Applying nanoindentation to measure micromechanical properties of phenol–formaldehyde microcapsules for self-healing cement-based materials

Leyang Lv[1,3], Jiaoning Tang*[1], Fusheng Xiao, Eric Schlangen[3], Guangming Zhu[1], Ningxu Han[2], Feng Xing[2]

[1]Shenzhen Key Laboratory of Special Functional Materials, College of Materials Science and Engineering, Shenzhen University, Shenzhen 518060, PR China,E-mail: tjn@szu.edu.cn;
[2]Department of Civil Engineering, Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering, Shenzhen University, Shenzhen 518060, PR China;
[3]Faculty of Civil Engineering and Geosciences,Delft University of Technology, 2628 CN Delft, The Netherlands.

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ABSTRACT

Incorporating microcapsules containing a rejuvenator in cement-based materials is one of the most promising strategies to heal cracks and prolong the materials' service life. The mechanical properties of the microcapsules have great influence on a material's survival during cement mixing and hydration, as well as the trigger efficiency when a crack traverses the material. In this work, a nanoindenter was successfully used to measure the micromechanical properties of the microcapsules with different physical features such as diameter and wall thickness. The results showed that both the elastic modulus and rupturing force of the microcapsules mostly depended on the shell thickness and shell-to-diameter ratio. Microcapsules with a higher elastic modulus required a larger mechanical force to trigger them to break open and release the healing agent.

1. INTRODUCTION

The incorporation of microcapsules in self-healing materials has been widely investigated [1]. Previous studies have demonstrated that urea–formaldehyde (UF) resin [2] and melamine–formaldehyde (MF) resin [3] can be used as wall materials for the fabrication of microcapsules containing dicyclopetadiene (DCPD) for self-healing polymers [4, 5] or asphalt [6]. While few studies have done on the preparation of microcapsules for the application in cement-based materials. Unlike polymer and asphalt, the microcapsules used in cement-based materials must resist not only mechanical agitation during the mixing process, but also long-term immersion in hazard environment [7]. PF resin has good mechanical strength, thermal stability, and water-resistance [8], which are the same characteristics required for self-healing microcapsules applied in cement-based materials.

In order to realize the self-healing function of microcapsules for cementitious materials, the microcapsules should have optimal mechanical properties [9, 10] that enable these particles to break by mechanical force generated from the crack in the matrix. It has been reported that the physical features of the microcapsules, such as diameter and shell thickness will affect their micromechanical properties [11, 12]. However, in order to develop guidelines for the preparation of microcapsules with more desirable mechanical properties, it is still necessary to understand the relationship between the microcapsules' physical features and the threshold rupturing force required to trigger their breakage. After that, the correlation between the formulation and processing conditions and the rupture probability can be established.

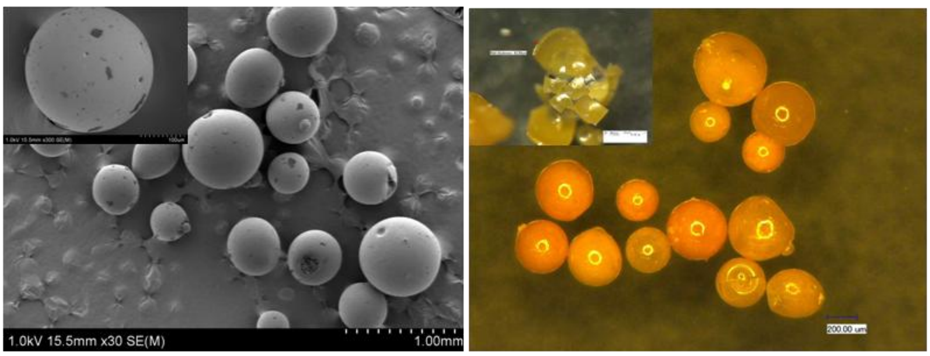
In this work, DCPD-containing phenol–formaldehyde(PF) microcapsules were synthesized by in situ polymerization. A typical load–displacement curve of a single microcapsule was obtained by nanoindentation [13]. PF shell microcapsules with different diameters and shell thicknesses were synthesized and selected to investigate the effect of physical features of microscapsule on the micromechanical properties.

2. MATERIALS AND METHODS

The surface morphology and shell thickness were examined using an optical stereoscopic microscope (OM; VHX-600K, Keyence, Japan) and a scanning electron microscope (SEM; SU-70, Hitachi, Japan) under an accelerated voltage of 5 kV. The micromechanical properties of the single microcapsules were obtained with a nanoindenter (G200, Keysight, USA). A Berkovich tip was used to stab the surface of the microcapsule to add a given load or to rupture it with a certain force. In this test, the allowable drift rate was 1 nm/s, the surface approach velocity was 20 nm/s, and the peak holding time was 10 s.

3. RESULTS AND DISCUSSION

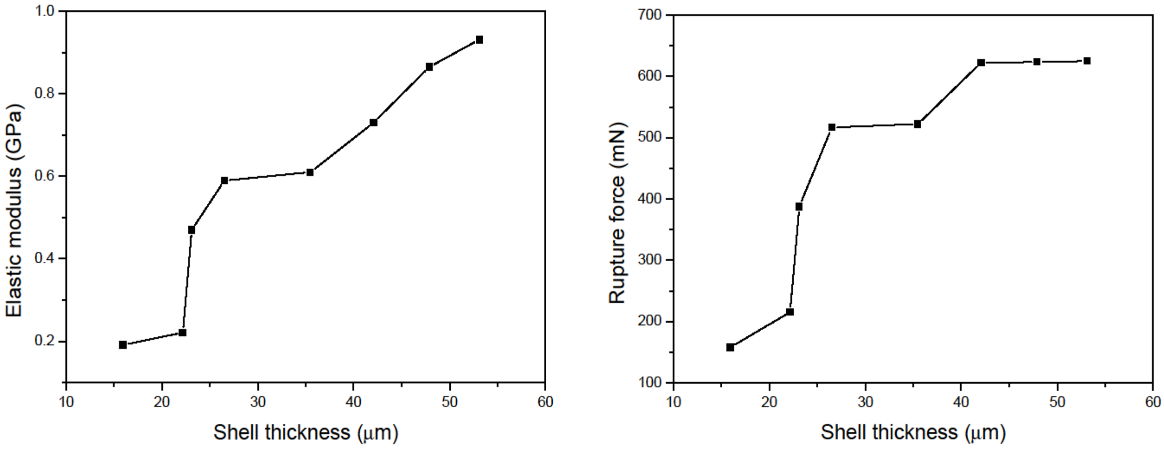
Fig. 1(a) shows that each microcapsule had a regular globular shape with a smooth surface. The OM image of microcapsules in Fig. 1(b) illustrates that the core material were completely covered by PF resin. The thickness of the shell was about 44 μm.



(a) (b)

Fig. 1. Images of PF microcapsules and the shell thickness, obtained by (a) an SEM and (b) an OM.

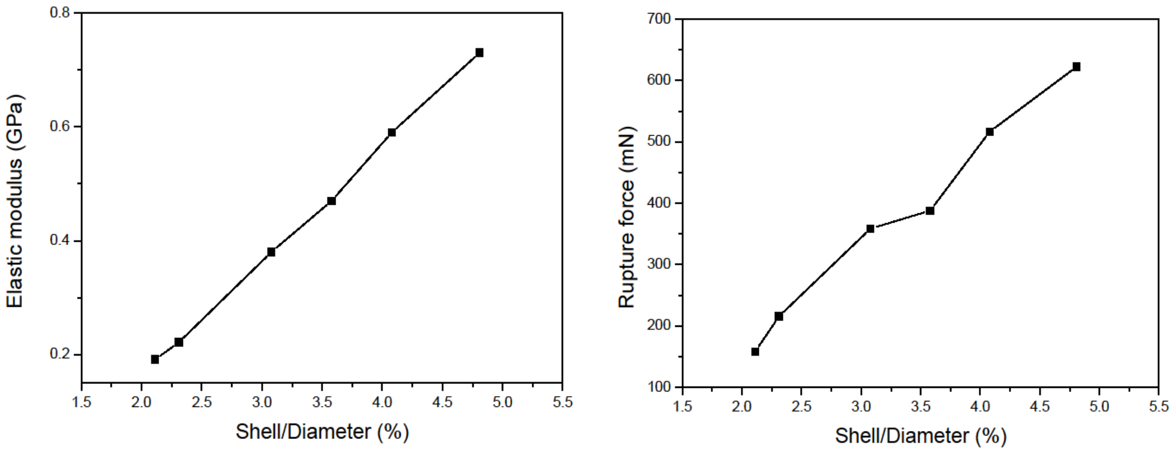
Fig. 2(a) shows the relationship between elastic modulus and shell thickness. As the shell thickness increased, the elastic modulus rose gradually, which means that elastic modulus obtained by the nanoindenter was largely affected by the properties of shell. In Fig. 2(b), the relationship between the rupturing force and shell thickness also shows a similar trend, which means that the thicker shells of microcapsules require bigger applied forces to rupture. It should be pointed out that when the wall thickness increased to about 43 μm, the rupturing force could not be measured because it exceeded the full-scale value (600 mN) of the nanoindenter.



(a) (b)

Fig. 2. Effects of shell thickness of PF microcapsules on the (a) elastic modulus and (b) rupturing force.

Since a larger microcapsule diameter does not necessarily indicate a thicker shell, the ratio of the shell thickness and diameter was taken into consideration in this. As shown in Fig. 5, the shell-to-diameter ratio was directly correlated with both the elastic modulus and rupturing force. A higher proportion of shell led to a larger elastic modulus of the microcapsule and microcapsule with higher shell-to-diameter ratio needed more energy to trigger its rupture by the mechanical force.



(a) (b)

Fig. 3. Micromechanical properties of microcapsules with different shell-to-diameter ratios.

4. CONCLUSION

nanoindentation test was carried out to establish the relationship between the physical features (diameter and shell thickness), micromechanical properties, and the rupturing force of a single microcapsule. It can be concluded that the wall thickness had a big impact on the elastic modulus of the shell and the force needed to rupture the microcapsule.The shell-to-diameter ratio was an important factor that could largely determine the micromechanical properties and the rupturing force of the microcapsule. A larger elastic modulus of a microcapsule means that it would need a bigger mechanical force for its rupture.

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