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Characterization of the Mechanical Properties of Urea−Formaldehyde Microcapsules

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Abstract: The mechanical properties of urea−formaldehyde (U−F) microcapsules were determined using a micromanipulation technique and a theoretical model. Loading−unloading, compressing and holding, and compressing to bursting tests at different speeds between two parallel plates for single microcapsules were carried out. It was found that the U−F microcapsules were visco-elastic (mainly elastic) at small compressive deformation, and plastic under large deformation. The transition point from elastic to plastic occurred at about (14±0.2)% compressive deformation. All the microcapsules would disrupt when compressed to about (17±0.2)% deformation, and the burst force increased linearly with their diameter. Compressing speed had no remarkable effect on both burst force and burst deformation. Liquid filled non-permeable and linear elastic spherical membrane model was used to simulate the uniaxial compression of single microcapsule, and its membrane modulus *Eh* was determined by fitting model prediction to experimental data. The average value of *Eh* was estimated to be (478±8) N/m.

Key words: urea−formaldehyde microcapsule; micromanipulation technique; mechanical properties; linear elasticity; Young′s modulus

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1 INTRODUCTION

Microcapsule is a kind of important special functional material, which has been widely used in pharmaceutical and medical delivery[1,2], adhesives and insecticides. Such microcapsules generally have a non-permeable or semi-permeable membrane wall, and a liquid-like core. As for its formulation, transportation and storage, the wall of capsules is desired to be more rigid. However, as for the applications such as drug delivery, prompt rupture is desired to make the endosome released on sites[3]. Understanding of the mechanical properties including relationship of stress-deformation and Young′s modulus are of interest for both preparation and usage. Some efforts such as pipette aspiration technique[4], micro-poking technique[5] and optical tweezers technique[6] have been made to probe the mechanical properties of micro-particles. However, most of the above techniques can only measure local mechanical stiffness at very small deformation.

Micromanipulation technique was mainly developed to measure the mechanical properties of single animal cells[7]. Its principle is compressing single particles between two parallel rigid smooth plates, one of which is connected with a sensitive force transducer. With this technique, the mechanical stiffness of some biological and non-biological particles[8−10] has been successfully investigated. Zhang et al.[11] also investigated burst force and burst displacement of melamine−formaldehyde (M−F) microcapsules with this technique. Sun et al.[12] investigated the influence of wall materials on stiffness of M−F and gelatin microcapsules. Urea−formaldehyde microcapsule has so far the largest commercial market in drug delivery, fragrance, carbonless copying paper[13] and self-healing materials[14] due to its impermeable wall, stability, cheap and easy-making[15]. The key feature of self-healing materials is the highly engineered microencapsulated healing agent. The microcapsules in self-healing polymers not only store the healing agent during quiescent states, but also provide a mechanical trigger for the self-healing process when damage occurs in the host material and the capsules rupture[16]. The microcapsules must possess sufficient strength to remain intact during processing of the host polymer, yet rupture when the polymer is damaged. However, little detail was known on its whole stiffness at extreme state, for example, whether it can be compressed to disruption, how and when it disrupts, whether it is elastic or plastic. Especially there is no information about the mechanical intrinsic parameters such as Young′s modulus of the U−F microcapsules. In this work, the micromanipulation

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technique was used to detect the stiffness of the U−F microcapsules and rheological behavior (elastic or plastic). And then liquid filled elastic membrane model was used to determine its Young′s modulus.

2 MATERIALS AND METHODS

Urea−formaldehyde microcapsules are kind gift from Dr. Allen Naddin, Central Science Laboratory, UK, which were made from dispersing kerosene in water and then encapsulated by urea−formaldehyde walls by in situ polymerization. The details of the preparation method are described in a US patent[17]. The molar ratio of formaldehyde to urea is 1.9. The average diameter of the samples is (82±2) μm, and wall thickness is estimated about 0.5~0.8 μm.

The micromanipulation rig is schemed in Fig.1. It is mainly composed of two microscopes (for both side and bottom views), a force transducer held by a fine micromanipulator, and a computer with a data acquisition system. The details of the technique are described elsewhere[9]. Single microcapsules were compressed to different deformation and held, compressed and released, or compressed to rupture at different speeds, the force imposed on microcapsule was measured by a force transducer (Model 403A, Aurora Scientific Inc, Canada) simultaneously. All micromanipulation experiments were conducted at room temperature. The diameters of single microcapsules were determined from microscopic images and a Leica image analyzer (Leica Q5001W, Leica Imaging Systems Ltd, UK).

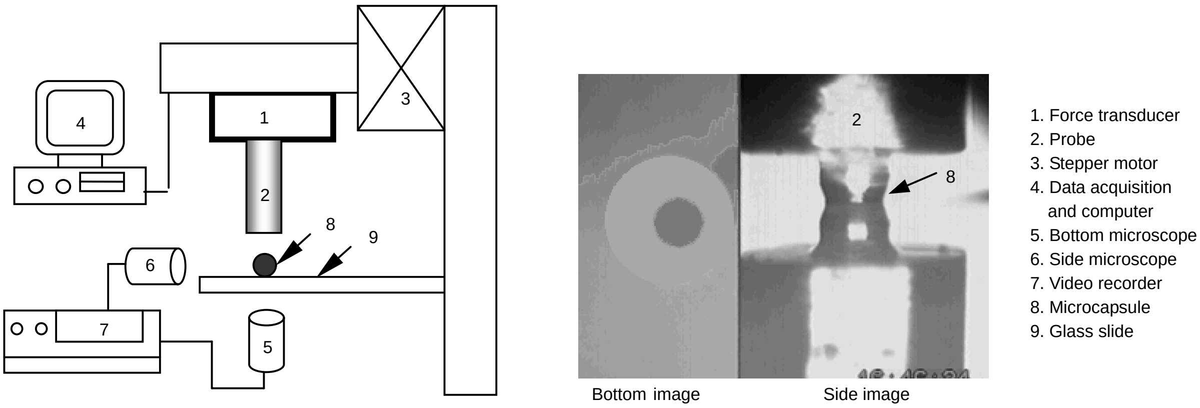

Fig.1 Schematic graph of the micromanipulation rig

3 RESULTS AND DISCUSSIONS

3.1 Compressing and Holding Mode

As the probe moved at a constant speed to gradually approach a microcapsule, touched (point *A*) and compressed it to pre-setup deformation (point *B*), and then the probe held (point *C*), the force imposed on single microcapsule would change with time as shown in Fig.2. It can be found that as soon as the probe touches the microcapsule, the force imposed on it increases quickly with the increase of deformation (displacement normalized by the diameter of microcapsule). The amount of the force is dependent on the mechanical strength of capsule and the degree of deformation. As the deformation reached the pre-setup deformation and the probe stopped to maintain its position, the force would not increase anymore. If the pre-setup final deformation was small, such as 11% and 13% of the capsule in the cases, the force almost kept constant during the holding time, which indicates no relaxation occurring under such compressive deformation. When the capsule suffered large deformation, as 18% in this case, a slight force decrease was detected as time elapsed. This indicates that the U−F microcapsules are either elastic or elastic-plastic at small deformation, and a little viscid under large deformation. It should be mentioned that the three compressing−holding curves

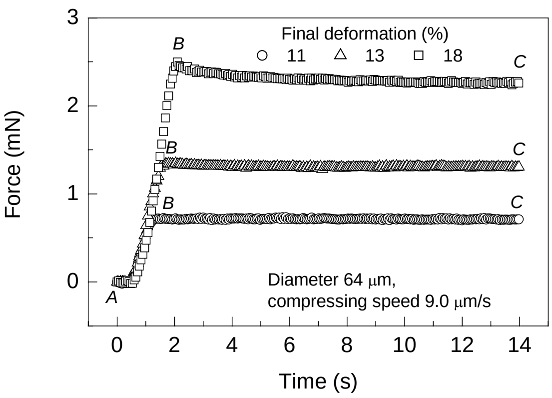

Fig.2 Compressing−holding curves for the same single U−F microcapsules

were obtained from the same capsule. The same touching point *A* of the three compressing–holding curves also implies a good elastic recovery of the capsule under small deformation.

3.2 Loading and Unloading Cycles

The loading and unloading curves of a same capsule in different deformation cycles are shown in Fig.3. It can be found that if the pre-setup deformation is small, as 8% of this case in the first cycle, the loading curve and unloading curves overlap very well without significant hysteresis. While the pre-setup deformation increases to about 17% in the second cycle, after the large loading deformation, the loading curve and unloading curves do not coincide because of the permanent deformation (about 5%). However, the small part of the loading curve of second cycle has a good agreement with the loading and unloading curves of first cycle. Therefore, the U−F microcapsule is considered as viscoelastic (mainly elastic) at such small deformation, and plastic at large compressive deformation.

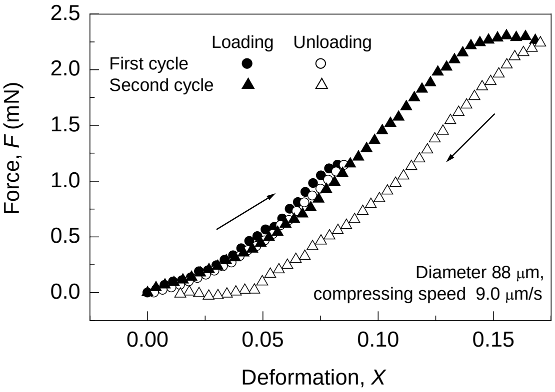

Fig.3 Loading–unloading curves for single U−F microcapsule

3.3 Compressing Single Microcapsules to Burst

The probe was first in its original position (point *A*′), far away the microcapsule (see Fig.4). As it was driven towards capsule till to touching point *A*, any further moving towards the capsule would cause the compression force increased and deformation of the capsule. When the microcapsule was compressed to point *B*, a quick force drop occurred, indicating the capsule disruption. The force imposed on the microcapsule at this moment was defined as burst force F_b, and burst deformation X_b was obtained correspondingly. As soon as the capsule ruptured, the force quickly reduced to point *C*. Points *C* to *D* is the compression of the debris of the microcapsule. The relationship between force and corresponding deformation from point *A* to *B* was also shown in Fig.4, which was important for the later modeling to determine instinct parameters such as Young′s modulus of microcapsules. Because the U−F microcapsule is visco-elastic (mainly elastic) at small deformation, and plastic at large deformation before rupture, there should be a transition point from elastic to plastic. This point is the yield point X_p, which can be determined by zero value of the second derivative of force to deformation, $d^2F/dX^2=0$. Figure 5 shows the transition deformation at yield point of all the experiments. It can be found that the transition deformation is independent of the diameter of the U−F microcapsules, and all the U−F microcapsules will present plastic yield when compressed to about (14±0.2)% deformation. Similar results have been obtained for melamine–formaldehyde microcapsules[18].

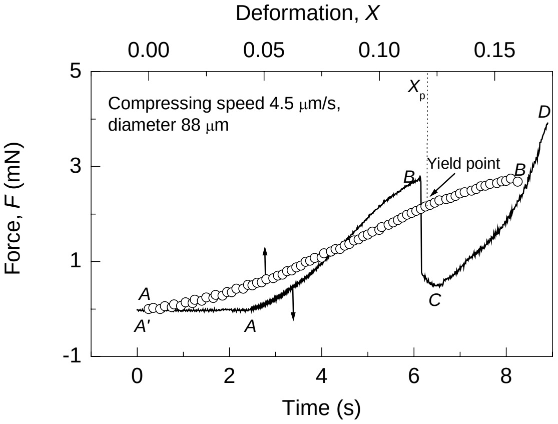

Fig.4 Force changes and corresponding force−deformation curve when compressing a single microcapsule

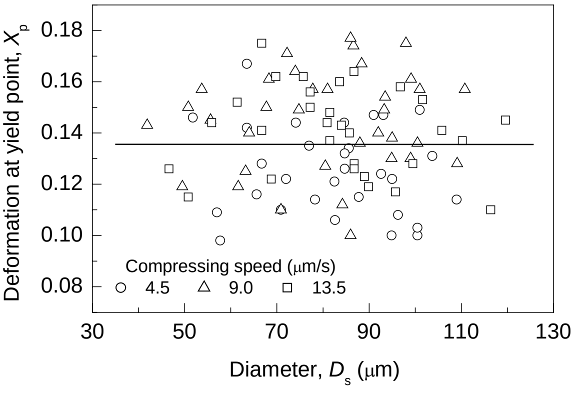

Fig.5 Transition points of the U−F microcapsules shifted from visco-elastic to plastic

3.4 Burst Force and Burst Deformation

Figure 6 shows the relationship of the burst force F_b and the diameter of microcapsules. There is a good linear relationship between the burst force and the diameter of the U−F capsules. Large capsules are more

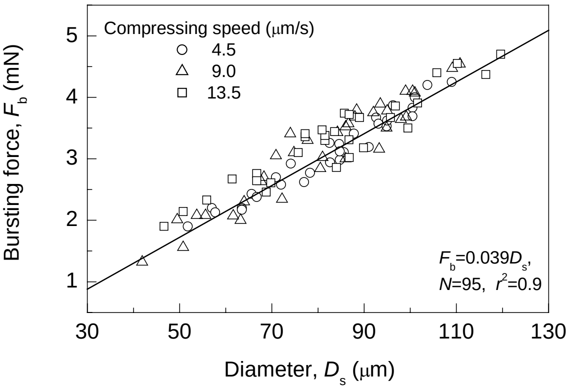

Fig.6 Relationship between the bursting force and microcapsule size

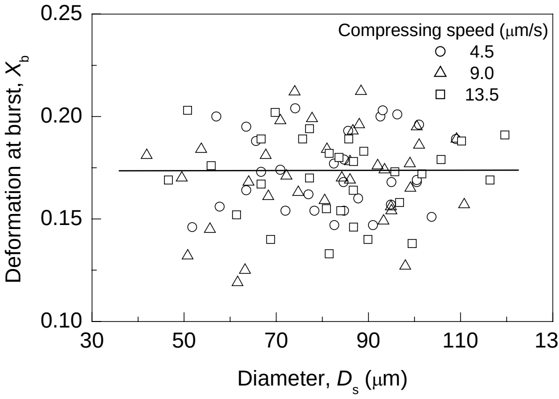

Fig.7 Deformation at burst point under different compressing speeds

rigid than small capsules. Figure 7 gives the burst deformation X_b of U–F microcapsules of different size at burst point. It is observed that the burst deformation is independent of the capsule size. All the capsules would be compressed to disruption when the compressive deformation reached about (17±0.2)%. Both F_b and X_b can be taken as the strength parameters of the microcapsules, and the results show that size control in microcapsule fabrication is an appropriate way to predict or control the microcapsule strength.

3.5 Theoretical Model and Young′s Modulus

Apart from the burst force and burst deformation, more interest is paid on the intrinsic mechanical parameters, such as Young′s modulus E and Poisson ratio υ. Forgoing result has demonstrated visco-elastic (mainly elastic) at small deformation of the U–F microcapsules, therefore single microcapsule was assumed to be a liquid filled, non-permeable spherical membrane[19,20], and linear elastic constitution equations[21] were used to simulate the uniaxial compression deformation between two smooth plates in this work. The compressed geometry of the capsule was divided into contact and non-contact regions, and governing equations of each region were obtained, in which compression force F and displacement η are connected with material properties of microcapsule including Young′s modulus E, Poisson ratio υ, and initial stretch ratio λ_s. More details of the model can be referred to Feng et al.[19] and Lardner et al.[20]. MATLAB program (Version 6.1, The Mathworks, Inc, USA) was used to solve the model equations and the relationship of compression force and deformation was obtained. Previous work[20] and our calculation have shown that the value of Poisson ratio υ has no remarkable effect on the deformation of such thin spherical membrane. Here the U–F microcapsule was assumed to be incompressible and therefore υ=0.50. The calculated results of the force F and compressive displacement η were integrated into two dimensionless groups, $Y=F/(EhR_0\lambda_s^2)$ and $X=1-\eta/R_0$, as shown in Fig.8. It can be found that with the increase of compressive deformation, the dimensionless force Y also increases, and the initial stretch ratio λ_s has a distinct effect on the relationship between the dimensionless force Y and deformation X.

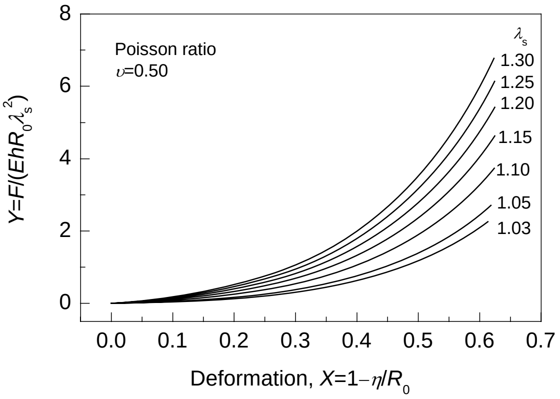

Fig.8 Dimensionless force and deformation at different initial stretch ratios of λ_s (R_0 is radius of microcapsule)

Due to the unknown wall thickness of individual microcapsules, here membrane modulus Eh was defined as the product of Young′s modulus and wall thickness, and it was determined by fitting experimental force-deformation results with the elastic model values by the least square method. Typical comparison of the model predictions with micromanipulation data of force versus deformation (corresponding to Fig.4) is plotted in Fig.9. It can be seen that till the plastic yield point, both are in very good agreement. The average derivation between the model prediction and experimental data is estimated about (8±1)%. The Eh of individual U–F microcapsules is given in Fig.10, and its mean value is (478±8) N/m. The initial stretch ratio λ_s, was also determined by the fitting method, and the average value is 1.09, which means that the U–F microcapsule has a little initial membrane tension by the internal pressure of liquid core. Future work will include investigation of the influence of wall thickness on capsule strength and development of elastic-plastic model to simulate the whole uniaxial compression.

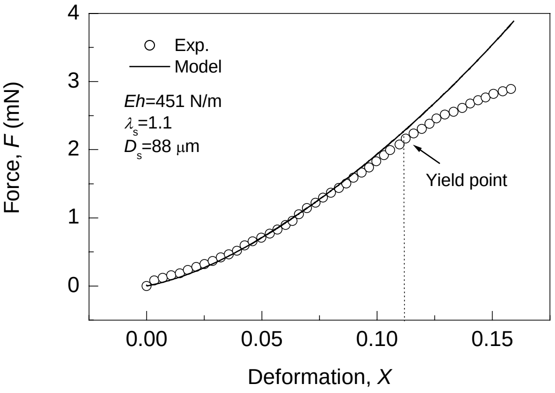

Fig.9 Comparison of the force versus deformation for both model prediction and experiment corresponding to Fig.4

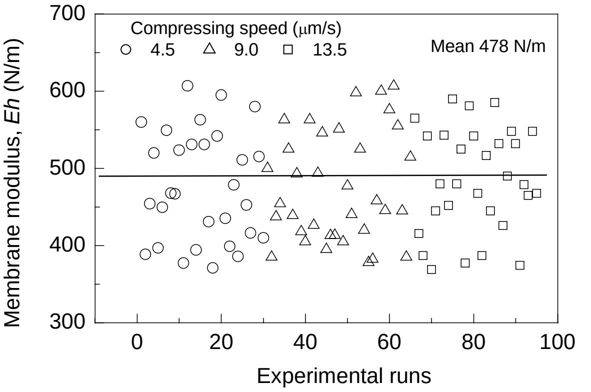

Fig.10 Membrane modulus *Eh* under three compression speeds

4 CONCLUSIONS

The mechanical properties of urea–formaldehyde microcapsules were determined using micromanipulation technique and linear elastic model. The results show that the U–F microcapsules demonstrate visco-elastic (mainly elastic) at small compressive deformation, and plastic under large deformation. The plastic yield occurs at about (14±0.2)% compressive deformation. All microcapsules would be compressed to disruption at about (17±0.2)% compressive deformation, and burst force varies linearly with the increase of capsule size. Compressing speed has no remarkable effect on both burst force and burst deformation. Liquid filled spherical membrane model in conjunction with linear elastic constitution equations was used to describe the elastic deformation of the microcapsules under uniaxial compression, and the membrane modulus, *Eh* was determined to be (478±8) N/m in average.

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