Materials Chemistry and Physics 215 (2018) 346–354

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Determination of elastic properties of urea-formaldehyde microcapsules through nanoindentation based on the contact model and the shell deformation theory

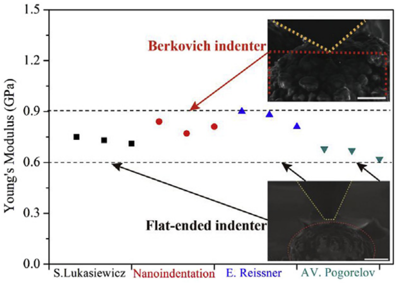
X.F. Wang*, R. Han, T.L. Han, N.X. Han, F. Xing**

College of Civil Engineering, Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen University, Shenzhen, 518060, PR China

HIGHLIGHTS

- Determination of Young's modulus of urea-formaldehyde microcapsules.
- Comparison between the result from the contact model and that from shell theory.
- The approach was validated by finite element method (FEM) simulation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Microcapsules
Mechanical properties
Nanoindentation
Contact theory
Shell theory

ABSTRACT

Characterization of the mechanical properties of urea-formaldehyde microcapsules filled with epoxy resin is of importance for achieving self-healing of cementitious composites. In this study, the morphology of microcapsules, including diameter and thickness, was characterized using scanning electron microscopy. The mechanical properties of single microcapsules, including Young's modulus and hardness, were determined through a nanoindentation technology based on the elastic contact theory using a Berkovich indenter. Moreover, to investigate the structural effects of microcapsules, a diamond plate indenter was used, and the Young's modulus of the microcapsule wall was calculated through the ordinary least square optimization method according to three analytical solutions on the basis of thin shell theory, namely Reissner, Pogorelov, and Lukasiewicz methods. It is shown that the results of the contact and thin shell theory were similar, in which the similarity occurs only in the case of a small deformation. When the deformation was large (indentation depth > 900 nm), the structural effect became significant. In addition, the finite element method was applied to simulate the mechanical response of the microcapsules using the results obtained. The validity of the approach was approved.

1. Introduction

Microcapsules containing core liquid encapsulated by a polymeric or inorganic wall are a type of micro/nanoparticles. A single microcapsule has a core-shell structure and its shell is considered to be compressible, isotropic, and homogeneous. Types of core materials and various trigger patterns directly determine the various applications of microcapsules. They have been extensively used to produce functional materials in the food [1,2], medicine [3,4], chemical [5,6], cosmetics [7], and printing industries [8]. In this study, urea-formaldehyde (UF)

---

* Corresponding author.
** Corresponding author.
E-mail addresses: xfw@szu.edu.cn (X.F. Wang), xingf@szu.edu.cn (F. Xing).

https://doi.org/10.1016/j.matchemphys.2018.05.041
Received 12 February 2018; Received in revised form 15 May 2018; Accepted 19 May 2018

microcapsules containing healing liquid E-51 epoxy resin were applied to self-healing cementitious composites [9,10]. The repair process of a self-healing cementitious composite can be triggered by a burst of microcapsules when cracks are generated. Cracks propagate until they penetrate the microcapsules which releases healing agent into the crack plane through capillary action. Ultimately, crack opening may be prevented by the cohesive force generated by the polymerization reaction between the microcapsule contained healing agent and catalyst [10]. It is known that there are different mechanisms to induce release, such as physical (temperature, ultrasound, mechanical deformation, magnetic and electric fields etc.), chemical (pH, salt and gases etc.) and biological (enzymatic degradation and biodegradability) stimulus [11]. These release mechanisms have also significant guidance for research, and the release of epoxy resin in this study is due to a mechanical trigger.

Therefore, the mechanical stability of the microcapsules must be maintained during preparation and storage, and their integrity could be destroyed so that the mechanically triggered healing agent can be properly released. The mechanical properties of microcapsules play a critical role in determining their deformation properties under applied external loads or internal osmotic pressure. A proper effect to these applied forces is essential to guarantee that the mechanical triggering process functions properly when cementitious materials are damaged [12]. During microcapsule design, it is crucial to align its mechanical characteristics with prospective applications. Two main approaches are applied when studying the mechanical properties of microcapsules, bulk and individual methods. For bulk methods, studies have focused on shear forces [13] and osmotic pressure [14,15], in an attempts to extract the average mechanical parameters across batches, such as shear elastic modulus.

However, for individual microcapsule measurements, the mechanical properties of a single microcapsule cannot be evaluated by compression tests of macroscopic samples due to size effects. Emerging experimental techniques, such as optical and magnetic tweezers [16,17], shear flow (spinning drop apparatus) [18], micropipette aspiration [19], atomic force microscopy (AFM) [20–25], and nanoindentation [26–33], have made the investigation of single microcapsules possible. Among these techniques, optical and magnetic tweezers as well as micropipette aspiration are usually used for biological samples [16,17,19]. Among these measurements, AFM and nanoindentation are also widely used to study the mechanical properties of minute particles. Cole et al. [26] examined the surface forces of Arbacia eggs (initial diameter 75 μm) between the parallel planes in the early 1930s, micromanipulation was not introduced to measure the bursting force of a single cell until 1991 by Zhang et al. [27,28]. The mechanical strength parameters including rupture force, deformation at rupture, and nominal rupture stress (the ratio of the rupture force to the initial cross-sectional area of the individual microcapsule) of melamine formaldehyde microcapsules containing a self-healing agent were determined by Hu et al. [29]. The nominal tension at rupture, a novel strength parameter, was proposed by Liu et al. [34]. These mechanical parameters depend on the diameter, thickness, and composition of microcapsules. Loading and unloading curves at small deformations were performed to determine the intrinsic material properties of microcapsules, such as their Young's modulus and hardness. In general, elastic contact theory, shell theory, and the combination of the finite elements method (FEM) and compression tests can be used to determine many mechanical parameters. For instance, Keller and Sottos [30] used micromanipulation tests to determine the elastic modulus and failure behaviour of a UF microcapsule. To quantify the Young's modulus, load-displacement data from micromanipulation compression tests were evaluated using the Hertzian half-space contact mechanics model [35]. MF microcapsules with different core/shell weight ratios were investigated using nanoindentation [33]. In addition, Ahangari et al. [32] investigated the elastic modulus of a UF microcapsule containing dicyclopentadiene (DCPD) using nanoindentation. A combination of compression and FEM tests were applied to determine the elastic properties of microcapsules by Ma et al. [31] and Mercade-Prieto et al. [36,37]. Recently, even though some pioneering studies have been conducted on determining the mechanical properties of a single microcapsule, the theoretical approaches based on thin shell theory and the microcapsule containing liquid healing agent have yet to be thoroughly investigated.

Regarding the key parameters of a material, Young's modulus is not only an important mechanical property, but also a significant indicator of the material stiffness, which should have much influence on the interaction between microcapsules and the imbedded matrix. Though other parameters such as rupture force, buckling or material aging could be equally important for the intended application, at the first stage, Young's modulus should be made clear. Hence in this study, the Young's modulus and hardness of a single UF microcapsule were determined based on elastic contact theory using a Berkovich indenter during nanoindentation. Moreover, to investigate the structural properties of single microcapsules, nanoindentation tests were performed using a diamond plate indenter. The data were analysed by combining the elastic solution of concentrated loads on the shallow spherical shells to determine the Young's modulus using the ordinary least square (OLS) method. In addition, the surface morphology, such as diameter and thickness, of UF microcapsules was evaluated using scanning electron microscopy (SEM). The mechanical response was simulated by the FEM based on the experimental results.

2. Materials and experimental methods

2.1. Preparation and characterization of the UF microcapsules

In this study, UF microcapsules containing the epoxy resin E-51 and butyl glycidyl ether (BGE) were synthesized using an *in situ* polymerization method at Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen University. The details of the synthesis can be found in Ref. [38]. Table 1 lists the specific parameters of the microcapsules, Fig. 1(a) and (b) show an SEM image (Quanta TM 250 FEG) of the microcapsules, and an image of microcapsule fragments, respectively. The diameter of microcapsules was calibrated by counting 300 intact microcapsules in the images. For Fig. 1(b), these microcapsules were broken on purpose in order to measure the thickness of the samples. The distributions of diameter and thickness of the UF microcapsules are shown in Fig. 2(a) and (b). Furthermore, the capsule core content was assessed by the chemical extraction method, which is detailed in Ref. [38]. The core content, ω_{cc}, can be determined by:

$$\omega cc = \frac{(Mcapsule - Mshell)}{Mcapsule} \times 100\% \tag{1}$$

where $M_{capsule}$ is the mass of a certain number of microcapsules and M_{shell} is the mass of the corresponding microcapsules shells.

2.2. Preparation of the microcapsule specimens for nanoindentation

The samples were measured using a diamond plate indenter. First, a microscope slide was sliced into 1cm × 1cm pieces using a glass cutter. Second, thin and uniform epoxy resin was fixed on the pre-diced pieces using a spin coater. Third, several similar microcapsules were selected and scattered on the 1cm × 1cm piece. Finally, the test piece was kept

Table 1
Specific parameters of the UF microcapsules.

Rotation velocity during synthesis (r/min)	Average diameter (μm)	Shell thickness (μm)	Capsule core content (%)
200	194.2	8.3	75