Mechanical-performance Investigation of a single DCPD/PF microcapsule with nanoindenter

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Keywords: microcapsule, mechanical properties, plastic deformation, nanoindenter

Abstract ID No : 142

ABSTRACT
An individual phenol-formaldehyde (PF) microcapsule containing dicyclopentadiene (DCPD) as healing agent was selected as a sample to investigate the relationship between deformation and mechanical properties of a microball with core/shell structure. Based on the load-displacement curves obtained with nanoindenter, a computational method was selected to deduce the Young's modulus and hardness of shell, and cracking load of the core/shell microcapsule. Indentation size, residual wall thickness and the ball diameter difference before/ after loading were measured by an optical microscope with super depth of focus to determine the amount of plastic deformation. It's found there is a linear dependence between plastic deformation amount and thickness of shell. The cracking load varies inversely with the ratio of particle size d and wall thickness δ. The Young's modulus of PF wall rests with the wall material itself only, has nothing to do with d or δ.

1. INTRODUCTION
Filled microcapsules have been developed for countless applications across a wide range of fields. They can potentially be used for drug delivery in pharmaceutical products, for protection of encapsulants in food and cosmetic industries, and even for self-healing in structural materials. Understanding the mechanical properties of such microspheres is essential because they may be exposed to mechanical forces during processing and in later applications.
Nanoindenter, known as instrumented for high-resolution and depth-sensing indentation involving the application of a controlled load to the surface of a material to induce local surface deformation, is a well-suited tool for the study of the mechanical properties [1].
Cured phenolic resin is hard and brittle, so well cross-linked phenol-formaldehyde (PF) should be an ideal shell material for the microcapsule used in self-healing concrete. In this work, PF microcapsule containing dicyclopentadiene (DCPD) as healing agent was selected as a sample to investigate mechanical properties of a micro-ball with core/shell structure.

2. MATERIALS AND METHODS
2.1 Materials
DCPD, Resorcinol were received from Aladdin-reagent, Shanghai, China. Phenol, 37wt% formaldehyde, sodium hydroxide, 37% HCl and sodium polyacrylate were purchased from Tianjin Chemical Plant, Tianjin, China.

2.2 Preparation of the PF/DCPD microcapsules

PF microcapsules filled with DCPD were synthesized by *in situ* polymerization. The details of encapsulation procedure are as follows: 15g sodium polyacrylate dissolved in 200ml deionized water, add 14g DCPD, 13g formaldehyde or 35ml 37wt% formaldehyde solution, adjust pH by 0.1M HCl and 0.1M KOH solution to 2, add 12g phenol, stirred at 800rpm for reaction. First react at 70°C for 3hrs, then at 90°C for another 3hrs. After washing and vacuum-drying, the product of PF/DCPD microcapsule was obtained.

2.3 Characterization of PF/DCPD microcapsules

microcapsule's morphology and shell's fracture surface were observed under SEM (SU-70, Hitachi, Japan). Micromechanical performance was determined on G200 nanoindenter (Keysight, USA) . For cracking load measurement, the nanoindenter worked on depth-step contrelled model by using a plate tip. When measure Young's modulus, the nanoindenter worked on continuous stiffness model (CSM) with a Berkovich tip. The testing procedure followed with the standard of ISO 14577[2]. The indentations were examined under optical stereoscopic microscope (VHX-600K, Keyence, Japan).

3. RESULTS AND DISCUSSION

3.1 Morphology of PF/DCPD microcapsules

PF/DCPD microcapsule is a perfect sphere with size from 40μm to 200μm. The shell is compact, smooth on both of interior and exterior, looks like brittle. The shell thickness is about 20μm evenly,

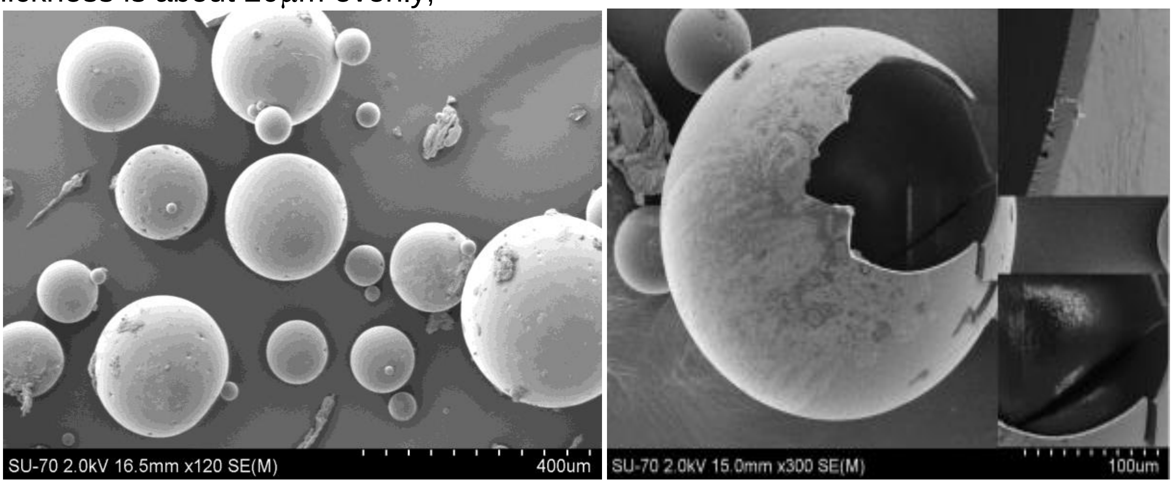

Fig. 1 SEM image of PF/DCPD microcapsule showing: (a) morphology, (b) fractured shell

3.2 Young's modulus of PF shells

The Young's modulus hardness of the microcapsule shells can be calculated by the nanoindentation instruments using well-established equations based on elastic contact theory[3]. During nanoindentation test on G200, the load and displacement are continuously examined resulting in a load–displacement curve, as shown in Fig. 2. The Young's modulus of PF shells (E) deduced from the curve was listed on Table1. It's clear that E does not change with microcapsule's diameter d or shell's thickness δ. It only rests with the wall material itself, has nothing to do with geometrical factors. The mean value of E is 2.47Gpa.

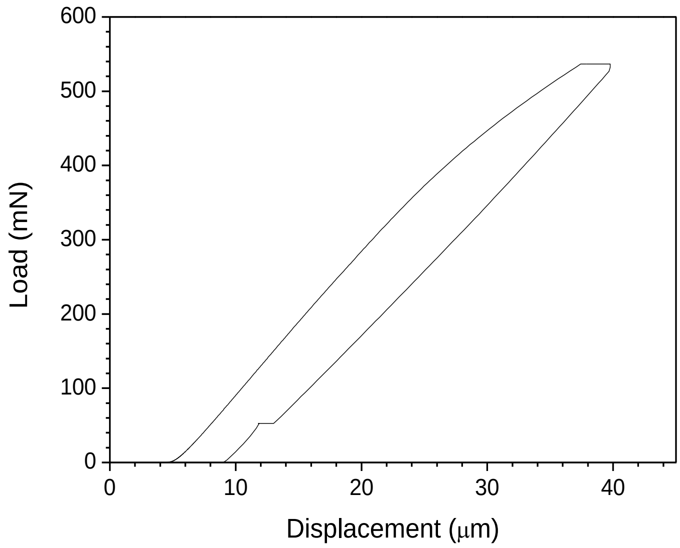

Fig. 2 the load–displacement curve of PF shell on continuous stiffness model

Table1.The Young's modulus of PF shell

Samples No.	PF shells' parameter		E (GPa)
	d(μm)	δ(μm)	
1	447.25	26.52	2.23
2	557.66	42.07	2.75
3	596.23	15.92	2.08
4	686.85	55.14	2.52
5	789.14	22.17	2.47
6	849.80	23.13	2.63
7	879.44	47.90	2.63
8	895.09	53.11	2.48
9	1105.18	35.47	2.33

3.3 Cracking load of PF/DCPD microcapsule

Cracking load is the maximum force the individual microcapsule bears during the test. As shown in Fig. 3, the load increases approximately with increaseing *δ* and decreasing *d.* In fact, Cracking load is varies inversely with the ratio of d/δ. There is a strict linear-relationship between them, as Fig.4 shows.

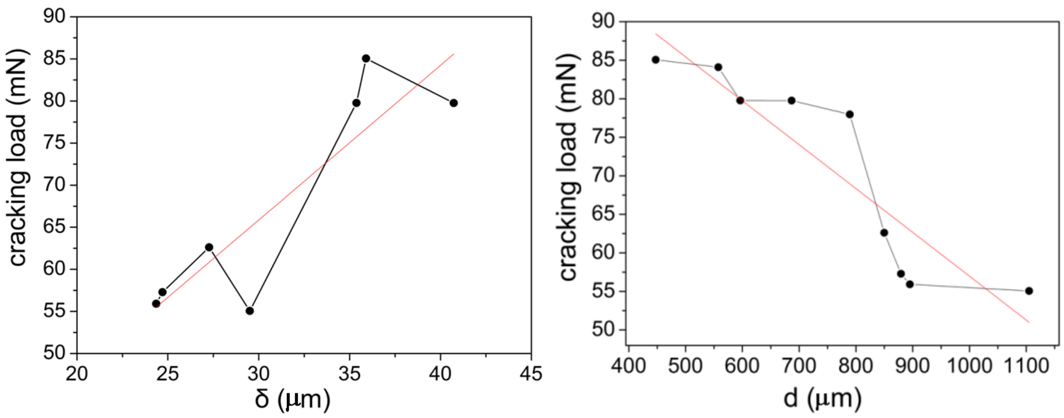

Fig. 3 Cracking load varies with (a) microcapsule's diameter *d*, (b) shell's thickness δ

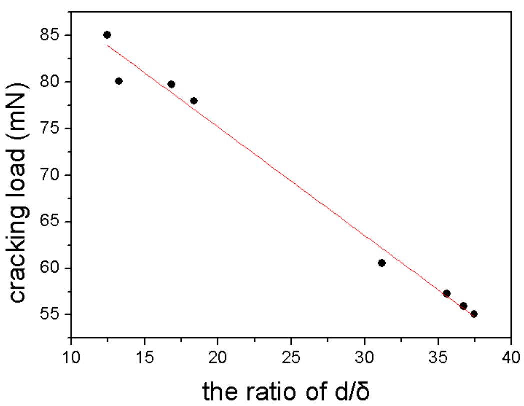

Fig. 4 The strict linear relationship between cracking load and *d/* δ

4. CONCLUSION

For a microball with core/shell structure like microcapsule, the maximum force it can bear is decreased with the ratio of ball's diameter to shell's thickness. it's confirmed Young's modulus of shell is foreign to structure parameters. Specially for PF/DCPD microcapsules, E value of PF shell is 2.47Gpa.

ACKNOWLEGDEMENTS

The authors would like to acknowledge financial support provided by National Natural Science Foundation of China (No.51120185002/U1301241), Science and Technology Project of Shenzhen City (JCYJ20140418091413518), and Collaborative Innovation Center for Advanced Civil Engineering Materials, Nanjing, P. R. China.

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