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Characterization of solvent-filled polyurethane/urea–formaldehyde core–shell composites

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HIGHLIGHTS

- An analytical model was used to extract Young's moduli from core–shell structures.
- The thickness of UF shells was independent of capsule diameter.
- PU shell thicknesses scaled with capsule diameter until a saturation thickness.
- Compared to UF shells, PU/UF shells had a five-fold lower Young's modulus.
- PU shells resisted well due to increased thickness and elongation at break.

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ABSTRACT

Encapsulation of liquid phases is a crucial step in many self-healing material systems where a healing agent has to be protected during processing and then released during a damage event. In this work, the mechanical properties of polyurethane (PU) reinforced urea–formaldehyde (UF) shells are characterized. It was found that shell thickness is both a function of PU content in the core phase and of the microcapsule diameter. Furthermore, a saturation thickness was found for high PU contents or high capsule diameters and this phenomenon had direct implications on the bursting force under compression of single microcapsules. With help of an analytical model, the Young's modulus of the hybrid PU/UF was determined and in general, PU-reinforced shells had a lower modulus but higher ductility in terms of elongation at break, leading to more resistant microcapsules overall.

1. Introduction

Protecting components for later use by an encapsulation process is of interest in many industrial applications in food industry [1,2] and pharmaceutical industry [3,4]. In general, the purpose of the encapsulation is the controlled release of the core components, which can be a triggered release or a sustained release. The different release modes can be driven by diffusion through membranes, chemical membrane dissolution and thermal or mechanical degradation (rupture) of membranes, amongst others [5].

Recently, self-healing polymeric composite materials were demonstrated. The self-healing capability can be achieved through intrinsic material properties (reversible covalent or non-covalent crosslinking) or extrinsic phases containing a healing agent [6]. In case of extrinsic self-healing materials, a small volume fraction of the polymeric material is occupied by the healing agent. Besides hollow channels or microvascular systems, mimicking a biological vascular system [7–9], this is commonly achieved by encapsulating a liquid component which is then dispersed into the polymer resin [10–12]. Common encapsulation procedures are batch processes relying on in-situ polymerization of a shell in an agitation stabilized emulsion [13,14] or more recently, using microfluidics [15–17].

For incorporation of these microcapsules into fiber composite materials, the requirements on the mechanical stability of the microcapsules are very high, as the microcapsules need to survive the stresses of processing. Keller et al. characterized the properties of monomer-filled urea–formaldehyde (UF) microcapsules by single capsule compression [18] and using an analytical model, the Young's modulus of the shell membrane was extracted. Unfortunately, the UF encapsulation protocol does not allow straightforward tuning of the shell thickness (which was reported to be in the 160–220 nm range [19]) and consequently mechanical properties cannot be changed. Later, Caruso et al. described a method to reinforce the UF shells by adding an aromatic diisocyanate to the

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core fluid which forms a polyurethane (PU) layer at the emulsion interface. These hybrid PU/UF shells were shown to increase the bursting force as well as thermal stability but the shells were not characterized using the aforementioned analytical model.

The goal of this work is to study how the morphology and mechanical properties of PU/UF composite shells change as a function of the shell thickness, composition and the capsule diameter. Therefore, polyurethane-reinforced PU/UF microcapsules filled with a solvent were produced and analyzed in detail. An analytical model was adapted to extract the Young's modulus of the hybrid shell and evaluate the mechanical properties' dependency on capsule diameter. This was accomplished using single capsule compression, then by fitting these results to the shell model developed by Feng et al. [20] which allows an accurate description of the Young's modulus of the PU–UF composite shell. The shell morphology was assessed using atomic force microscopy (AFM) and scanning electron microscopy (SEM) while the thermal stability was investigated using thermogravimetric analysis (TGA).

2. Experimental methods

2.1. Encapsulation protocol

Pure UF capsules were produced using the protocol developed by Brown et al. [19] and Blaiszik et al. [21], with a core composed of 97.5% ethyl phenylacetate (EPA) and 2.5% epoxy resin. The following chemicals have been used: EPON 828 (Brenntag Schweizerhall AG), ethyl phenylacetate (99%, Acros), urea (Acros), ammonium chloride (Fluka), resorcinol (Sigma Aldrich), formaldehyde (37%, Sigma Aldrich), ethylene maleic copolymer solution (2.5%, Sigma Aldrich), sodium hydroxide (20%, Acros) and octanol (Sigma Aldrich).

For PU-reinforced capsules, the same encapsulation procedure was followed, but a commercial polyisocyanate precursor (Desmodur L75, Bayer) was dissolved into the core mixture before addition to the stirring bath [22]. Different amounts of PU precursor were added, namely 2.5, 5.0 and 7.5 g per 60 ml of core fluid. All batches were produced using a stirring rate of 400 rpm and size fractions <90, 90–125, 125–180, 180–250 and 250–355 μm were separated by manual sieving and retained.

2.2. Thermogravimetric analysis

The thermal stability of pure UF and of PU-reinforced microcapsules was tested using TGA on a Mettler Toledo sDTA851e. The samples were kept at room temperature for about 1–2 weeks and 10–15 mg were transferred to alumina crucibles which were then subjected to a temperature ramp at 10 °C min^{-1} from 30 °C to 400 °C. The relative mass loss was then computed to investigate the critical temperatures of these microcapsules.

2.3. Evaluation of capsule diameter and shell thickness

To obtain the capsule size distribution, 100 optical measurements were performed on each type of capsules. Furthermore, scanning electron microscopy (XLF-30 FEG, FEI) was used in order to characterize the diameter-dependent shell thickness of microcapsules. For each type of capsules, five different size fractions (<90, 90–125, 125–180, 180–250 and 250–355 μm) were analyzed. Prior to imaging, capsules were slit using a razor blade, washed with acetone several times and dried with compressed air followed by 2 h storage in vacuum. A layer of carbon coating of about 10 nm was then deposited onto the samples. On the micrographs, a total of 35 thickness measurements were taken on 5 different capsules within each diameter fraction and averaged. Particular care was taken to acquire images of the shell sections at a perpendicular angle in order to limit the error due to an oblique observation angle.

2.4. Atomic force microscopy

Atomic force microscopy (Multimode Nanoscope, Veeco) was used in tapping mode in order to check and confirm the capsule shell composition through phase contrast imaging. Samples were prepared by mixing 5 wt% of capsules in a resin/hardener mixture composed of EPON 862 (Brenntag Schweizerhall AG) and diethylenetriamine (DETA, Sigma Aldrich) in a 100:12 weight ratio; the compound was then degassed for 10 min and poured into a silicone mold for ultramicrotomy samples.

Curing at room temperature for 24 h and post-curing at 35 °C for 24 h then followed. These samples were then cut into 300 nm thin slices by using an ultramicrotome device (PowerTome X, Cordouan Technologies). The slices were collected in water and then put onto glass slides for drying and further imaging. Slices consisted in sheets of matrix with holes corresponding to sectioned embedded capsules, as depicted in Fig. 1(a). Images of a folded slice acquired by SEM after sputter coating with carbon, as well as an optical image, are shown in Fig. 1(b) and (c), respectively. The shell could then be observed at the air/matrix interface.

2.5. Single capsule compression

For single capsule compression, a motor driven indenter (1.5 μm s^{-1} displacement rate) compresses a single microcapsule with known diameter, placed on the sample holder. Force–displacement data were acquired using a Futek LMP200 load cell (0–100 mN). An analytical model was then used to extract the Young's modulus of the shell material by fitting the modeled response to the experimental data, as described in Appendix A. Fig. 2 shows a schematic of the geometrical deformation with the corresponding parameters. An incompressible liquid filled shell of radius r_i is compressed by a flat indenter. Thereby a flat contact zone and a stretched non-contact zone are defined by the contact angle Γ. The stretch ratios ($\lambda = \varepsilon + 1$) in latitudinal and longitudinal direction are called λ_1 and λ_2, respectively and are, once computed, used to calculate the geometry for a given Γ through the η_Γ and $\rho_\Gamma(\psi)$ coordinates.

3. Results and discussion

3.1. Capsule diameter

The size distribution of each batch of microcapsules was optically measured and the corresponding average diameters as well as standard deviations are found in Table 1.

3.2. Thermogravimetric analysis

Fig. 3 shows the mass loss of UF and PU-reinforced microcapsules as a function of temperature. In UF microcapsules, a small evaporation of moisture occurred between 70 and 100 °C, followed by a mass loss at a gradually increasing rate, peaking at about 280 °C. Beyond, only the shell material remained.

Concerning PU-reinforced capsules, the results suggest a very low moisture content in all three batches. As opposed to pure UF shells, PU/UF shells offer very high thermal stability, with no significant mass loss until 240 °C, well above the boiling point of core solvent EPA (229 °C). Beyond 240 °C, the capsules release the solvent and at 275 °C, almost all the solvent had evaporated for all three types of PU/UF capsules. Note that for higher PU contents, the residual weights after solvent evaporation are also higher. At