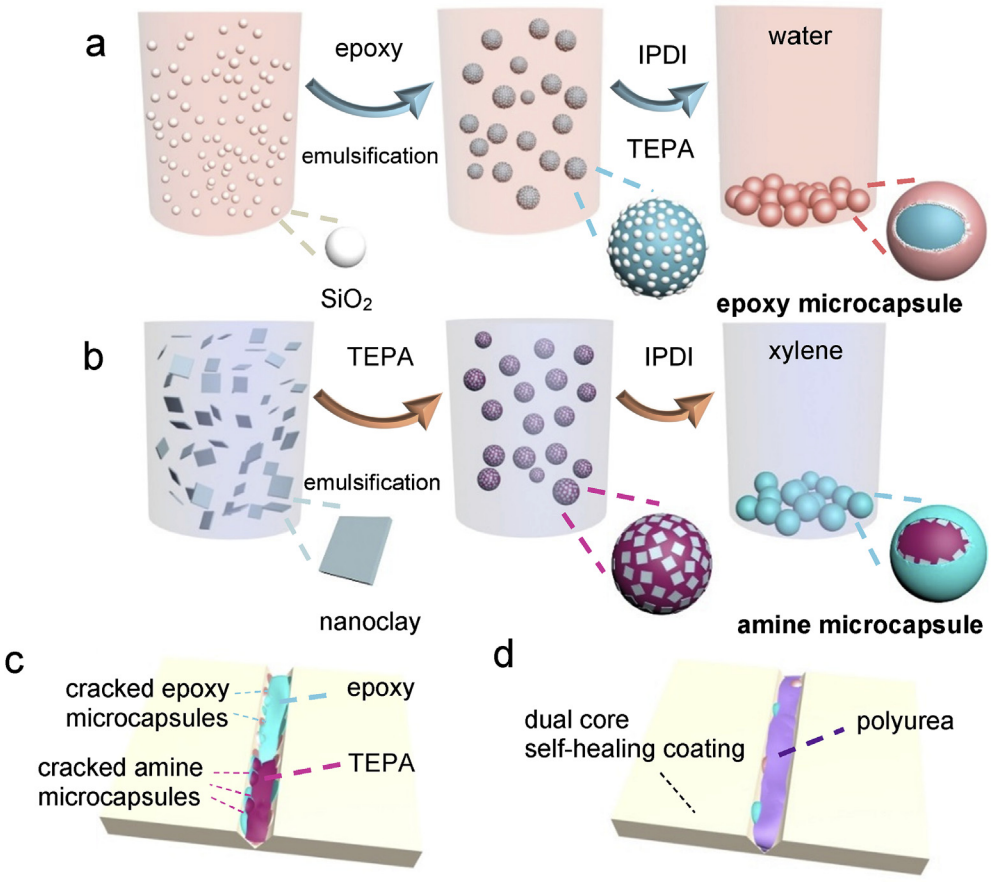

Fig. 1. Synthesis process of (a) epoxy microcapsule and (b) amine microcapsule. Self-healing process: (c) microcapsules embedded in self-healing coating crack upon damage, core materials outflow. (d) TEPA reacts with epoxy to form polyurea and repair the coating.