Determination of the rupture stress of microcapsule and the Young's modulus of its shell materials by nanoindenter

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ABSTRACT
As a core/shell structure, the deformation of microcapsule under stress is consisting of two parts: the shell deformation and the structure deformation. It will complicate the calculation of Young's modulus of shell materials and rupture stress of whole microcapsule if the data is acquired by a nanoindenter. In this paper, a discrete step working model of the nanoindenter was developed to determine the rupture stress of microcapsule from load-displacement curves, and another novel working model was employed to measure the Young's modulus of the shell. The accuracy of results was discussed.

1. INTRODUCTION
Micromechanical parameters are extremely important to the microcapsules used in self-healing materials. Only when the microcapsules were triggered at a given stress, the healing process can be carried out, and the self-healing materials can be useful. In most applications, it's required the shell materials are hard and strong enough to ensure the microcapsule survive in the composite formation, and meanwhile crispy enough to be broken [1].

Due to small size and wide size-distribution of microcapsules, there are few instruments and methods available for the investigation of microcapsule's mechanical performance. Although much pioneering work has been done on modeling and simulation, to the best of our knowledge, there are few studies reported in literatures on the mechanical behaviour of microcapsules under nanoindenter [2–4].

Normally, Nanoindenter can works on different models. In each model, the equipment records the load and displacement. How to calculate the strength or Young's modulus from these data is a challenge, because nanoindenter is so sensitive that the results are affected by many factors, such as, loading regime, substrate, deformation of indenter and specimen shape, etc. In this work, a special method for the nanoindenter was designed to acquire the load-displacement curves that are able to determine the ruptured stress of microcapsules. A novel working model of the nanoindenter was employed to measure the Young's modulus of the shell materials by using a Berkovich nanoindenter continuously contacting the sample surface.

2. MATERIALS AND METHODS
The samples tested are DCPD/PF microcapsule which is made by ourself. Before testing, each microcapsule and the shell obtained from a fractured microcapsule

were inspected and selected under optical stereoscopic microscope, then fixed firmly on the sample stage by a heat-cured gum.

The nanoindentation tests were conducted on G200 Nanoindenter (Keysight, USA) in isolated conditions. For rupture force measurement, the equipment works on depth-step-controlled model with a plate tip. To determine Yong's modulus and Hardness of the shell materials, it works on continuous-stiffness model (CSM) with Berkovich indenter. Both of models are displacement-contrelled procedures, but the former increases the displacement step by step, the latter increases the displacement continuously.

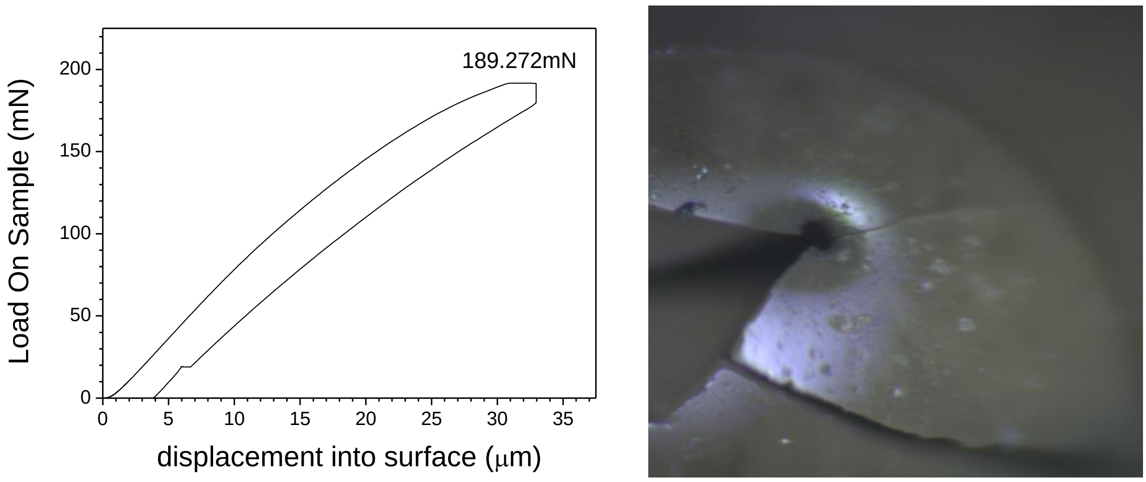
As a comparison, the shell of microcapsules was also tested on traditional medel. It's a load-contrelled procedure, quite different from models we developed.

3. RESULTS AND DISCUSSION

3.1Rupture force of the whole microcapsule

Depth-step-controlled model actually is a strain-stepper procedure. In each step, the nanoindenter records the resisting force of sample automatically. When the sample is broken, the force will fall down suddenly. The crest value will be the rupture force we want.

As most of the microcapsules are shelled by anelastic polymers, the data obtained by this model shoud be more precise than traditional method. In Fig. 1(a), the rupture force of tested microcapsule is 189.272mN. Fig.1(b) tell us the rupture is typically brittle.



(a) (b)

Fig.1 (a) load-displacement curve of the microcapsule (b) the image of ruptured microcapsule after test

3.2 Young's modulus (E) of the shell

In order to prevent errors from structural deformation of microcapsule, the measurement of Young's modulus was conducted only on phenolic aldehyde (PF) shell, not on the whole microcapsule. As the shell is so thin that, it's deformation will be affected strongly with the substrate. Continuous-stiffness model is a dynamic nanoindentation procedure, by which a true stress – strain curve can be derived from the real - time load-displacement data. So substrate effect could be overcome by the model[5].

The general principle of elastic modulus (E) measurement by CSM is as follows: In order to calculate E, the elastic stiffness of the contact, S, must be known. Traditionally, S is determined from the slope of the load-displacement data acquired during unload. However, such a calculation to determine S only can be done at the maximum penetration depth. The CSM option enables a continuous measure of S during loading, and not just at the point of initial unload. This is accomplished by superimposing a small oscillation onthe primary loading signal and analyzing the resulting response of the system by means of a frequency-specific amplifier. With a continuous measure of S, hardness and elastic modulus as a continuous function of surface penetration can be obtained.

Fig. 2 illustrates the principle. Fig. 2(a) shows the local deformation of shell materials in the vicinity of Berkovich indenter at a moment of testing, on which, P_{max} is the maximum load, h_{max} is the maximum penetration depth, h_c contact depth, h_f final depth. These parameters are important to characterize the real-time deformation. They can be determined from the dynamic load–displacement curve, as shown in Fig. 2(b).

Define the slope of the beginning unloading curve as contact stiffness (H), it is given by

$$H = \frac{P_{max}}{A_C}$$

where A_c is integral of the unloading curve[6].

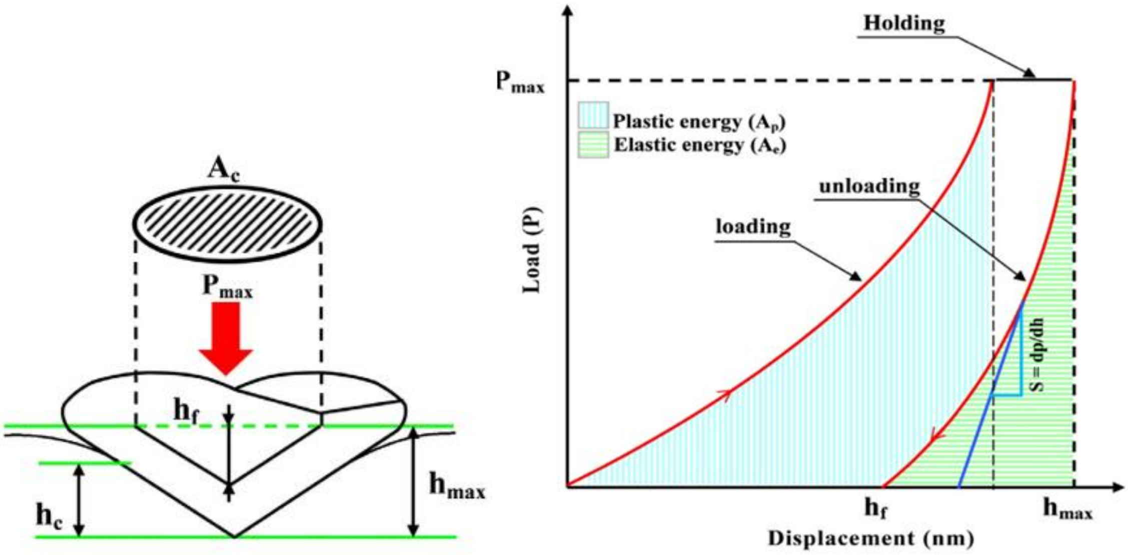


Fig.2 (a) the shell deformation under the pressure of Berkovich indenter on continuous-stiffness model, (b) schematic diagram of load–displacement curve on continuous-stiffness model

Table 1 Young's modulus value E of PF shell

Sample's No.	E by TM, GPa	E by CSM, GPa
1	0.07	2.23
2	4.12	2.75
3	2.25	2.08
4	1.36	2.52
5	2.22	2.47
6	2.61	2.63
7	0.47	2.63
8	5.08	2.48
9	3.01	2.33

To calculate Young's modulus (E) accurately, the elastic deformation of indenter must be token into account. From the slope of the linear portion, i.e. dP/dh upon unloading in Fig. 2(b), E_r, the reduced modulus of the indentation contact, is given by[6] :

$$E_r = \frac{\sqrt{\pi}}{2}\frac{dP}{dh}\frac{1}{A_C}$$

E_r is related to the elastic modulus of the sample and the elastic modulus of the indenter by the following equation[6]:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}$$

Where E and ν are the elastic modulus and Poisson's ratio of specimen respectively. E_i is ν_i are the elastic modulus and Poisson's ratio of indenter respectively. For Berkovich diamond indenter, E_i and ν_i are 1140 GPa and 0.07, respectively. Table 1 shows the calculation results from from the load-displacement data acquired by continuous stiffness model (CSM) and traditional method(TM). It is clear the PF shell's moduli acquired by CSM are more uniform. The mean value is 2.46GPa, close to the value obtained from the standard tensile test, 2.8±0.7Gpa.

4. CONCLUSION

on G200 Nanoindenter, the ruptured stress of microcapsules can be measured with a plate tip in depth-step-contrelled working model, the Young's modulus of shell materials can be calculated from the load-displacement curve obtained by applying continuous stiffness measurements (CSM) working model and a Berkovich indenter. The results are very reliable.

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REFERENCES

[1] M.W. Keller, N.R.Sottos, Mechanical properties of microcapsules used in a self-healing polymer. Exp Mech 2006; 46(6):725–33.

[2] A. Fery, R. Weinkamer, Mechanical properties of micro- and nanocapsules: single-capsule measurements. Polymer 2007; 48(25):7221–35.

[3] J. Lee, M. Zhang, D. Bhattacharyya, Y.C. Yuan, K. Jayaraman, Y.M. Mai, Micromechanical behavior of self-healing epoxy and hardener-loaded microcapsules by nanoindentation. Mater Lett 2012;76:62–5.

[4] M.M. Shokrieh, M.R. Hosseinkhani, M.R. Naimi-Jamal, H. Tourani. Nanoindentation and nanoscratch investigations on graphene-based nanocomposites. Polymer Test 2013; 32(1):45–51.

[5] J.L. Hay, P. Agee, and E.G. Herbert, Continuous stiffness measurements during instrumented indentation testing. Experimental Techniques 34, 86 (2010).

[6] W.C. Oliver, G. M. Pharr, An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, Journal of Materials Research:7 (1992)1564–1583.