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Thermal softening of superswollen polyelectrolyte microcapsules

Byoung-Suhk Kim,^a Tai-Hsi Fan^b and Olga I. Vinogradova^{*cd}

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We study the effect of temperature on the mechanical properties of polyelectrolyte microcapsules assembled by layer-by-layer (LbL) deposition of polystyrene sulfonate (PSS)/polyallylamine hydrochloride (PAH). Capsules are initially significantly swollen (superswollen) as a result of the osmotic effect caused by *in situ* polymerization of inner PSS. It is well known that hollow PSS/PAH microcapsules are insensitive to temperature changes. However, we show that the heat treatment of superswollen capsules introduces additional plastic deformation and leads to an additional softening of a highly stretched polyelectrolyte shell. A simple model is provided to characterize the elasto-plastic behavior of the microcapsules under consideration. This finding suggests an alternative method to control mechanical properties of the multilayer shell.

1 Introduction

Electrostatic self-assembly^{1,2} offers a simple means to build functional materials from the bottom up and is promising in making micro- and nano-capsules for various applications in cosmetic, pharmaceutical, and biomedical industries. The general procedure for assembly of microcapsules is based on a layer-by-layer deposition of oppositely charged polyelectrolytes on a colloidal template.³ After several layers of deposition, the template is dissolved to form a shell with the required nanosize thickness.

The assembly of microcapsules is an established research area, so that a large body of publications have described capsules' physical properties such as deformability (*elastic* or *elastoplastic* deformation) (see ref. 4,5 for recent reviews), adhesion and interaction,⁶ or permeability.^{7–9} Several methods have been proposed to study their mechanical properties. They involve the observation of osmotically induced buckling of capsules immersed in a polyelectrolyte solution,¹⁰ measurements of the deformation of microcapsules by using an atomic force microscope (AFM),^{11–13} and the studies of swelling of microcapsules filled with strong polyelectrolyte solutions.^{14,15} In the latter, depending on the concentration of the encapsulated polyelectrolyte, the swelling can be moderate, so that the shell deformation is kept in the *linear elasticity* regime,¹⁴ or it could be very large to involve *plastic* deformation.¹⁶ In the last case, superswollen capsules are found to be much softer than both multilayer shells used for their preparation and the elastically swollen capsules filled with polyelectrolyte of relatively low concentration.

The mechanical properties of polyelectrolyte multilayer shells can be tuned by exposing materials to aqueous solutions with

different pH values,^{7,15,17,18} organic solvents,^{9,19,20} and solutions with different ionic strength.^{21–25} Besides, one also expects that thermal post-treatments could help to tune the multilayer shell properties. It is natural to expect such an effect for capsules based on thermoresponsive polyelectrolytes. Indeed, it has been shown that incubation at temperatures above 35 °C leads to changes in the thermosensitive (polydiallyl dimethyl ammonium chloride (PDADMAC)/PSS, poly(*N*-isopropylacrylamide) (PNIPAM)/PSS, and poly(2-diethylaminoethyl methacrylate) (PDEAEMA)/PNIPAM) capsules' morphology^{26–28} and mechanical properties.²⁹ However, in the case of polyelectrolyte pairs which are insensitive to temperature, such as PSS/PAH, no changes in mechanical properties of capsules due to their heating should be expected. Indeed, prior work has shown only a slight (less than 10%) shrinking of corresponding hollow capsules after treatment at 80 °C for 5 h, which is comparable to measurement error.¹⁶

Here we report a new observation of thermal softening of PSS/PAH capsules, the shell of which is already highly stretched due to the inner osmotically active solution. During the heat treatment, an additional elasto-plastic deformation of the shell is induced due to the increase of the inner osmotic pressure. A simple theoretical model is proposed to quantify the mechanical behavior according to the experimental observations. This study suggests a new means of tuning mechanical properties of filled polyelectrolyte microcapsules.

2 Experimental

2.1 Materials

Shell-forming polyelectrolytes poly(sodium 4-styrenesulfonate) (PSS; $M_w \sim 70$ kDa) and poly(allylamine hydrochloride) (PAH; $M_w \sim 70$ kDa) were purchased from Sigma-Aldrich Chemie GmbH, Germany. 4-Styrenesulfonic acid sodium salt (SSNa) as a monomer and potassium peroxydisulfate ($K_2S_2O_8$) as an initiator were used for standard radical polymerization. All chemicals were of analytical purity or higher quality and were used without further purification. Water used for all experiments was purified by a commercial Milli-Q Gradient A10 system containing ion exchange and charcoal stages, and had a high resistivity of 18.2 M Ω cm.

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Suspensions of monodisperse and weakly cross-linked melamine formaldehyde particles (MF particles) with a radius of $r_0 = 2.0 \pm 0.1 \mu\text{m}$ were purchased from Microparticles GmbH (Berlin, Germany). Glass bottom dishes (0.17 mm/diameter 30 mm) with optical quality surfaces were obtained from World Precision Instruments Inc. (USA). Glass spheres (radius $20 \pm 1 \mu\text{m}$) were purchased from Duke Sci. Co., California.

2.2 Methods

2.2.1 Preparation of capsules. The positively charged MF particles (50 μL of 10 wt% dispersion) as a template were incubated with 1 mL of PSS solution (1 mg mL⁻¹ containing 0.5 mol L⁻¹ NaCl, pH 6) for 10 min, followed by three centrifugation/rinsing cycles, and finally dispersed in water. 1 mL of a PAH solution (1 mg mL⁻¹ containing 0.5 mol L⁻¹ NaCl, pH 6) was then added to the particle dispersion. After 10 min given for adsorption three centrifugation/wash cycles were performed. The PSS and PAH adsorption steps were repeated four times each to build multilayers on the MF particles. The microcapsules were obtained by dissolving the MF template in HCl at pH 1.2–1.6 and washing with water three times as described before.³

Filled capsules have been prepared by using *in situ* polymerization techniques^{16,30} (see Fig. 1) since it gives the largest stretching of the shell as compared with other methods.^{7,11,19,31} Polymerization was carried out at various SSNa concentrations in the presence of hollow capsules for 5 h at 80 °C under nitrogen atmosphere according to a reported method.^{16,30} 1% of K₂S₂O₈ as an initiator, related to the monomer concentration, was used. The total monomer concentration was varied from 0.1 to 0.5 mol L⁻¹. Optically sensitive polymers were prepared by copolymerisation of SSNa and 0.5 mol % fluorescein O-methacrylate (Aldrich, adsorption maximum at $\lambda = 490 \text{ nm}$, emission maximum at $\lambda = 520 \text{ nm}$) in 20% methanol. After polymerization, the capsules were separated from the PSS in the bulk solution by centrifugation. Several washing cycles with pure water were repeated.

With this technique of encapsulation we assume that the initial concentration of PSS inside the capsules (monomer units) is approximately equal to that of a monomer used for a synthesis.

2.2.2 Confocal laser scanning microscopy (CLSM). We used a commercial confocal microscope unit FV300 (Olympus, Japan) together with an inverted fluorescence microscope Olympus IX70. To make confocal images of capsules an argon laser ($\lambda = 488 \text{ nm}$) and a high-resolution (60 \times) bright (NA = 1.45) immersion oil objective were used. The size of the capsules was

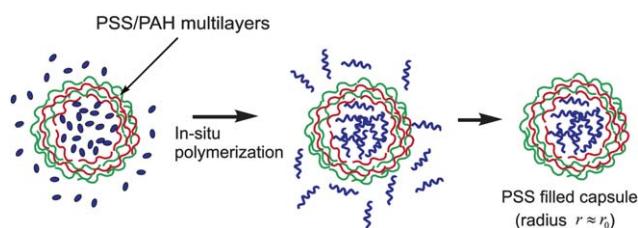


Fig. 1 Encapsulation by *in situ* polymerization in the interior of capsules. The radius of the capsule is approximately equal to that of the initial template, $r \approx r_0$.

determined as an average of at least 10–15 capsules with an accuracy of $\pm 0.2 \mu\text{m}$.

3 Results and discussion

A scheme of capsule swelling and post-treatment, with the illustration of changes in capsule size, is shown in Fig. 2. The initial swelling caused by inner osmotic pressure at room temperature reflects several effects including initial elastic deformation, strain-softening during the plastic deformation, partial reversibility, and reduced elastic modulus after large deformation (sketch in Fig. 3). After the equilibration of swelling at room temperature, we incubate capsules at temperature 90 °C for 1 h. Fig. 4. shows the dependence of the equilibrium radius of the swollen capsules before and after heat treatment as a function of initial concentrations of the inner polyelectrolyte. The equilibrium radius increases with the initial concentration of the inner PSS, confirming earlier observations.¹⁶ To inspect the reversibility of deformation, we immersed a part of swollen capsules into NaCl solution with a concentration of 2 mol L⁻¹. At this salt concentration the excess osmotic pressure of the inner counterions is entirely suppressed, but there is no dissociation of the multilayer shells.²² The average size of capsules is smaller after salt water treatment but never reaches the size of the original template used for capsule preparation. This suggests that the stretching/swelling of the shell is only partially reversible (Fig. 3), and a plastic deformation occurs during the room temperature swelling process. Another part of swollen capsules exhibited further expansion due to the heat treatment for 1 h followed by cooling to room temperature (Fig. 4). Radii of capsules after the heat post-treatment are always larger than those of not-heated capsules. This suggests that superswollen microcapsules exhibit an additional plastic deformation.

A simple quasi-steady model is presented to quantify the thermal softening effect. Since the capsules are large enough to take into account the leak-out of counter-ions,³² the excess osmotic pressure inside the capsules can be estimated by $\Pi = \phi cRT$, where the osmotic coefficient ϕ accommodates the reduction of osmotic pressure Π due to the counter-ion condensation,³³ R is the gas constant, T is the absolute temperature, $c = (r_0/r)^3 c_0$ is the molar concentration determined by the radius r at later stages of the processes, r_0 is the initial radius, and c_0 is the initial PSS concentration within the capsule. At the super-swollen state A where $r = r_A$ (Fig. 3), the assumed isotropic

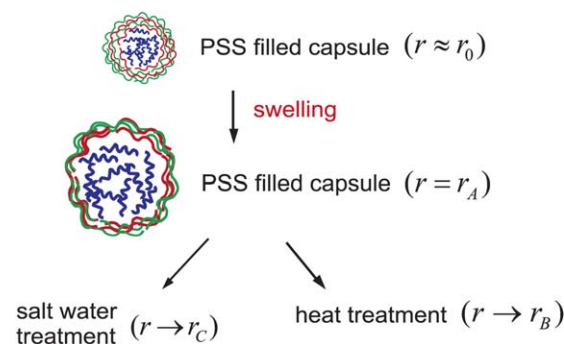


Fig. 2 Corresponding capsule sizes at various processing stages.

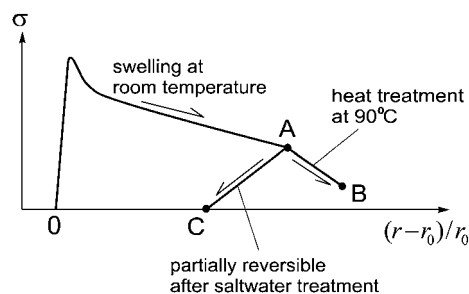


Fig. 3 Schematic stress–strain curve showing the end states. A: the equilibrium state of superswollen capsules before heat-treatment. B: the equilibrium state of superswollen capsules after heat-treatment (further irreversible swelling). C: the equilibrium state of superswollen capsules after salt-treatment (partially reversible shrinking).

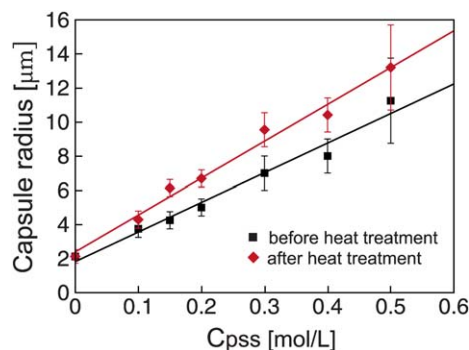


Fig. 4 The equilibrium radius of the superswollen capsules *versus* the initial concentration of PSS.

membrane tension stress σ_A is balanced by the excess osmotic pressure, expressed as

$$\Pi_A = \varphi(r_0/r_A)^3 c_0 RT_A. \quad (1)$$

For a thin membrane with thickness $h \ll r_0$, the bending effect is negligible and the Laplace equation is applicable for the spherical capsule,

$$\Pi_A \approx 2\sigma_A h_A / r_A \quad (2)$$

where r_A^{-1} is the mean curvature of the membrane shell. Thus the tension stress can be formulated as

$$\sigma_A \approx \frac{\Pi_A r_A}{2h_A} \text{ or } \frac{\varphi r_0^3 c_0 RT_A}{2r_A^2 h_A}. \quad (3)$$

Assuming that the Poisson ratio of the shell is about 0.5, the linear approximation of the corresponding Young's modulus can be calculated by using

$$E_A \approx \frac{\Pi_A r_A}{4\varepsilon h_A}, \quad (4)$$

where ε is the elastic in-plane longitudinal strain.

After the heat treatment at 90 °C for 1 h, the capsules expand to the end state B where the force balance gives $\Pi_B \approx 2\sigma_B h_B / r_B$. By substituting the initial concentration c_0 we can ensemble two stress–strain curves to demonstrate the thermal softening effect

caused by the heat treatment (Fig. 5). The overall strain (x -axis) including the elastic and plastic deformation is obtained by direct observation of the capsule size. We assume that the membrane thickness remains unchanged throughout the swelling process and during the heat treatment, and the static model does not account for the complicated membrane viscous effect during deformation. The small variation of the membrane thickness is compromised in the model presented above because it can only be calculated as if the membrane structure remains homogeneous and incompressible during the swelling process. Fig. 5 shows that the plastic stress–strain curve shifts downward after the heat treatment, meaning the elevated temperature essentially enhances the strain-softening effect that makes the filled capsules behave like a plastic material when the stress goes beyond the corresponding yield point. The partially reversible strain after the saltwater treatment further confirms the existence of the plastic deformation. A similar test for hollow capsules did not show observable changes in capsule size (less than 10%) and the elastic modulus (measured by AFM) after the heat treatment (data not shown, capsules behave like a rigid material with fixed size). We speculate that for hollow capsules the pre-tension force does not exist in the LbL structure after the self-assembly process. Those capsules initially filled with PSS, on the other hand, are pre-stressed such that the additional high temperature treatment results in stress release and is perceived as membrane softening and deformation.

The elastic strain ε in eqn (4) can be estimated by suppressing the osmotic effect.¹⁶ If ε is approximately the same for cases considered in Fig. 4 and Fig. 5, the modulus E is expected to be scaled as $1/r^2$ for a given initial PSS concentration. This indicates that the heat treatment may slightly modify the modulus, and the thermal softening actually happens by way of an enhanced osmotic effect. To reduce the modulus, one only needs to increase the strain by, for example, the osmotic pressure that increases with concentration and temperature. Further studies are required to validate this hypothesis. Considering that ε is about 20%, the apparent Young's modulus is on the order of 1 MPa, which is typical for highly elastic polymers. Before, such a value of Young's modulus was observed only for capsules after their plastification¹³ by a treatment in a mixture of special organic

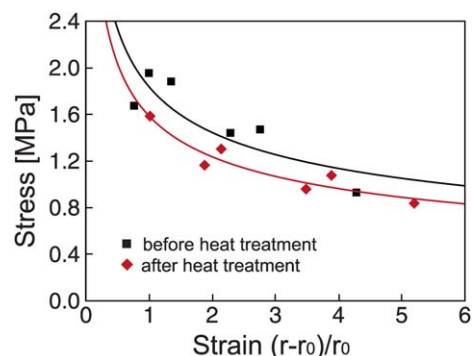


Fig. 5 The stress–strain curves before and after the heat treatment at 90 °C for 1 h. The 6 data pairs correspond to the data shown in Fig. 4 except the initial point. The osmotic coefficient is around 0.2 (taken from ref. 34–36) and the estimated membrane thickness is about 10 nm for all microcapsules.⁴

solvents⁹ or as a result of salt softening.^{22,23} In all other situations^{10,12–14} Young's modulus was much larger. This result indicates that the Young's modulus strongly depends on the degree of stretching. In other words, the smaller the stretching the larger is the apparent Young's modulus extracted from the micro-mechanical experiments. Thus, the modulus of the order of GPa is observed when stretching was negligibly small.^{10,37,38}

In summary, heat treatment may provide a useful means to control the multilayer structure and thus the physical properties through the rearrangement processes of the polyelectrolytes, and be able to tailor specific properties required for many potential applications. For the future work we suggest investigation of the microstructure of the polyelectrolyte membrane before and after the heat treatment and the permeability control in a high temperature aqueous environment for applications with controlled release of chemical agents.

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