MICROENCAPSULATION OF VARIOUS REACTIVE MONOMERS BY IN SITU POLYMERIZATION

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ABSTRACT

Advances in the study of composite polymeric materials for structural applications have suggested the possibility of an early elimination of cracks to avoid macroscopic damage of the material. Hence, the concept of self-healing composite materials has been introduced to reduce the maintenance cost and frequency, to increase the life in service and to expand the applications of these materials. One of the most successful and versatile approach consists on embedding an encapsulated haling agent inside the matrix.

One of the key features for the effectiveness of the healing system is the microcapsule design. The release properties depend on the healing agent properties, wall materials, the microencapsulation method, the physico-chemical parameters of the process, the mean particle size and the shell thickness. In order to have a successful self-healing performance, it is important to synthesize microcapsules with rough surface morphology to assure a good adhesion with de polymer matrix, low core material permeability, appropriate diameter and core content, and adequate shell thickness.

The aim of this work was to synthesize poly (urea-formaldehyde) microcapsules filled with different reactive monomers: dicyclopentadiene and two epoxy monomers with different viscosities. This parameter is important for the release properties and the healing performance of the resulting capsules. Microcapsules were prepared by in situ polymerization in oil-in-water emulsion and the best experimental conditions were selected to optimize the subsequent healing efficiency. Several reaction conditions were analyzed, by changing the following parameters: the rate of agitation, the concentration of surfactant and the viscosity of the encapsulated phase. The effect of the addition of nanoclay along the shell was also studied. The final step of filtering and washing the obtained capsules with different solvents was analyzed as well.

1. INTRODUCTION

Microcracking is a critical problem for polymers and polymer composites during their service in structural applications. The ability of self-healing materials to repair cracks is necessary to retain structural integrity. The route based on dispersing microcapsules filled with a healing agent which rupture upon a crack event, mimicking a biological ‘bleeding’, seems to be very promising due to its versatility. Therefore, the objective of this work was to synthesize and characterize poly (urea-

formaldehyde) microcapsules containing different reactive monomers and to establish the best reaction conditions for each case.

2. MATERIALS

Urea (Anhedra), 40% w/v aqueous solution of formaldehyde (Biopack), ammonium chloride (Timper) and resorcinol (Biopack) were used as shell forming materials. Poly (ethylene-alt-maleic anhydride) (EMA), 1-octanol and dicyclopentadiene were purchased from Sigma-Aldrich. A bisphenol A epoxy resin (Epon 826, epoxy equivalent weight 178 a 186 g/eq) and a bisphenol F epoxy resin (Distraltec (RBF170), epoxy equivalent weight 182.8 g/eq) were also used. Figure 1 shows the chemical structures of the encapsulated monomers.

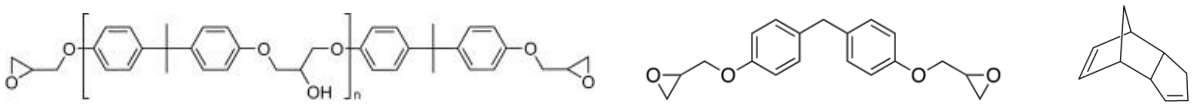

Figure 1: Encapsulated monomers.

3. METHODS

Microcapsules were prepared in oil-in-water emulsion by in situ polymerization [1], as it is shown in Figure 2.

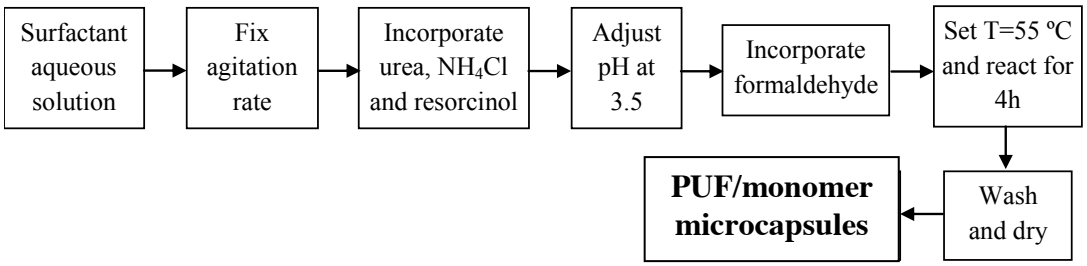

Figure 2: Microencapsulation procedure.

The prepared microcapsules were observed by scanning electron microscopy (JEOL JSM 6460 LV). Surface morphology and microcapsule size were studied. Infrared Spectroscopy (FTIR) spectra were obtained on a Perkin–Elmer Spectrophotometer model Spectrum 100 in attenuated total reflection (ATR) mode. Spectra, averaged over 16 scans, were taken in the range of 4000–600 cm^{-1}at a resolution of 4 cm^{-1}

4. RESULTS

Syntheses of microcapsules have been successfully performed for all encapsulated monomers. Regarding PUF/DCPD system, different agitation rates between 300 and 600 rpm previous to the incorporation of formaldehyde were studied; the emulsion was stabilized for 15 min in all cases. At 300 rpm the agitation rate was not enough to stabilize the droplets in the emulsion. The best results were obtained for samples synthesized at 450 rpm. Figure 3 displays the characterization of these capsules.

Spherical and high quality microcapsules with a normal and narrow size distribution were obtained. The measured values of mean diameter and standard deviation of the outer diameter were 282.3 μm and 50.9 μm, respectively. The microcapsule shell has a smooth inner wall and a rough porous morphology on the outer surface (Figure 3b). The presence of DCPD was evidenced by FTIR (Figure 3c).

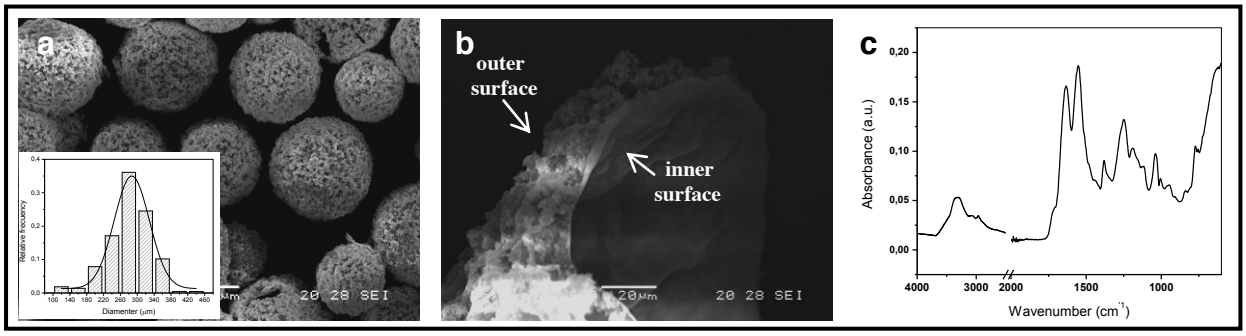

Figure 3: Characterization of PUF/DCPD microcapsules obtained at 450 rm: a) SEM micrograph, b) SEM micrograph of a broken capsule, c) FTIR spectrum.

As regards PUF/DGEBA systems, higher stirring rates were required to stabilize the emulsion due to the considerably higher viscosity of the epoxy monomer (12400 cP at 25 ºC) compared with DCPD. The best results were registered at 600 rpm. Different washing solvents were employed: water, ethanol, acetone and ethanol-acetone (80:20). As water and ethanol were unable to remove the excess of epoxy, microcapsules with a smooth wall were observed by SEM (Figure 4a). On the other hand, acetone and ethanol-acetone (80:20) were more suitable for the washing step and a “cleaner” and rougher microcapsule surface can be observed (Figure 4b). The measured values of mean diameter and standard deviation of the outer diameter were 31.3 μm and 6.8 μm, respectively.

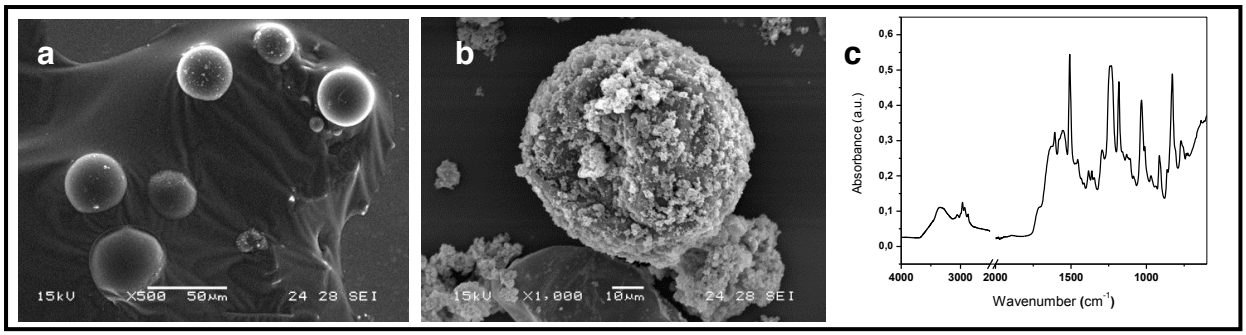

Figure 4: Characterization of PUF/DGEBA microcapsules obtained at 600 rpm: a) SEM micrograph of microcapsules washed with ethanol b) SEM micrograph of microcapsules washed with acetone, c) FTIR spectrum.

Regarding PUF/DGEBF systems, the same agitation rate of 600 rpm was used; this rate was selected owing to the higher viscosity of DGEBF monomer compared with DCPD. However, the viscosity of this epoxy monomer is lower than DGEBA monomer (6170 cP a 25ºC), which is an advantage for the release properties of the resulting microcapsules, once they have been embedded in an epoxy matrix and a propagating crack provokes its rupture. In this case, the emulsion was stabilized for 1 h in order to obtain a homogenous distribution of resin droplets. The characterization

is displayed in Figure 5. Once again, different solvents were evaluated in the washing procedure and the best results were observed when microcapsules were washed with acetone. A white free-flowing powder was obtained, but an agglomerated yellow powder was obtained when it was washed with ethanol. The measured values of mean diameter and standard deviation of the outer diameter were 136.9 μm and 22.3 μm, respectively.

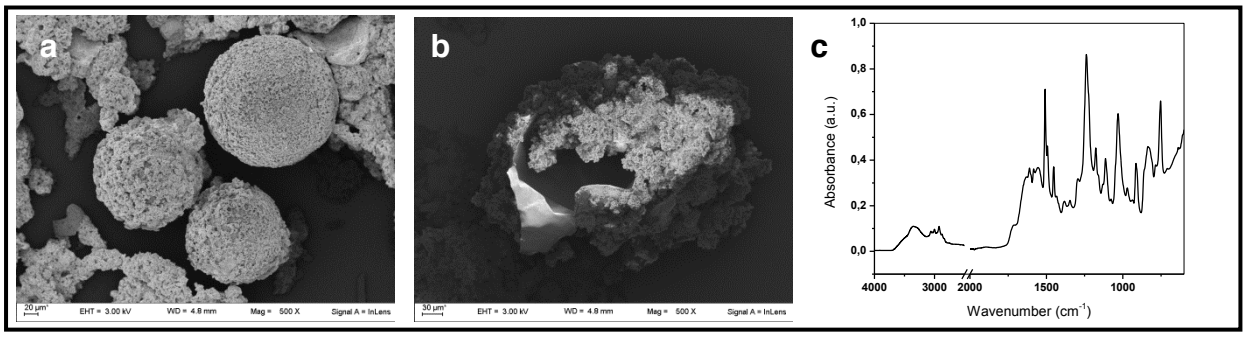

Figure 5: Characterization of PUF/DGEBF microcapsules obtained at 600 rpm: a) SEM micrograph of microcapsules washed with acetone, b) SEM micrograph of a broken capsule, c) FTIR spectrum.

Samples including bentonite were also prepared. The presence of clay was evidenced by FTIR, thermo gravimetric analysis and X-Ray Diffraction (not shown). It was found that the addition of clay did not affect the surface morphology but it changed the thermal behavior of the microcapsules (studied by TGA). Future works regarding the incorporation of the clay on the microcapsules will be carried out.

CONCLUSIONS

Poly (urea-formaldehyde) microcapsules with different encapsulated reactive monomers (dicyclopentadiene and two epoxy monomers: DGEBA and DGEBF) were successfully synthesized. This was evidenced by SEM and FTIR. It was demonstrated that the washing steps have a very important effect on the final morphology and the cleanness of the microcapsules surface. For each case, optimal agitation rate and emulsion stabilization were established according to the monomer properties. Regarding epoxy containing capsules we believe that DGEBF is more suitable for self-healing applications due to its lower viscosity.
Future works regarding the effect of the incorporation of clay in the microcapsules on the barrier properties and rupture behavior once embedded in the epoxy matrix are being carried out.

ACKNOWLEDGEMENTS

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