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Mechanical behaviour of micro-capsules and their rupture under compression

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H I G H L I G H T S

- We investigate deformation and rupture of micro-capsules under compression
- Force-deformation data from nano-indentation experiments agrees with simulations
- Simulations give a detailed picture of the stress distribution in the shell
- Micro-capsules are found to rupture along meridian lines from the equator

A R T I C L E I N F O

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A B S T R A C T

Understanding the deformation of micro-capsules (MCs) and especially the mechanism of their rupture is of crucial importance for their performance in various applications. Mechanical instability can on the one hand be a failure mechanism, resulting in undesired release, but can on the other hand be used as a release trigger. In this work, finite element analysis together with nano-indentation experiments is applied to characterize the deformation of single filled MCs made of melamin–formaldehyde. The simulations reveal that the capsules undergo different deformation regimes: starting from linear elastic deformation, upon further compression the MCs yield and are plastically deformed. The final step is a strain hardening regime, where the maximum stress rapidly increases till the MCs rupture. Finally, we describe the MCs rupture mechanism obtained from numerical simulation and experimental results. We show that the axial and radial stresses cause significant thinning of the shell at the MC's equator, and that the circumferential stress leads to rupture along the meridians of the MC.

1. Introduction

Micro-capsules (MCs) are primarily used to encapsulate a gel, solid or liquid core by a coating shell. There are numerous shell materials that are selected with respect to the chemistry of the core, and the specific functions that MCs are expected to perform. This long list includes gums, starch, cellulose, beeswax, copolymers, resins, lipids, and carbohydrates (Bansode et al., 2010; Sri et al., 2012).

MCs have been widely used in a variety of applications such as polymer composites (Carlisle et al., 2006), agro-chemicals industry (Tsuji, 2001), flame retardants (Wang et al., 2015), perfume containers in washing powders, health products and cosmetics (Carvalho et al., 2015), food industry (Gibbs et al., 1999), paint coatings (Koh et al., 2014), building construction materials (Tyagia et al., 2011; Schossiga et al., 2005), self healing materials (Brown et al., 2004), and corrosion inhibitors (Mac et al., 1989). Additionally, many researchers consider them as promising candidates for further applications like smart micro-containers (Bedard et al., 2010), magnetically (Carregal-Romero et al., 2015; Degen et al., 2015), chemically, and mechanically triggered active release (Peyratout and Dähne, 2004), biomimetic MCs in drug delivery systems and micro-biotechnology (He et al., 2009; Verberg et al., 2007; Masoud and Alexeev, 2012).

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Mechanical behavior of MCs, along with the chemistry of their constituents, and the physical properties of their shell, highly influences their performance. For example in polymer composites, MCs are commonly used to enhance their compression and impact strengths (Carlisle et al., 2006). In biomedical applications, when they are used in cartilage and bone replacements, MCs are expected to endure a high level of compression. In blood vessels where they may function as drug delivery agents, their stability under shear forces is of main interest (Nguyen et al., 2009). Recent results as well indicate that the mechanical properties of microcapsules influence endocytosis and internalization pathways in a controllable way, offering new opportunities in cellular medicine research and cancer therapy (Hartmann et al., 2015). A review article providing a broader overview of the relevance of microcapsule mechanics and of methods for mechanical characterization of microcapsules can be found in Neubauer et al. (2014).

Understanding the mechanical behavior of MCs, especially their rupture is of crucial importance in order to control the quality of the products and the efficiency of their performance. In this context, single microcapsule experiments are of major importance. Historically, the first single-capsule experiments were carried out on egg cells by Cole in the 1930s by compressing the cells between two parallel plates while monitoring the force as a function of the compression (Cole and Michaelis, 1932). Recent experiments follow a similar scheme (Hu et al., 2009; Gouadec et al., 2004; Carlisle et al., 2006; Mercadé-Prieto et al., 2011; Stenson et al., 2009; Nguyen et al., 2009; Mercadé-Prieto et al., 2012; Pan et al., 2013; Vella et al., 2012): the MCs are placed under a flat or pointed probe that moves toward a stationary metal substrate until the capsule is completely flattened (for highly plastic like phenolic capsules) or crashed (for brittle materials such as glass or carbon). The maximum force experienced by the MC at its burst and the corresponding displacement of the probe can be readily obtained from such experiments. However, in order to complete MCs rupture characterization it is necessary to relate this data to the proper stress and strain distribution in the shell thickness.

Mathematical models have been considered as useful tools to fill this gap. However, the so far proposed analytically tractable models can only describe very simple scenarios which are rarely of practical interest in micro-capsule technology. One example of these models is Reissner's shell theory (Reissner, 1946, 1946). This model was originally developed to calculate the displacement of shallow spheres under a point force, but has also successfully been applied for flat probes at small deformations. It has been applied to estimate the compression force of an empty elastic capsule with a very thin shell ($h/r \ll 0.1$) from the displacement of the probe for sufficiently small deformations ($d/h \ll 0.1$) through the following equation:

$$\frac{F}{Ehr} = \frac{4}{\sqrt{3(1-\nu^2)}}\frac{h}{r}\alpha \tag{1}$$

where F is the compression force, h is the wall thickness of the shell, d is the displacement, r is the inner radius of the shell, E is Young's modulus, ν is Poisson's ratio, and ($\alpha = \frac{d}{2r}$) is the fractional displacement. In fact, a general mathematical model that accounts for the mechanical behavior of a filled MC in larger deformations is not available. This is partly due to the possible complexity of the shell material properties, and the geometrical non-linearity of MC deformation (Neubauer et al., 2014). Numerical analysis such as finite element method offer the opportunity to address such a theoretically complex, nevertheless practically very important problem.

Several researchers have studied the mechanical deformations and the collapse mechanisms of similar spherical systems with dimensions bigger than 0.1 mm ("macro-balloons") under compression. For instance, Lim et al. (2002) presented experimental results of a single macro-balloon compression together with an appropriate Finite Element analysis to investigate the deformations and the failure of single macro-capsules made of stainless steel. For this analysis they assumed a simple linear elastic model with rate-independent plasticity for the material. These studies inspired further numerical research on the mechanics of smaller systems when the suitable experimental data was available.

In 2007, Carlisle et al. (2007) used a linear elastic model to predict the burst location of carbon micro-balloons (MBs) with the size of 20 μm. Using this method they concluded that, in contrast to the previous studies which assumed a simple flexural stress to be responsible for the failure of MBs and hence predicted the burst location to be at the equator of the balloon, the failure was most likely to be initiated on the MB's inner wall, directly under the contact region. While considering a completely linear elastic deformation without plasticity is a reasonable choice for carbon as a brittle material, it cannot account for the complex deformation of polymeric systems under compression (Fery and Weinkamer, 2007).

For instance, in the case of melamine–formaldehyde (MF) capsules, by assuming a linear elastic model, one can get a good agreement with compression test results only for small displacements of the probe ($d/r < 0.1$) Mercadé-Prieto et al., 2011. However the prediction of such a simple model deviates dramatically in larger deformations (Fery and Weinkamer, 2007; Mercadé-Prieto et al., 2011, 2013). Therefore, considering plasticity for this system is inevitable.

Recently, for MF capsules, Mercadé-Prieto et al. (2012) proposed an elastic-perfectly plastic model as the simplest scenario that could predict the compression force versus the displacement of a micromanipulator probe in good agreement with the experimental results. In this analysis the shell material is modeled as a linear elastic solid that yields by further compression. Thereafter, a strain hardening stage is considered to account for the observed increase of stress in larger displacements ($d/2r > 0.5$). Using this model, they concluded that the position of maximum strain, and stress and hence the rupture location is at the equator of the MCs.

In this work, a similar model will be examined for studying the mechanical behavior of a single MC under uniaxial compression. The MCs that are used for this study are particularly made to serve as perfume oil micro containers in washing machine powders. Failure under compression is considered the most likely mechanism of their rupture and the release of their contents.

Rupture due to shear forces would require excessively large flow velocities and/or attachment between the tip of the microcapsules and a second fibre, both of which are unlikely to occur. First, an elastic-perfectly plastic model with suitable parameters will be validated by comparing the Finite Element Method (FEM) simulation results with the relevant nano-indentation experimental data. Finally, their rupture mechanism and its localization will be discussed using the stress profiles at rupture together with corresponding after burst micrographs that clearly show its shape.

2. Methods

2.1. Sample preparation and experiments

2.1.1. The composition of micro-capsules

The investigated micro-capsules consist of a melamine–formaldehyde (MF) shell and a perfume oil core. The core material was produced by Henkel AG & Co. KGaA (Krefeld, Germany). Then it was encapsulated with MF by Follmann GmbH & Co. KG (Minden, Germany). Two groups of these MCs with four capsules from each group are studied in this work.