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Note

Mechanical strength of microcapsules made of different wall materials

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Abstract

The mechanical strength of microcapsules made of three different wall materials, including melamine–formaldehyde resin, urea–formaldehyde resin and gelatin-gum arabic coacervate, were measured by a micromanipulation technique. Single microcapsules were compressed to large deformations or rupture and the force being imposed on them were measured simultaneously. Melamine–formaldehyde and urea–formaldehyde microcapsules showed clear bursting under compression, and their bursting force, deformation at bursting and deformation at a pesudo yield point were determined. Gelatin microcapsules did not show clear bursting under compression, and their mechanical strength was characterized by the force required to cause their deformation to 50%. The mechanical strengths of these three types of microcapsules are compared in this paper.

Keywords: Microcapsules; Mechanical strength; Micromanipulation; Melamine–formaldehyde; Urea–formaldehyde; Gelatin

Microcapsules have been widely used for making carbonless copying paper, functional textiles, preservation or targeted delivery of agrochemical, chemical, food, pharmaceutical etc. Microcapsules for such applications should have appropriate mechanical strengths. Due to their small size, little was known about the mechanical strength of single microcapsules until recently a micromanipulation technique was developed (Zhang et al., 1991; Liu et al., 1996; Zhang et al., 1999; Sun and Zhang, 2001). This technique was used to measure the bursting force and deformation at bursting of single melamine–formaldehyde microcapsules (Zhang et al., 1999) and to determine the visco-elastic-plastic behaviours of the microcapsules (Sun and Zhang, 2001). Following the success, the technique has been applied to measure the mechanical strength of urea–formaldehyde and gelatin microcapsules, and the results of these three types of microcapsules are presented in this paper.

Melamine–formaldehyde (M–F) and urea–formaldehyde (U–F) microcapsules were prepared by in situ polymerization, and the details are given in Sun and Zhang (2001) and Foris et al. (1978) respectively. The amount of M–F wall

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materials used was 50% of the core materials in weight, and that of U–F was 42%. Gelatin microcapsules were made by complex coacervation (Kroschwitz, 1995). The amount of gelatin-gum arabic wall materials used was 50% of the core materials in weight. The core material encapsulated in the M–F microcapsules was a 10:1 (w/w) mixture of HB40 and kerosene, the former being a mixture of technical grade partially hydrogenated terphenyls (Monsanto Limited, Brussels, Belgium). In the U–F and gelatin microcapsules, the core materials were dibutyl phthalate and dimethyl phthalate (Fisher Scientific, Leicester, UK), respectively.

The principle of the micromanipulation technique is to compress single microcapsules between two parallel surfaces. The schematic diagram of the micromanipulation rig is shown in Fig. 1. The details of this technique is described elsewhere (Zhang et al., 1999; Sun and Zhang, 2001). Single microcapsules were compressed and held, compressed and released, and compressed to large deformations or rupture at a pre-set speed. Simultaneously, the force being imposed on them and their deformation were determined.

M–F and U–F microcapsules were dried before their mechanical properties including strengths were determined. When single M–F and U–F microcapsules were compressed and held, the force imposed on them increased when they were compressed and decreased slightly when they were held. When both types of the microcapsules were compressed to a small deformation and then released, e.g. 12% (ratio of the microcapsule displacement to original diameter) for M–F and 15% for U–F microcapsules, there was only marginal hysteresis found from the force versus displacement curve. The force being imposed on the microcapsules dropped to zero only when the force probe returned to its original position. Therefore, M–F and U–F microcapsules can be considered to be visco-elastic (mainly elastic) for such small deformations, which is consistent with the experimental results of 'compress and hold'. However, when their deformation was relatively large, e.g. 39% for M–F (Fig. 2a) and 29% for U–F microcapsules (Fig. 2b), there was a more profound hysteresis, and the force corresponding to unloading had already reduced to zero even if the force probe was still far away from its original position. This indicates that the microcapsules had a permanent (plastic) deformation after the force on them was completely released. Since M–F and U–F microcapsules were visco-elastic (mainly elastic) at small deformations and plastic at relatively large deformations, there was a pseudo yield point at which the plastic behaviour began to occur. For M–F microcapsules, the deformation corresponding to this yield point was found to be $19 \pm 1\%$ (Sun and Zhang, 2001), and for U–F capsules, the deformation was $17 \pm 1\%$.

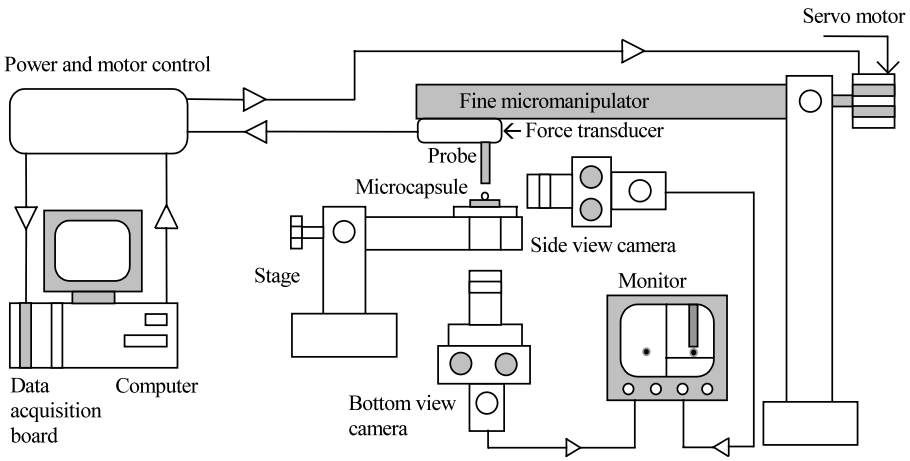

Fig. 1. Schematic diagram of the micromanipulation rig.

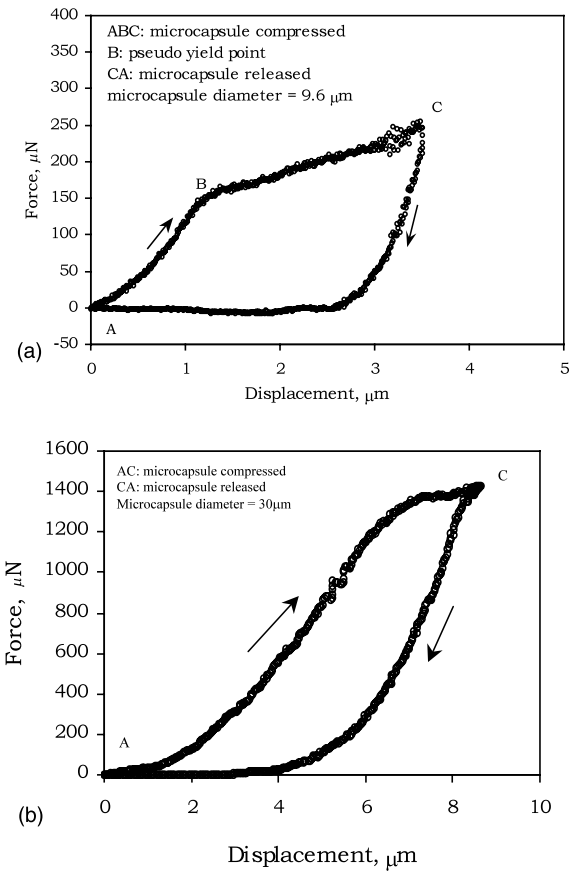

Fig. 2. Force vs. displacement curve when single microcapsules were compressed to a relatively large deformation and then released. The compression speed was 1 μm/s. (a) M–F microcapsule; (b) U–F microcapsule.

Gelatin microcapsules were in water suspension when their mechanical properties were characterised, since their wall appeared to collapse and core materials were released after they were dried, indicating that their wall was highly permeable to the core materials. When single gelatin microcapsules were compressed and held, the force imposed on them increased first and then decreased slightly. When the microcapsules were compressed to a deformation of up to 50% and released, there was no significant hysteresis observed. This indicates that gelatin microcapsules were mainly elastic up to this deformation. The drop in force being imposed on the microcapsules when they were held might be due to the loss in core materials from the wall.

Understanding of these elastic, visco-elastic or plastic behaviors of single microcapsules is essential to determination of the constitutive equations of the materials. Furthermore, the intrinsic mechanical property parameters of the microcapsules, such as Young's modulus, Poisson ratio, relaxation time, yield stress, etc. may be determined by mathematical modeling and micromanipulation measurements (Feng and Yang, 1973; Lardner and Pujara, 1980; Liu et al., 1996; Smith et al., 2000).

When M–F microcapsules were compressed to a deformation around $68 \pm 1\%$ they exhibited a clear bursting, represented by point 'C' in Fig. 3a. Under compression U–F microcapsules also showed a clear bursting, represented by point 'B' in Fig. 3b where the core material was observed to be released. In addition, after the U–F microcapsules were ruptured, further compression resulted in cracking and yielding of the ruptured wall, which is reflected by the second peak in Fig. 3b, point 'C'.

On average, the bursting force and deformation at bursting of U–F microcapsules increased proportionally with their diameter, as shown in Fig. 4. Similar results have been obtained for M–F microcapsules (Sun and Zhang, 2001). However, the U–F microcapsules burst when they were deformed by only $35 \pm 1\%$, much smaller compared with $68 \pm 1\%$ for M–F microcapsules (Sun and Zhang, 2001). The mean bursting force of U–F microcapsules (Fig. 4a) was also significantly smaller than that of M–F microcapsules for the same size (Sun and Zhang, 2001).

Gelatin microcapsules did not show clear rupture under compression. The force required to deform this type of microcapsules is much smaller than that for M–F and U–F microcapsules with same diameters. It is believed that when gelatin microcapsules were compressed the core materials were quickly released, thus significantly reducing the pressure inside. The force required to cause 50% deformation of single gelatin microcapsules appeared to increase proportionally with their diameter, as shown in Fig. 5.

In summary, the mechanical strengths of microcapsules with three different wall materials were

measured by a micromanipulation technique. M–F and U–F microcapsules showed viscoelastic (mainly elastic) behaviours at small deformations, and plastic beyond a yield point corresponding a deformation of $19 \pm 1\%$ and $17 \pm 1\%$ respectively. They both burst under compression, and the deformation at bursting were $68 \pm 1\%$ and $35 \pm 1\%$, respectively. Gelatin microcapsules showed an elastic behaviour, and did not burst under compression. This may be due to that the wall of gelatin-gum arabic coacervate was highly permeable to the core material. The bursting force and deformation at bursting for both M–F and U–F microcapsules increased proportionally with their diameter. The force required to cause gelatin microcapsules to deform by 50% also increased with their diameter. It is believed that these results can be used to understand better the functions of the microcapsules in industrial applications or to modify their formulation in order to optimise their mechanical strengths.

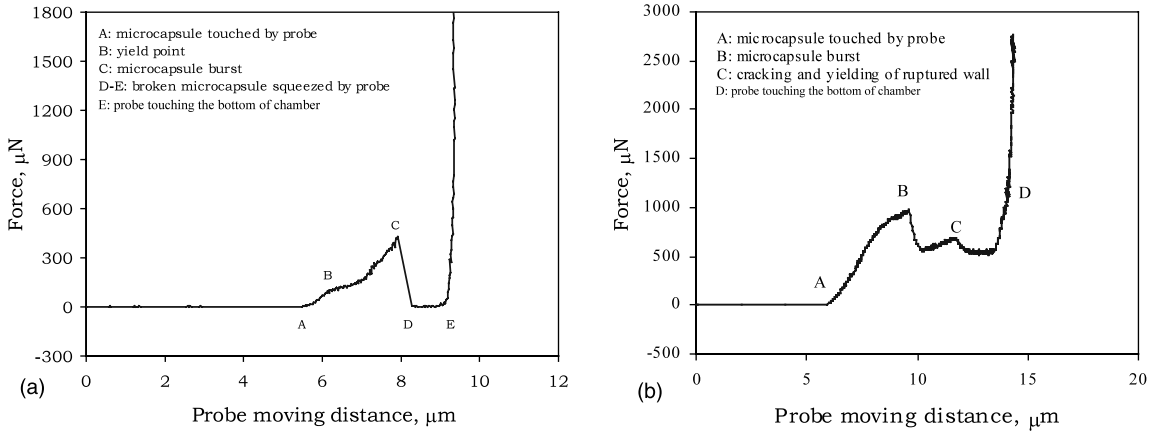

Fig. 3. Force versus probe moving distance for compressing single microcapsules to rupture. (a) M–F microcapsules; (b) U–F microcapsules.

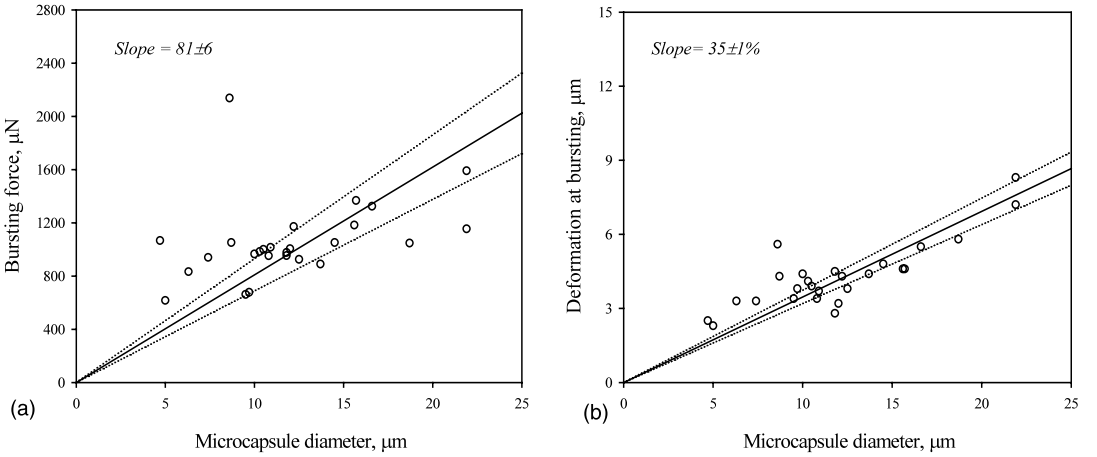

Fig. 4. Bursting force (a) and deformation at bursting (b) vs. diameter for U–F microcapsules. The compression speed was 1 μm/s. The solid lines in Figs. 4 and 5 represent the linear regression passing through the origin, and the dash lines show the 95% confidence limit of the regression.

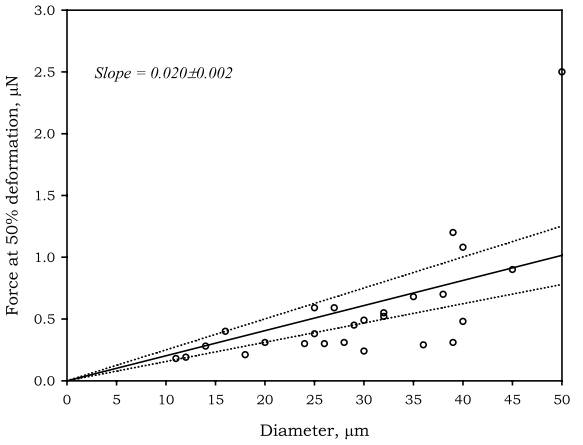

Fig. 5. Force required to cause 50% deformation versus diameter for gelatin microcapsules. The compression speed was 1 μm/s.

Acknowledgements

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