SYNTHESIS OF NANOCONTAINERS FOR SELF-HEALING REACTIONS BASED ON ROMP

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ABSTRACT

Most of the capsule-based healing systems possess diameters ranging from 10 to 100 µm. Such sizes are ideal for healing large cracks, but not suitable for healing damage events in the nanometer scale, i.e. in thin films or coatings. Nanocapsules are required for these applications that can be produced by the miniemulsion technique.

Miniemulsion is a special class of emulsion, for which coalescence and Ostwald ripening are suppressed by using a surfactant and an ultrahydrophobe, respectively. The miniemulsion technique allows the formation of small (50-500 nm) and narrowly distributed droplets by use of high shearing processes, for example sonication. The miniemulsion droplets were further used for polymerization reactions [1] and for the encapsulation of hydrophobic [2] or hydrophilic liquid substances [3]. Core-shell nanoparticles with liquid core and a polymer shell were then obtained. The polymer shell could be formed by a phase separation between the liquid and the polymer induced by polymerization [2] or by solvent-evaporation [4].

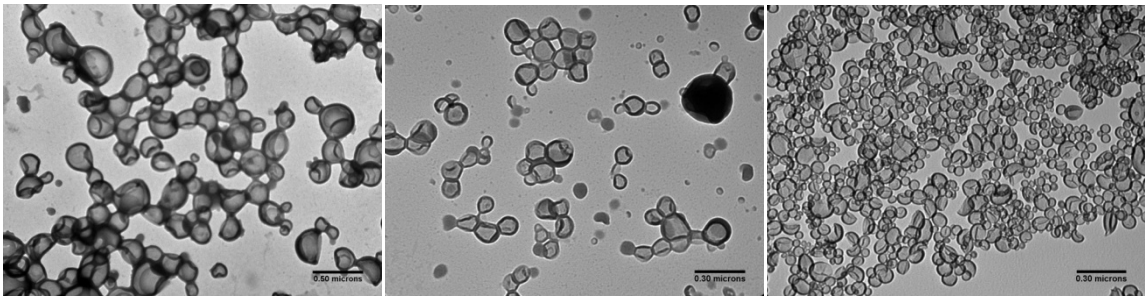
We used three different methods to encapsulate separately Grubbs catalysts and liquid monomers suitable for Ring Opening Metathesis Polymerization (ROMP). The encapsulated reagents can be released out of the capsules to yield a healing reaction.

Firstly, nanocontainers with polymer shell were formed by free-radical copolymerization of hydrophobic monomer with small amounts of hydrophilic monomers (Fig. 1a). Functional groups could hence be introduced on the surface of the nanocapsules.

Secondly, the emulsion solvent-evaporation technique was used to encapsulate sensitive healing agents such as solution of Grubbs catalysts. Homogeneous droplets containing polymer, healing reagent, solvent, and antisolvent for the polymer were produced and the solvent was subsequently evaporated. Phase separation between the polymer and the antisolvent occurred at the interface of the droplets, yielding core-shell nanoparticles (Fig. 1b). The core consisted of the antisolvent and one healing reagent.
Finally, we produced inorganic nanocontainers with silica shells from aqueous minemulsions of silica precursors (Fig. 1c).

The size and shell thickness of the nanocontainers were controlled by the concentration of the surfactant and monomers, respectively. It is shown that an efficient encapsulation of the ROMP monomer was mainly dependent on the functionality of the polymer used for building the capsule shell.

Preliminary experiments of self-healing reactions could be successfully demonstrated.



a b c

Figure 1: TEM micrographs of the nanocontainers synthesized by a: free-radical polymerization, b: emulsion solvent-evaporation, c: condensation of silica precursors at the interface of miniemulsion droplets.

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