Superswollen Ultrasoft Polyelectrolyte Microcapsules

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ABSTRACT: We study mechanical properties of polyelectrolyte multilayer microcapsules filled with polyelectrolyte solutions of high concentration. The osmotic pressure of counterions leads to a superswelling of microcapsules. The suppression of excess osmotic pressure causes a shrinking of capsules, which however do not return to their original, i.e., before swelling, size. To quantify these large and only partly reversible stretching of the shells, we develop a simple model, in which the stress—strain relation is constructed by mapping a linear model to two equilibrium, swollen and shrank, states. Fitting to predictions of this model allows one to conclude that the presence of plastic deformation at large stretching is equivalent to a dramatic decrease in apparent Young’s modulus, down to ~1 MPa in our experiment. This is in agreement with force—deformation profiles measured with the atomic force microscope, which show that superswollen capsules are ultrasoft.

1. Introduction

Recently there has been much interest in studying physical properties of polyelectrolyte multilayers.1,2 In particular, there have been recent attempts to explore mechanical behavior of supported multilayer films.3–6 Another system of special interest is polyelectrolyte multilayer microcapsules.7 The shell of these capsules is nothing more than a free-standing multilayer film. The free film geometry allows one to study properties not accessible in bulk or supported films. In this way one might gain better understanding of polyelectrolyte multilayers. For example, recent experimental studies of microcapsule mechanics allowed one to raise such questions as the interplay between elasticity and permeability in determining shell stiffness, whether a postmodification of multilayers can change their mechanical properties and physical state (rubber, glass, or bulk plastic) and more8–13 (see ref 14 for a recent review).

One of the important issues that has been raised recently and still awaits clarification is whether and under what conditions the multilayer shell deformations become plastic, i.e., only partially reversible, and how to describe these changes quantitatively. Indeed, there have been some indications of plastic behavior of multilayer shells at large degree of swelling/stretching.9,13,16 However, all theoretical models8,10,13,14 to describe capsule deformation experiments suggested so far are based on the crucial assumption that multilayer shell deformation is elastic. This assumption is correct only if deformation is completely reversible. To our knowledge, stretching of a multilayer film is reversible and was proven to be elastic for very small strain.10,11 It is one of the goals of this paper to study the reversibility of multilayer deformation at larger strain and to accommodate the earlier theoretical model13,14 for the case of elastoplastic stretching.

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Direct experimental studies of elastoplastic properties of free-standing polyelectrolyte multilayers are very difficult to perform. In this paper we propose a new method based on studying the swelling and shrinking of microcapsules filled with the solution of strong polyelectrolyte with relatively high concentration. Capsules swell due to excess osmotic pressure of the inner solution created by counterions.13,16 They shrink when this excess pressure is entirely suppressed. Therefore, by performing this swelling/shrinking test, we mimic the mechanical loading/unloading. If capsules do not shrink down to their original (before swelling) size, plastic deformations come into play. In such a case a general model describing swelling of capsules might also be rather involved.9 The standard description is normally based on a solution of nonlinear equations based on a constitutive relationship, which, besides Young’s modulus, E, contains the plastic modulus and the yield stress at transition from elastic to plastic.17 The non-linearity and a large number of unknown parameters make the problem essentially numerical. Here we propose an alternative way to attack the problem by adopting a simplified approach, which leads to explicit formulas that can be easily handled. We suggest a simple theoretical model, in which the stress—strain relation is constructed by mapping the linear elastic model to two, swollen and shrank, equilibrium states. Fitting the experimental data to the prediction of our model allows one to conclude that the presence of plastic deformations is equivalent to a significant decrease in apparent Young’s modulus. Before, by studying low strain deformations, we concluded that mechanically the behavior of polyelectrolyte multilayers is confined between a rigid cross-linked rubber18 (E = 10 MPa) and soft plasticized glass18 (E = 1000 MPa).11,14,19 Here we show that elastoplastic behavior at large stretching is equivalent to what would be expected in the case of much softer elastic shells (E = 1 MPa). This conclusion is confirmed by force vs deformation profiles studies with the atomic force microscope that show that super-swollen capsules are ultrasoft.
2. Experimental Section

2.1. Materials. Shell-forming polyelectrolytes poly(sodium 4-styrenesulfonate) (PSS; \( M_w \approx 70 \, \text{kDa} \)) and poly(allylamine hydrochloride) (PAH; \( M_w \approx 70 \, \text{kDa} \)) were purchased from Sigma-Aldrich Chemie GmbH, Germany. 4-Styrenesulfonic acid sodium salt (SSNa) as a monomer and potassium peroxodisulfate (K\(_2\)S\(_2\)O\(_8\)) 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\(\Omega\)cm.

Suspensions of monodisperse weakly cross-linked melamine formaldehyde particles (MF particles) with a radius of \( r_0 \approx 2.0 \pm 0.1 \, \mu\text{m} \) 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. Glass spheres (radius 20 \(\pm\) 1 \(\mu\text{m}\)) were purchased from Dukew Sci. Co., San Jose, CA.

2.2. Methods. Preparation of Hollow Capsules. The positively charged MF particles (50 \(\mu\text{L}\) of 10 wt \% dispersion) as the template were incubated with 1 \(\text{mL}\) of PSS solution (1 mg/mL containing 0.5 mol/L NaCl, pH 6) for 10 min, followed by three centrifugation/rinsing cycles, and finally dispersed in water. 1 \(\text{mL}\) of a PAH solution (1 mg/mL containing 0.5 mol/L NaCl, pH 6) was then added to the particle dispersion. After 10 min given for adsorption three centrifugation/wash cycles were performed (as above). 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.\(^{10}\)

**Polymer Synthesis inside Hollow Capsules.** Polymerization was carried out at various SSNa concentrations in the presence of hollow capsules for 5 h at 80 °C under a nitrogen atmosphere according to a method.\(^{21}\) 1% of K\(_2\)S\(_2\)O\(_8\) as an initiator was used for standard radical polymerization. All chemicals were of analytical purity or higher quality and were used without further purification.

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**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 \(\times\) \times 1.45) immersion oil objective were used. The size of the capsules was determined as an average of at least 10–15 capsules with an accuracy of \( \pm 0.2 \mu\text{m} \).

**Scanning Electron Microscopy.** For scanning electron microscopy (SEM) analysis a drop of each sample solution was applied to a silicon wafer with sequential drying at room temperature for 2–3 h. The measurements were performed using a Gemini Leo (Zeiss) 1530 instrument operating at a working distance of 2 mm and an acceleration voltage of 0.5 kV. Since the samples were not covered with a gold layer before inspection, this low acceleration voltage was applied in order to avoid charging of the sample. The images were recorded using the InLens detector.

**Cantilever Deformation Experiment.** The experimental setup for the force measurements was described before.\(^{10,11,22}\) Briefly, load (force) vs deformation curves were measured with the Molecular Force Probe device (MFP) 1D (Asylum Co., Santa Barbara, CA), which has a nanopositioning sensor. This sensor can correct piezoceramic hysteresis and creep of the AFM piezotranslator. For force measurement we used V-shaped cantilevers (Micromash, Estonia, spring constants \( k \approx 3 \, \text{N/m} \)). The spring constant of the cantilever was estimated from the resonance frequency calibration plot (Cantilevers catalog, Micromash, Estonia). Glass spheres were glued onto the apex of cantilevers with an epoxy glue (UHU Plus, Germany). The capsule deformation experiment has been described before. Here we performed the measurements at a piezotranslator speed of 20 \(\mu\text{m/s} \). The result of measurement represents the deflection \( \Delta \) vs the position of the piezotranslator at a single approach. The load force \( F \) was determined from the cantilever deflection, \( F = k\Delta \). As before, we assume that the zero of separation is at the point of the first measurable force.\(^{10,11,22}\) Then the deformation is calculated as the difference between the position of the piezotranslator and cantilever deflection. The diameter of the capsule was determined optically with an accuracy of 0.2 \(\mu\text{m} \) and from the AFM load vs deformation curves (like in refs 10, 11, and 22). The relative deformation \( \epsilon \) of the capsule was then calculated as \( \epsilon = 1 - H/(2r) \), where \( H \) is the minimum sphere/substrate separation and \( r \) is the equilibrium capsule radius.\(^{10}\) To get reliable results, we have performed several series of force measurements. Every series included at least 10–15 experiments for each initial concentration of the inner polyelectrolyte. Then the average of all force vs deformation curves for each series was calculated.

3. Results and Discussion

Figure 1 shows confocal fluorescence images of swollen capsules. The fluorescence intensity suggests a uniform concentration in the capsule’s interior. The bright interior of capsules does not change with time, and there is no fluorescent signal from water. This confirms that capsules are in an impermeable (for PSS) state. One can see that filled with PSS capsules are always larger than original hollow capsules and that the equilibrium radius of the swollen capsules increases with the initial (i.e., before swelling) concentration of PSS.
PSS, or $C_{\text{PSS}}$. Note that this conclusion is different from results published before, where the shrinkage of the capsules filled with PSS of the concentration range from 0.1 to 0.5 mol/L was observed, and swelling took place only at concentration above 0.6 mol/L. The reason for disagreement is likely connected with the fact that the shells used in ref 21 have shown a considerable (up to 40%) decrease in size after heating in conditions corresponding to the PSS synthesis. This shrinking effect is acting opposite to a swelling. To rule out a similar effect for our experimental conditions, we studied the size of hollow capsules treated at 80 °C for 5 h. A slight shrinking of the capsules (less than 10%) was observed, which is however comparable with the error of optical measurements.

The change in intensity of the fluorescent signal coming from the capsule interior indicates that the final (after swelling) concentration decreases with the final radius of the capsules. Taking into account the conservation of mass, the final value of the PSS concentration can be evaluated as $C(r) = (r/r_{\infty})^3C_{\text{PSS}}$.

The dependence of the equilibrium radius of the swollen capsules on the initial concentration of the inner polyelectrolyte is shown in Figure 2. The equilibrium radius increases with the initial concentration of the inner PSS. To check the reversibility of deformation, we have immersed swollen capsules into a solution of NaCl with a concentration of 2 mol/L. At this salt concentration the excess osmotic pressure of the inner counterions is entirely suppressed, but there is no dissociation of the multilayer shells. The averaged radii of shrunk capsules are included in Figure 2. One can see that radii of capsules are getting smaller but never reach the size of original templates used for capsule preparation. This suggests that the large stretching/swelling of the multilayer shell is only partially reversible, so that plastic deformations are coming into play. However, several cycles of washing in pure water with the consequent exposure to water for several days lead to a full recovery of the size of the swollen capsules, although a larger scatter in the size of reswollen capsules was observed. Therefore, the deformation can be treated as elastoplastic. In other words, swelling can be considered as quasi-elastic, but with the reference point corresponding to the size of shrunk capsules.

The plastic changes in the multilayer shells are indirectly confirmed by SEM images of the dried superswollen capsules. SEM images of dried capsules filled with PSS by means of different encapsulation techniques were taken and studied before. We have observed that capsules collapse upon drying by forming structures with sharp folds and creases. The morphology of dried superswollen capsules prepared by in-situ polymerization seems to be very different (Figure 3). SEM images of these capsules do not reveal any structure with discernible folds. These observations are consistent with the plastic deformations of the shells.

A simple model accounts for these experimental observations. The excess osmotic pressure inside the capsules is equal to $\Pi = \varphi CRT$, where $R$ and $T$ have their usual definitions, and the osmotic coefficient $\varphi$ is a phenomenological parameter that accommodates the reduction of osmotic pressure $\Pi$ due to the counterion condensation. According to various studies, $\varphi$ has a value ranged from 0.2 to 0.8 for PSS. At the fully swollen equilibrium state, we assume that the excess osmotic pressure $\Pi = \varphi (r/r_{\infty})^3 C_{\text{PSS}}RT$ is balanced by the isotropic tension stress $\sigma$ of the multilayer shell with an averaged radius $r$ and shell thickness $h$. According to Landau’s derivation for the linear deformation of a thin-shell hollow sphere, the isotropic tension stress induced by the excess pressure is consistent with a simple Laplace formula $\Pi \sim 2\varphi h/r$, where $2/r$ is the total surface curvature. So for a similar system with small deformation, one can further prove that the tension stress can be approximated by the linear constitutive equation $\sigma \sim E\varepsilon(1 - \nu)$, where $E$ is the Young’s modulus, $\nu$ is the Poisson ratio, and $e = (r - r_0)/r_0$ is the in-plane longitudinal strain. Here we assume that the elastic model can be adapted for the partially reversible process with the shrinkage state $r_0$ as a reference point. We thus redefine an effective strain using $\varepsilon = (r - r_0)/r_0$. By assuming $\nu = 1/2$, the force-balance model for the reversible process becomes

$$\Pi = \varphi \left(\frac{r_0}{r}\right)^3 C_{\text{PSS}}RT \sim \frac{2\varphi h}{r} \sim 4\varepsilon \frac{hE}{r} \left(\frac{r - r_0}{r_0}\right)$$

Experimentally we only consider two equilibrium states corresponding to a single concentration $C_{\text{PSS}}$: (1) a fully swollen microcapsule in water and (2) a completely relaxed capsule after saltwater treatment. Equation 1 is applicable from state 1 to 2 when both the osmotic pressure and the tension stress gradually vanish, and only the elastic part $\varepsilon = (r - r_0)/r_0$ of the
true longitudinal strain \( e = (r - r_0)/r_0 \) can be fully recovered. Since we measured \( r \) and \( r_0 \), \( C_{\text{PSS}} \), and \( h \) are known, we are now on a position to evaluate a ratio of apparent Young’s modulus to the osmotic coefficient, \( E/\tilde{\varphi} \). The results of calculations are presented in Figure 4 and suggest that the elastoplastic swelling of polyelectrolyte microcapsules causes a dramatic softening of their shells. Indeed, the apparent Young’s modulus is getting of the order of 1 MPa, which is typical for highly elastic polymers.\(^\text{18}\) Before, such a value of Young’s modulus was observed only for capsules after their plastification\(^\text{2}\), by a treatment in a mixture of special organic solvents\(^\text{10}\) or as a result of salt softening.\(^\text{14,15}\) In all other situations Young’s modulus was much larger. This result indicates that the measured Young’s modulus might depend on the degree of stretching. In other words, the smaller the stretching the larger is the apparent Young’s modulus extracted from the micromechanical experiments.

If \( \tilde{\varphi} \) is known, we can calculate \( E \) or \( \sigma \) to place end-state 1 in the stress–strain plot. The elastoplastic deformation curve shown in Figure 5 (\( \tilde{\varphi} \sim 0.2 \)) is simply constructed by connecting the first (swollen) end-state (shrunken) points for several tests with various \( C_{\text{PSS}} \). Dashed lines here simply connect swollen and shrunk states and do not represent a real pass (almost likely qualitatively resembling a dash–dotted curve) from these two experimental situations. We also remark that beside data from our swelling test (squares) Figure 5 includes a low-strain experimental point (a triangle) taken from our previous publication.\(^\text{10}\)

Figure 6 shows typical load vs deformation curves measured for superswollen capsules with various initial concentration of the inner PSS solution. The deformation profile of initial “hollow” capsules is also included. On can see that the superswollen capsules show deformation profiles qualitatively different to those previously observed for “hollow” capsules\(^\text{13,16}\) and capsules filled with PSS using another technique.\(^\text{11,24,20}\) Another observation is that the superswollen capsules are much softer than “hollow” ones. This is consistent with the decrease in apparent Young’s modulus of the shells predicted by our model. We remark and stress, however, that there is no correlation between the stiffness of “filled” capsules and the initial PSS concentration. This result, in contrast to the decreasing shell modulus, remains an open question for future study. Another important point to note is that the force vs deformation curves (both the shape and values of forces) are very similar to what was recently observed for living cells.\(^\text{31}\)

It has to be also stressed that the ultrasoft nature of superswollen capsules studied here is not due to a heating of capsules used for a synthesis of PSS. No influence of a preheating at conditions corresponding to the PSS synthesis on mechanical properties was found (the force curve is not shown). Thus, the preheating of capsules definitely cannot affect either our theoretical estimates or conclusions.

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References and Notes

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