

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/27269950>

Mechanical Properties of Polyelectrolyte Microcapsules Filled with a Neutral Polymer

ARTICLE *in* MACROMOLECULES · APRIL 2003

Impact Factor: 5.8 · DOI: 10.1021/ma0259719 · Source: OAI

CITATIONS

62

READS

27

4 AUTHORS, INCLUDING:



[Gleb Sukhorukov](#)

Queen Mary, University of London

318 PUBLICATIONS **19,379** CITATIONS

SEE PROFILE



[Olga I Vinogradova](#)

Russian Academy of Sciences

111 PUBLICATIONS **3,383** CITATIONS

SEE PROFILE

Mechanical Properties of Polyelectrolyte Microcapsules Filled with a Neutral Polymer

Valentin V. Lulevich,^{†,‡} Igor L. Radtchenko,[§] Gleb B. Sukhorukov,[§] and Olga I. Vinogradova^{*,†,‡}

Max Planck Institute for Polymer Research, Postfach 3148, 55021, Mainz, Germany; Laboratory of Physical Chemistry of Modified Surfaces, Institute of Physical Chemistry, Russian Academy of Sciences, 31 Leninsky Prospect, 117915 Moscow, Russia; and Max Planck Institute for Colloid and Interface Research, 14424 Golm, Potsdam, Germany

Received December 17, 2002; Revised Manuscript Received February 12, 2003

ABSTRACT: We study the deformation of “filled” (with a neutral polymer) polyelectrolyte microcapsules under applied load using an atomic force microscope (AFM)-related force-measuring device. The experimental setup allows combining dynamic force measurements with high-resolution optics. The “filled” capsules are prepared from “hollow” ones (water inside) by changes in their permeability for a high molecular weight polymer by adding organic solvent. At low applied load, capsule deformation was found to be elastic, reversible, and independent of the concentration of the inner polymer, being entirely controlled by the shell properties. Above a certain load capsules deform substantially and partly irreversibly. They start to show variability in the behavior and dependence of their deformation profiles on the driving speed and concentration of the inner polymer solution, which is likely due to the enhanced permeability of the stretched shell. The “filled” capsules were found to be always several times softer than the preformed “hollow” ones, which is shown to be a consequence of the treatment of the shell by organic solvent.

Introduction

Polyelectrolyte multilayer capsules have been recently introduced as a novel type of nanoengineered microstructure.^{1,2} These capsules are made by layer-by-layer (LbL) adsorption³ of oppositely charged polyelectrolytes on surfaces of colloidal particles⁴ with subsequent removal of the template core and can be filled with a wide class of molecules (for a review see ref 5). The well-defined shape of these capsules, their mechanical stability, and an easy way of preparation allow employing them as a model system for basic and applied studies. A novel and promising area of research is connected with the investigation of the elasticity and the mechanical properties of such microstructures. Indeed, deformation and rupture of polyelectrolyte capsules may limit their use. In contrast, controlled stiffness and mechanical properties may lead to a variety of novel applications.

To our knowledge, there have been only three attempts to study the deformation behavior of polyelectrolyte microcapsules.^{6–8} The first approach⁶ involves generating and observing a plastic shrinkage by means of the micropipet aspiration technique. The second method⁷ is based on studying osmotically induced buckling of “hollow” (water inside) capsules immersed in a polyelectrolyte solution. The third, more recent, approach⁸ is based on measuring the deformation of microcapsules under applied load with an atomic force microscope (AFM). One advantage of this method is that it increases the level of details obtained from the experiment. In particular, it is possible to distinguish between different regimes in load-deformation profiles, characterized by different behavior (reversibility, elasticity, plasticity, etc.). It also allows one to judge about

contact deformation and adhesion. Another advantage of the AFM technique is that it can be applied for studying not just “hollow” but also “filled” (polymer inside) capsules.

In this paper we extend and develop the (AFM) approach suggested in ref 8. Our measurements are performed in conditions that differ from our previous study.⁸ We drastically increase the range of speeds used for our experiment, which allowed us to address the rate-dependent phenomena connected with the loading. We also use a new optical scheme, which opened a possibility to work in a fluorescence mode. Beside that, some special technical arrangements allowed us to reduce the experimental errors.

The method is applied to study a novel class of capsules. A new development concerns both the type of encapsulated polymer and the way for encapsulation. In the previous paper⁸ we compared the deformation behavior of “hollow” and “filled” capsules prepared by a controlled precipitation,⁹ i.e., by an assembly of the inner layer of polyelectrolyte shell by means of multivalent ions, with the consequent extraction of these ions and charged polymer release into the capsule interior. The “filled” capsules have been considerably swollen due to counterion osmotic pressure of an inner polyelectrolyte solution. They showed a different mechanical behavior and have been found to be much stiffer than “hollow” ones, which reflects a combined effect of excess osmotic pressure, irreversible changes of the mechanical properties of the stretched shell, and, possibly, formation inside capsules of electrostatically stabilized 3D net. In this paper we make the “filled” capsules from “hollow” ones by regulation of their permeability¹⁰ by solvent variation. The preformed “hollow” capsules are permeable for water but impermeable for high molecular weight polymers. The shell permeability for polymers changes at low pH¹⁰ and in a water/ethanol mixture,¹¹ which has already been used to encapsulate macromolecules. Here, to fill “hollow” capsules with polymers of

[†] Max Planck Institute for Polymer Research.

[‡] Russian Academy of Sciences.

[§] Max Planck Institute for Colloid and Interface Research.

* To whom correspondence should be addressed. E-mail: vinograd@mpip-mainz.mpg.de.

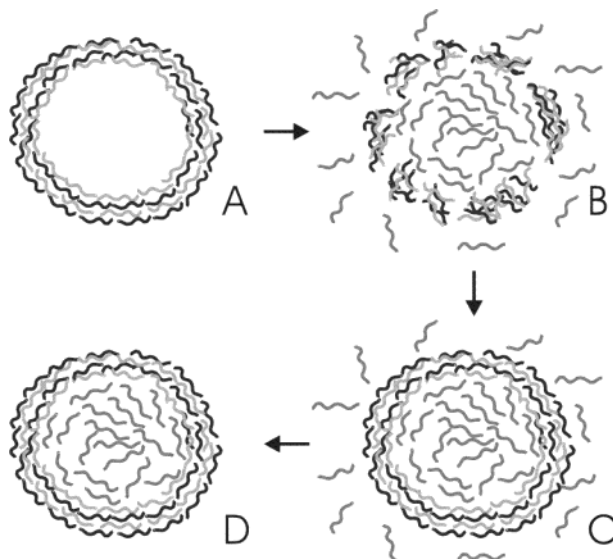


Figure 1. Scheme illustrating the preparation of the "filled" microcapsules.

various concentrations, we use a water/acetone mixture. This technique allows one to encapsulate a wider class of macromolecules than before.⁸ As an initial application of our novel encapsulation technique, we have chosen to study mechanical properties of capsules filled with a neutral polymer. One question of interest is what is the role of the concentration of encapsulated neutral polymer in determining the stiffness of the capsules? Another one is to which extent are the properties of the shell itself responsible for the mechanical stability of the capsules? We also briefly address an issue of reversibility of a transition from the "closed" and "open" state of the capsules and of a mechanism for permeability changes.

Materials and Methods

Materials. Sodium poly(styrenesulfonate) (PSS, $M_w \sim 70\,000$) and poly(allylamine hydrochloride) (PAH, $M_w \sim 50\,000$) were obtained from Aldrich. Rhodamine 6G was purchased from Sigma. Acetone was purchased from Merck.

Fluorescein isothiocyanate–dextran (FITC–dextran, $M_w \sim 500\,000$) purchased from Sigma was used as a neutral polymer.

Dispersions of monodispersed weakly cross-linked melamine formaldehyde (MF) particles with a diameter of $4.5 \pm 0.1\ \mu\text{m}$ were purchased from Microparticles GmbH (Berlin, Germany).

Thin glass slides (0.17 mm) with optical quality surfaces were obtained from World Precision Instruments (Victoria, Australia). Glass spheres (radius $20 \pm 1\ \mu\text{m}$) were purchased from Duke Sci. Co., California. Glass surfaces were cleaned by ethanol and plasma treatment.

Experiments were carried out in water prepared using a commercial Milli-Q system containing ion exchange and charcoal stages.

Capsule Preparation. The "filled" capsules were made from the preformed "hollow" capsules. The original "hollow" capsules have been produced by LbL assembly of four pairs of poly(styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) layers on MF particles. MF particles coated with PSS/PAH multilayers were dissolved in 3 M HCl, and MF oligomers were removed by washing, as described in ref 2. Then the encapsulation of a polymer included several steps (Figure 1). The original "hollow" capsules (Figure 1A) were exposed to an acetone/water mixture (30%) in order to make the polyelectrolyte multilayer permeable for high molecular weight polymer. Then the neutral polymer (FITC–dextran) molecules were added to the capsules in such a solvent mixture. The "open" state of the capsule wall allows the

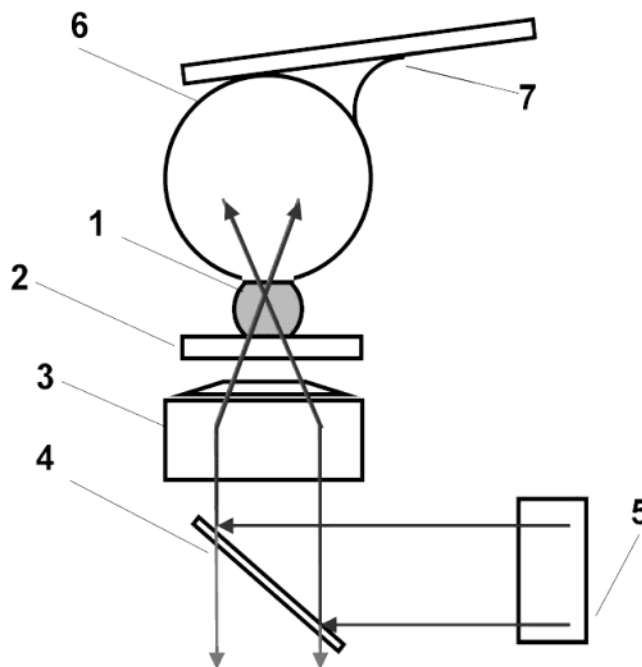


Figure 2. Schematic of the AFM force experiment.

polymers to penetrate inside (Figure 1B). After 30 min this mixture was diluted with pure water, and the multilayer composed shell is assumed to return to the "closed" state (Figure 1C). After washing in pure water, the capsules contain polymer solution (Figure 1D). We have used FITC–dextran solutions of several concentrations below 10 g/L.

Atomic Force and Optical Microscopy. Load (force) vs deformation curves were measured with the Molecular Force Probe (MFP) 2D AFM (Asylum Co., Santa Barbara, CA). The MFP is equipped with a nanopositioning sensor that can correct piezoceramic hysteresis and creep when operating in a closed loop. The MFP was used in combination with an inverted fluorescence microscope Olympus IX70 with a high-resolution immersion oil objective (100 \times), especially adjusted for the MFP 2D.

We used V-shaped cantilevers (Micromash, Estonia, spring constants $k = 2.5\ \text{N/m}$). The constant of the cantilevers was determined by a resonance frequency calibration plot (Cantilevers catalog, Micromash, Estonia). Glass spheres were glued onto the apex of cantilevers with epoxy glue (UHU Plus, Germany).

To determine the 3D shape of the capsules and to measure the concentration of FITC–dextran inside the capsules, we used a commercial confocal microscope manufactured by Carl Zeiss (Jena, Germany) consisting of the module Confocor 2 in combination with the inverted microscope model Axiovert 200 and equipped with a 40 \times water immersion objective. The excitation wavelength was chosen according to the label Rhodamine (525 nm). The z -position scanning was done with steps of $0.1\ \mu\text{m}$. The concentration measurements were performed via the fluorescence intensity coming from the interior of the FITC–dextran containing capsules. In this case we assumed that fluorescence is directly proportional to FITC–dextran concentration and used a calibration curve of fluorescence intensity of free polymer in the bulk solution.

Schematic of Experiment. A schematic of the experiment is presented in Figure 2. A drop (50–100 μL) of water suspension of polyelectrolyte microcapsules (1) was deposited onto a thin glass substrate (2) fixed over the oil immersion objective (3) of the inverted fluorescence microscope, which included a dichroic mirror (4) and a mercury lamp (5). For fluorescence we used the fluorescent dyes Rhodamine 6J and fluorescein. The optical image was recorded by an Olympus E-20P camera. The colloidal sphere (6) attached to a cantilever (7) was centered above the apex of a capsule with accuracy of $\pm 0.5\ \mu\text{m}$, using the graticule line(s) in the optical image for

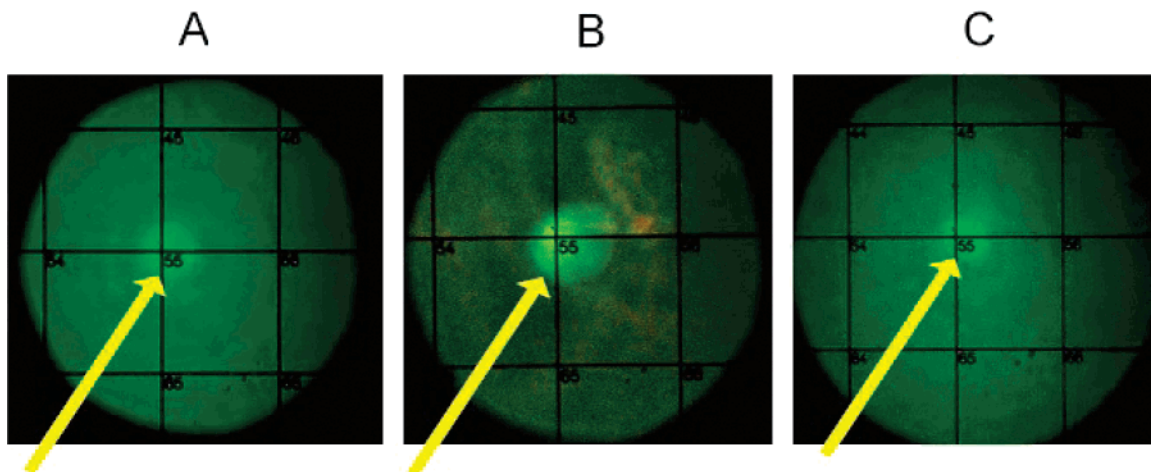


Figure 3. Typical optical reflection images for a “filled” capsule obtained for different stages of deformation. The capsule is located at the intersection of graticle squares 44–45–54–55; the size of a graticle square is 10 μm . (A) A sphere is far from the capsule; a spherical capsule is not deformed. (B) A capsule is compressed between a sphere and a substrate ($\epsilon \sim 50\%$). The darker background is due to a shadow from the sphere. On the right of the capsule one can see the red speck from the AFM laser. (C) A sphere is away from the crushed capsule. One can see its nonspherical rest on a substrate.

alignment (see Figure 3). Measurements were performed at a speed in the range from 0.2 to 20 $\mu\text{m/s}$. The maximum loading force was up to 1 μN . To quantify the force data, the results of measurements were calibrated from the “constant compliance” region of force curves between the glass probe and the glass substrate in a region free from immobilized polyelectrolyte capsules.

Calculation of the Deformation Curve. The result of measurements represents the deflection Δ vs position of the piezotranslator at single approach (loading)/retraction (unloading). The force (F) acting between the glass sphere and the polyelectrolyte microcapsule was determined from the cantilever deflection $F = k\Delta$. The main difficulty with the AFM measurements on deformable systems is that there is normally no sharp transition between contact and no contact due to the extended range of surface forces. In this study we simply assume that the zero of separation is at the point of the first measurable force.¹² Then the deformation can be calculated as the difference between the position of the piezotranslator and cantilever deflection. The height of the capsule (AFM diameter) was determined as a difference between the position of the apex and the substrate and was used as an independent way to determine the capsule diameter. The relative deformation ϵ of the capsule was then defined as a ratio of deformation to its height (or AFM diameter) as before.⁸

Results and Discussion

The 3D confocal scanning suggested that the original “hollow” capsules are of a spherical form and of the size of the original colloidal template. Confocal images of capsules filled with FITC–dextran suggested that they are also not swollen, and their confocal radius is the same as for “hollow” capsules. Here, we also have not found any deviations of the capsule shape from the spherical one within the accuracy of the confocal 3D scanning. The absence of discernible swelling for “filled” capsules suggests that the excess osmotic pressure of the inner polymer solution is too small to change the size of the capsules. This is not surprising, taking into account that for a neutral polymer the osmotic pressure is proportional to the concentration divided by a chain length, which gives values of the order of 10^{-4} Pa for our solutions of FITC–dextran.

A confocal fluorescence image in Figure 4 illustrates that polymer was encapsulated. The interior of the capsules was found to be bright and constant over time, and there is no fluorescence signal from water. This

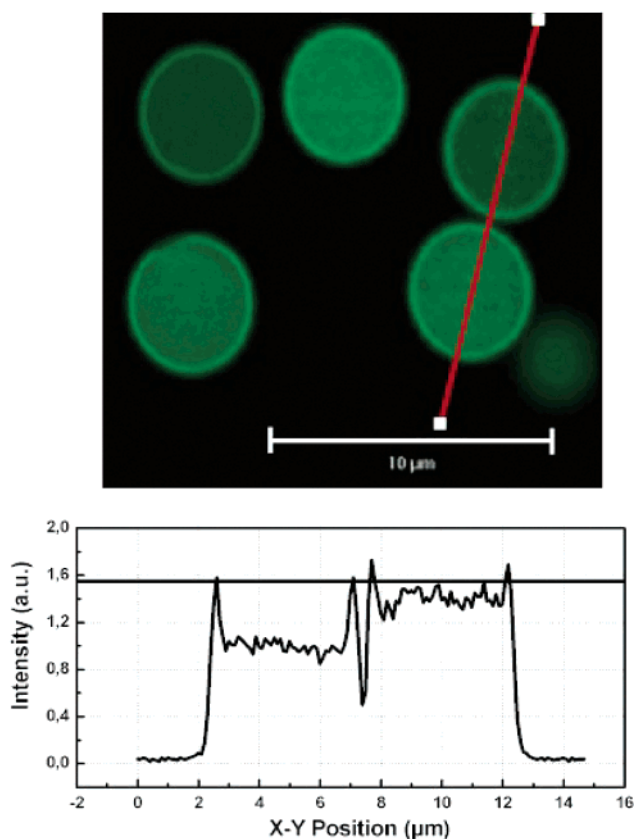


Figure 4. Typical fluorescent confocal images of capsules loaded with FITC–dextran (top) and fluorescent profile along the line indicated in the images (bottom). The line on the profiles (bottom) illustrates the intensity of fluorescence of 3 g/L FITC–dextran bulk solution used for encapsulation.

proves that the capsules are in the “closed” state. For some capsules the intensity of fluorescence from the interior was up to 20–30% less than that of bulk polymer solution used for encapsulation. However, for the majority of them it was found to remain equal to the bulk value or was only a few percent lower.

We have performed several series of experiments; each included the measurements of about 10–20 capsules. As before,⁸ we found some variability in similar

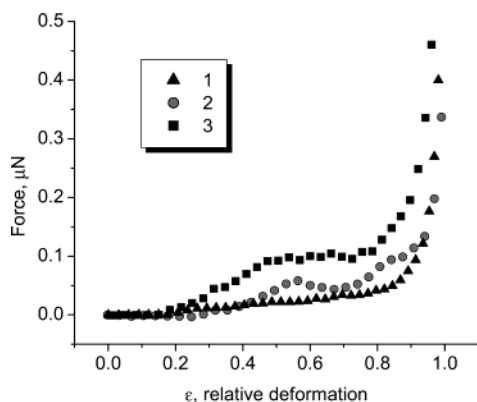


Figure 5. Load vs deformation curves for “filled” capsules measured at driving speed $2 \mu\text{m/s}$. Only every 10th point is shown. Concentration of the FITC–dextran solution is 1 (1), 3 (2), and 10 g/L (3).

capsule behavior, so that the so-called typical results we report below represent a generalization (averaging) of many observations. Some percent of the capsules had a tendency to be broken (up to two capsules in the series). In this case we have not observed the typical force curves (quantitatively), and these data were ignored in our analysis.

We remark that in all the cases the pull-off force was equal to zero, which means negligibly small adhesion to the glass substrate. Also, the AFM diameter used to calculate ϵ was always found to be equal to an optical (confocal) one. Similar observations have been made before,⁸ so that we do not discuss that in detail here.

Figure 5 shows typical load vs deformation profiles measured for capsules with different concentration of inner FITC–dextran solution. These measurements have been performed at the same (low) speed as before.⁸ The essential observations are these:

(i) One can observe some tendency for capsules to become slightly stiffer with the increase in concentration (although the difference between concentration 1 and 3 g/L is within an experimental error). Therefore, there exists a contribution to mechanical properties coming from the inner polymer solution. The reason for this contribution cannot be connected with the osmotic pressure of the FITC–dextran solution, which is negligibly small.

(ii) We also see that capsules with different concentration of FITC–dextran show qualitatively similar deformation profiles, the same as was previously observed for “hollow” capsules,⁸ namely, that the deformation profiles always include three distinct regimes. In the *first regime*, with low applied load (ϵ up to ~ 0.2 – 0.3), the capsules become stiffer after the load is increased. The deformation is elastic and reversible and does not depend on the concentration of the inner polymer. Importantly, because of an improved optical scheme and a possibility to control the shape of the capsule, we dramatically decreased the variability in load vs deformation profile for the first regime. The *second regime* ($\epsilon \sim 0.3$ – 0.8) is characterized by a change in slope in the load–deformation profiles, which now reveals a dependence on concentration of the inner polymer solution and only partial reversibility. The load–deformation profile includes different sectors (from substantial deformation at the quasi-constant load to noisy regions in the data and, sometimes, a change in the sign of the slope). Another important feature of this regime is a much higher hysteresis and variability in

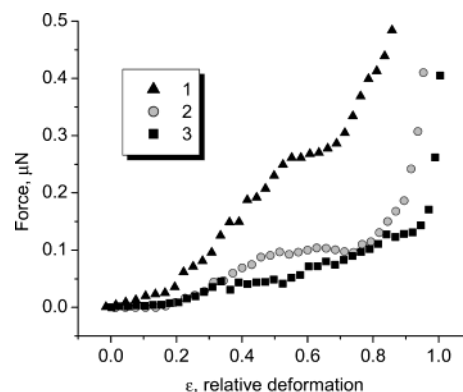


Figure 6. Load vs deformation curves measured at low drive speed of $2 \mu\text{m/s}$ (only every 10th point is shown) for original “hollow” capsules (1) and capsules after treatment in a water/acetone mixture: “hollow” (3) and “filled” (10 g/L) with FITC–dextran (2) capsules.

behavior. We stress that this variability is due to different properties of different capsules and is not connected with experimental error. After substantial deformation the capsules enter the *third regime* ($\epsilon \sim 0.7$ – 1.0), in which major damage is caused by higher load.

(iii) Another result is that the capsules filled with FITC–dextran are very soft compared with the capsules studied in our previous publication.⁸

These observations deserve more comments and detailed investigations. We start with the question of a stiffness of the capsules. Figure 6 illustrates the difference of capsules filled with FITC–dextran from the original “hollow” capsules. Indeed, the “filled” capsules are much softer than those used for their preparation. More precisely, the load required to cause the same deformation of “filled” capsules is from 3 to 5 times lower than that for the original “hollow” ones, depending on regime of deformation and on concentration of the inner polymer solution. To understand the reasons for such a decrease in stiffness, we have treated the original “hollow” capsules in the same water/acetone mixture used for encapsulation of a polymer. One can see that this led to a dramatic decrease in the “hollow” capsule stiffness. Essentially, the “hollow” capsules treated by organic solvent are softer than “filled” capsules only in the second and third regimes of deformation. We have not found any difference between these two types of capsules in the first regime of deformation.

These results indicate that the treatment of the capsules by organic solvent results in decreases in the stiffness of the shells, and this effect is entirely responsible for the mechanical properties of the “filled” capsules deformed in the *first regime*. Some aspects of the behavior of the capsules at small deformations can be better understood by analyzing the data plotted in log–log scale (see Figure 7). The experimental data presented in this scale look somewhat like straight lines. This indicates that the relationship between the load and the relative deformation approximates a power law, which is in agreement with our theoretical model.¹³ The data for “filled” and treated by solvent “hollow” capsules are superimposed, while the results for preformed “hollow” capsules plotted in this scale are shifted toward higher values of a force. According to our predictions,¹³ the force is linear in Eh , where E is Young’s modulus of a polyelectrolyte multilayer and h is the shell thickness. Therefore, the softening of the capsules after

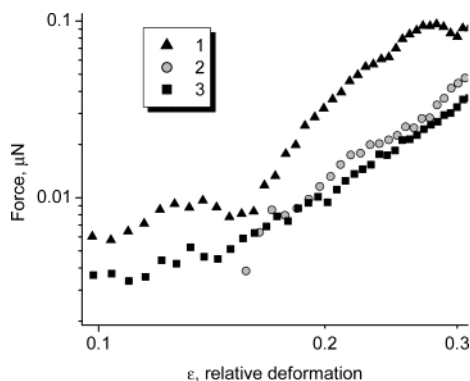


Figure 7. Data for small relative deformations for the same systems as in Figure 6 plotted in a log–log scale. Only every second point is shown.

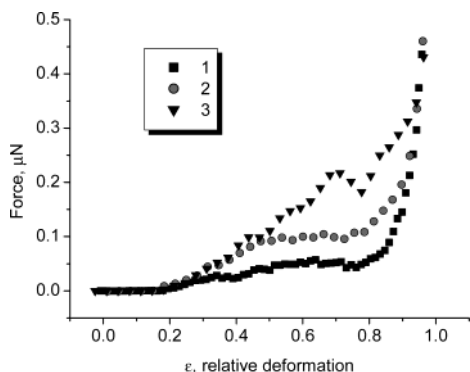


Figure 8. Load vs deformation curves for capsules filled with FITC–dextran (10 g/L) measured at driving speed 0.2 (1), 2 (2), and 20 $\mu\text{m/s}$ (3). Only every 10th point is shown. The change in slope for the high-speed curve (3) is likely due to a local rupture of the shell (and/or buckling).

treatment in organic solvent is due to either structure changes (leading to a decrease in E) or partial dissolution of the shell (leading to smaller h), or both. Once again, the encapsulated neutral polymer itself does not give any contribution to the mechanics of elastically deformed capsules.

In the *second regime*, the behavior of capsules depends on both the shell properties and concentration of the inner polymer solution. In addition, the deformation profiles are getting rate dependent as illustrated by Figure 8. More precisely, there is no speed dependence in the first regime of deformation, but the deformation profiles for the second regime are very sensitive to the driving speed. One can see that the “filled” capsules become stiffer with the increase in the rate of deformation. The same qualitative behavior was found for “hollow” capsules treated by a water/acetone mixture although a slightly lower load was required to cause the same deformation. However, we were unable to observe any significant dependence on the driving speed when it was below 15 $\mu\text{m/s}$ for original “hollow” capsules. These results indicate that the capsules treated in organic solvent are different from the original “hollow” capsules and that the second regime of deformation is, indeed, controlled by phenomena that are not related to the elasticity of the shells. The rate-dependent deformation profiles were previously observed in the AFM force experiment and have been interpreted in favor of plastic¹⁴ and/or viscoelastic^{15,16} deformation. The impact of the inner polymer allows us to rule out these types of deformation for the multilayer shells. We therefore conclude that the mechanics of the “filled”

capsules deformed in the second regime is different from what was found before⁶ (as a reaction to micropipet suction). We should also exclude similar phenomena coming from the capsule interior because both concentration and viscosity of encapsulated polymer are relatively low. So, the reasons for the observed behavior of highly deformed capsules are not very clear. One can, however, surmise that at some load the “filled” capsules become more permeable for an inner solution. If so, the deformation would be controlled by its drainage through the shell pores. Such a hypothesis is consistent with the softening of the multilayer shells after treatment by organic solvent, which could lead to a lower value of a “tensile strength” for the pore/defect formation. It will also predict the increase in the force with the viscosity of the inner polymer solution (or polymer concentration) and driving speed, which is also in agreement with our observations. However, more detailed investigation of this regime is required to finally conclude on the reasons for such a mechanical behavior. This work is in progress and will be published elsewhere.

In summary, the experiment we have reported suggests that the encapsulation of a neutral polymer changes the mechanical properties of polyelectrolyte microcapsules toward their softening. This softening is due to treatment by organic solvent required to induce a transition from the “closed” to “open” state of the capsules. As a result, in a small deformation regime the behavior is entirely controlled by the elasticity (and its changes) of a shell-forming polyelectrolyte complex. At larger deformations the capsule mechanics is likely determined by the drainage of the inner solution through the nanopores of the stretched shell. The role of organic solvent in permeability changes and softening of the shell has hardly begun to be considered theoretically in any depth and raises questions of some interest. The pH-induced opening of the pores of the order of several nanometers and more in a polyelectrolyte multilayer has been studied before.¹⁷ It follows from our results that organic solvent ought to have a similar role to play in setting ultrastructure of the polyelectrolyte multilayer shell.

Acknowledgment. We are grateful to Professor A. R. Khokhlov and Professor H. Möhwald for valuable remarks on the manuscript. We also thank Dr. K. Mitsui for suggestions concerning the optical scheme and A. A. Antipov for a help with the polymer encapsulation. We have benefited from valuable discussions with Dr. D. Andrienko and Dr. H. Schiessel. This work was partly supported by the Sofia Kovalevskaya Program of the Alexander von Humboldt Foundation and by the German Ministry of Education and Research.

References and Notes

- (1) Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S.; Möhwald, H. *Angew. Chem.* **1998**, *37*, 2202–2205.
- (2) Sukhorukov, G. B.; Donath, E.; Davis, S.; Lichtenfeld, H.; Caruso, F.; Popov, V. I.; Möhwald, H. *Polym. Adv. Technol.* **1998**, *9*, 759–767.
- (3) Decher, G. *Science* **1997**, *277*, 1232–1237.
- (4) Sukhorukov, G. B.; Donath, E.; Lichtenfeld, H.; Knippel, E.; Budde, A.; Möhwald, H. *Colloids Surf. A* **1998**, *137*, 253–266.
- (5) Sukhorukov, G. B. In *Novel Methods To Study Interfacial Layers*; Mobius, D., Miller, R., Eds.; Elsevier: Amsterdam, 2001; pp 384–414.
- (6) Bäuml, H.; Artmann, G.; Voigh, A.; Mitlöhner, R.; Neu, B.; Kiesewetter, H. *J. Microencapsulation* **2000**, *17*, 651–655.

- (7) Gao, C.; Donath, E.; Moya, S.; Dudnik, V.; Mohwald, H. *Eur. Phys. J. E* **2001**, *5*, 21–27.
- (8) Lulevich, V. V.; Radtchenko, I. L.; Sukhorukov, G. B.; Vinogradova, O. I. *J. Phys. Chem. B* **2003**, *107*, 2735–2740.
- (9) Radtchenko, I. L.; Sukhorukov, G. B.; Leporatti, S.; Khomutov, G. B.; Donath, E.; Mohwald, H. *J. Colloid Interface Sci.* **2000**, *230*, 272–280.
- (10) Sukhorukov, G. B.; Antipov, A. A.; Voigt, A.; Donath, E.; Möhwald, H. *Macromol. Rapid Commun.* **2001**, *22*, 44–46.
- (11) Lvov, Y.; Antipov, A. A.; Mamedov, A.; Möhwald, H.; Sukhorukov, G. B. *Nano Lett.* **2001**, *1*, 125–128.
- (12) Aston, D. E.; Berg, J. C. *J. Colloid Interface Sci.* **2001**, *235*, 162–169.
- (13) Lulevich, V. V.; Andrienko, D.; Vinogradova, O. I., submitted for publication.
- (14) Butt, H. J.; Doeppenschmidt, A.; Huettl, G.; Mueller, E.; Vinogradova, O. I. *J. Chem. Phys.* **2000**, *113*, 1194–1203.
- (15) Pittenger, B.; Fain, S. C.; Cochran, M. J.; Donev, J. M. K.; Robertson, B. E.; Szuchmacher, A.; Overney, R. M. *Phys. Rev. B* **2001**, *63*, Art. No. 134102.
- (16) Gillies, G.; Prestidge, C.; Attard, P. *Langmuir* **2002**, *18*, 1674–1679.
- (17) Mendelsohn, J. D.; Barrett, C. J.; Chan, V. V.; Pal, A. J.; Mayes, A. M.; Rubner, M. F. *Langmuir* **2000**, *16*, 5017–5023.

MA0259719