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Self-healing microcapsules containing rejuvenator with an organic nanocomposite shell

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Novel self-healing microcapsules containing bituminous rejuvenator with nano-calcium carbonate/organic composite shells were developed by in situ polymerization.

In recent years, microcapsules containing healing agents (i.e., that repair damage to the surrounding material) have attracted increasing attention due to their applications in polymeric self-healing materials.[1] Self-healing materials are a class of smart materials into which the capability to repair damage (caused by mechanical usage over time) is structurally incorporated. The inspiration behind these materials originates from the ability of biological systems to heal after being damaged.[1–3] Among such self-healing approaches, the use of self-healing microcapsules relies on the release of an encapsulated healing agent into the damage zone. This is generally a one-off process, as the functionality of the encapsulated healing agent cannot be restored. Nevertheless, these systems are able to restore material integrity to almost 100% and remain stable over the material lifetime.[4]

In recent years, microcapsules containing a 'rejuvenator' material have been applied to enhance the self-healing capability of bitumen. Bitumen, which usually has an application temperature of 180°C in a melting state, is used as a binder between mineral aggregates. Both the mechanical properties and the thermal stability therefore play important roles in determining the deformation and durability of the microcapsules when subjected to external mixing forces with bituminous aggregates, and under high temperatures. Research in this area has indicated that the the addition of inorganic particles—such as nanoclays, nanoparticles (e.g., silicon dioxide, SiO_2, calcium carbonate, $CaCO_3$, and aluminum oxide, Al_2O_3), and carbon nanotubes—can control the behavior (i.e., the thermal stability, mechanical properties, and chemical resistance) of the microcapsules.[5–7] Some pioneering studies have focused on the design of the shell microstructure but, to the best of our knowledge, there are a limited number of studies in the literature that investigate the compactibility of nano-inorganic/organic composite microcapsules containing a liquid healing agent. Nanoparticles can increase the mechanical properties and thermal properties of microcapsules, but are not expected to reduce the compactness of the shell structure.

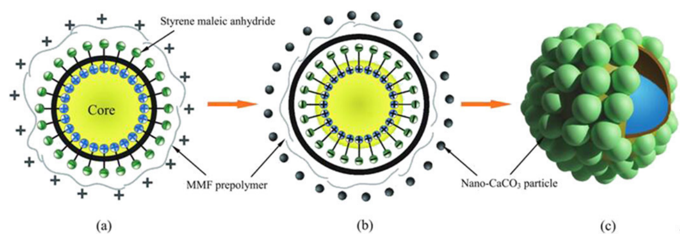

Figure 1. *Illustration of the microcapsule formation process. (a) Hydrated styrene maleic anhydride molecules arrange on core droplets. (b) The methanol modified melamine-formaldehyde (MMF) prepolymer and nanoparticle (calcium carbonate, $CaCO_3$) condensation process occurs. (c) The structure of the final microcapsule is achieved, with a nanoparticle/polymer composite shell structure encapsulating the rejuvenator.*

In our work,[8] we have investigated an approach for exploring simple, inexpensive, robust, and environmentally friendly microcapsules with enhanced mechanical properties, thermal stability, and compactibility for application in bitumen. Our main motivation was to design reliable microcapsules with a nano-inorganic/organic shell structure. We achieved this by fabricating a shell composed of methanol-modified melamine-formaldehyde (MMF) resin and $CaCO_3$ nanoparticles. The structure of our microcapsules can be adjusted by altering the polymerization process and nanoparticle content.

We fabricated microcapsules containing rejuvenator by a coacervation process consisting of three steps: see Figure 1. We reported a similar forming mechanism in our previous work.[4] First, the oily rejuvenator is dispersed by styrene maleic anhydride (SMA) molecules. In this core-material emulsion step, SMA molecules are hydrolyzed by sodium hydroxide (NaOH) and are then inserted as a dispersant into

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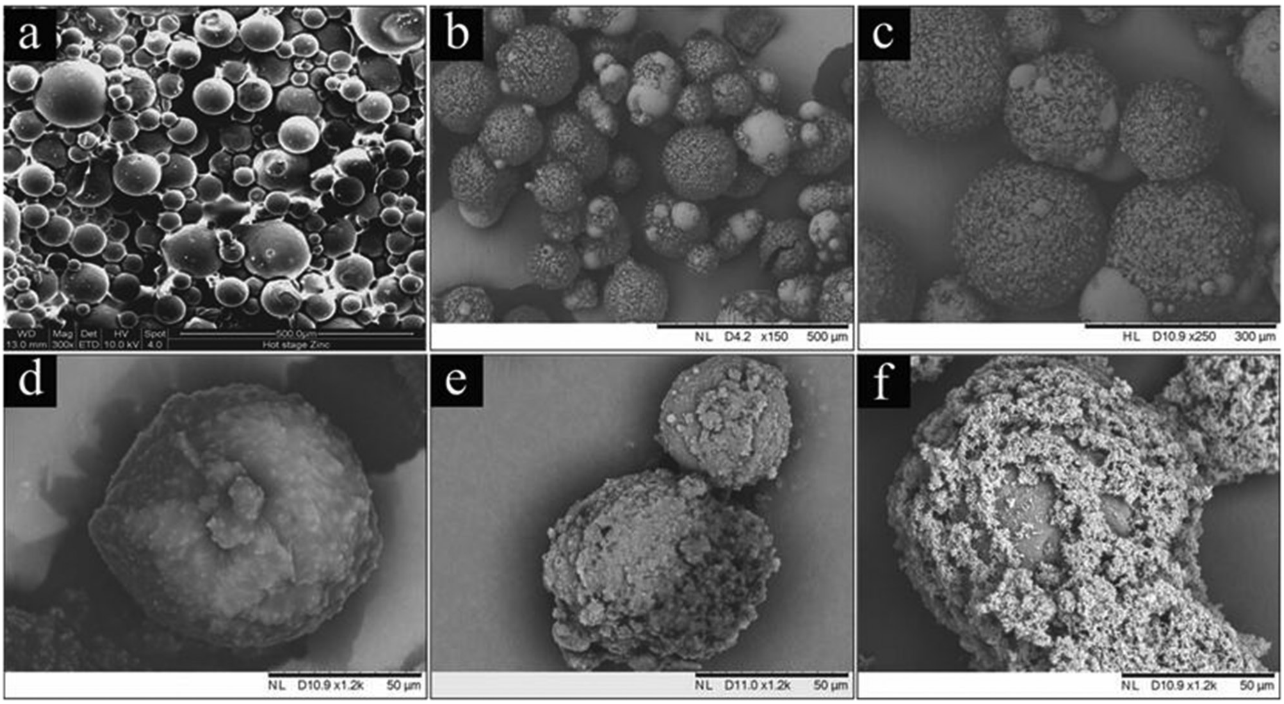

Figure 2. *Environmental scanning electron microscope morphologies of microcapsule samples with nano-$CaCO_3$ contents of (a) 1%, (b, c) 2%, (d) 3%, (e) 5%, and (f) 8%.*

the oil droplets. Because of the directional arrangement (hydrophobic groups oriented toward the center of the droplets and hydrophilic groups oriented outward), a strong electron (i.e., negative) charge layer is formed on the surface of the droplets. The MMF molecules then assemble on the surface by electrostatic attraction. Under suitable polymerization conditions, the inner layer of the shell is formed with a cross-linked MMF structure. After titration of $CaCO_3$ nanoparticles and half of the MMF-prepolymer hybrid, the MMF-prepolymer molecules attach to the surface of the inside layer with the help of the remnant electrostatic force.[9] At the same time, the nano-$CaCO_3$ particles promote chain entanglement (due to electrostatic attraction), thus causing them to adhere to the droplet surface. At an equilibrium point, the other half of the MMF-prepolymer molecules are cross-linked to form the outer layer of the nano-inorganic/organic shells.

We analyzed the morphologies of the microcapsules with and without nanoparticles using an environmental scanning electron microscope (see Figure 2). The microcapsules with nanoparticles included nano-$CaCO_3$ at weight contents of 1, 2, 3, and 5% (MS-1, MS-2, MS-3, and MS-5, respectively). When piled together, the microcapsules have a mean size of about 50μm. Because microcapsule formation in this study is a coacervation process, the addition of nanoparticles can greatly affect the morphology of the shells. Optimization of the $CaCO_3$

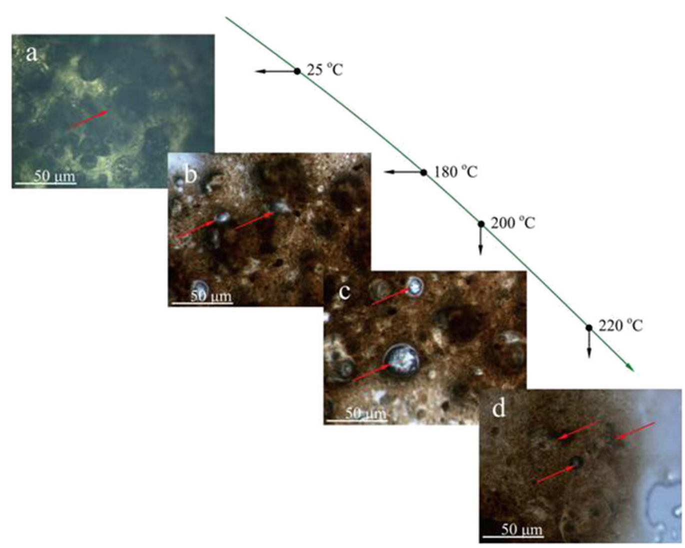

Figure 3. *Optical morphologies of a polymer/nano-$CaCO_3$ microcapsule (with a nano-$CaCO_3$ loading of 5wt%) in bitumen under temperatures of (a) 25, (b) 180, (c) 200, and (d) 220°C.*

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nanoparticle content is therefore necessary to ensure that the core material is well protected by its shell. We carried out this optimization directly by employing the simple method of observing the microcapsules' surface morphology, and find that excess nano-$CaCO_3$ particles are not able to adhere to the shells. This phenomenon may be attributed to two factors: one is the lower bonding strength between the MMF resin and the nano-$CaCO_3$ particles; and the other is the weak adhesive force (due to the unbalanced electrostatic attraction of MMF prepolymer). These factors lead to excess nano-$CaCO_3$ particles that are not attached to the surface, but remain in the environment, and can thus negatively effect the properties of the microcapsules. The addition of excess nano-$CaCO_3$ particles must therefore be avoided to maintain microcapsules with excellent thermal stability and mechanical properties.

We also investigated the thermal stability of microcapsules in bitumen. We analyzed the optical morphologies of a microcapsule sample (MS-5) mixed with bitumen under temperatures of 25, 180, 200, and 220°C (see Figure 3). We found that microcapsules containing rejuvenator are not destroyed during mixing with hot bitumen,[10] and can be homogeneously dispersed. Nearly all microcapsules survived the mixing process without breaking or decomposition, and maintained their original spherical shape. This result indicates that the rejuvenator is indeed well protected by the nano-$CaCO_3$/polymer composite shells.

In summary, we prepared novel microcapsules containing rejuvenator by using a nano-inorganic/organic composite method and then systematically studied the structure–property relationship in the resultant microcapsules. Our investigations show that an oily rejuvenator is well protected by the nano-inorganic/organic composite shell. We found that the addition of nano-$CaCO_3$ particles did not greatly influence the mean size of microcapsules. Additionally, thermal tests showed that the nano-$CaCO_3$/polymer microcapsules survived mixing in 220°C bitumen for a long service time under radical conditions without damage, thanks to the good thermal stability of the shells. In the next stage of our work, we will investigate the self-healing capability of these microcapsules when added to asphalt.

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