Eur. Phys. J. E **5**, 21–27 (2001)

THE EUROPEAN PHYSICAL JOURNAL E

EDP Sciences

Elasticity of hollow polyelectrolyte capsules prepared by the layer-by-layer technique

C. Gao[1,2], E. Donath[2,a], S. Moya[2], V. Dudnik[2,3], and H. Möhwald[2]

[1] Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, P.R. China
[2] Max-Planck Institute of Colloids and Interfaces, 14424 Potsdam, Germany
[3] Department of Chemistry, University of Toronto, Toronto, Ontario M55 3H6, Canada

Received 25 January 2000 and Received in final form 18 May 2000

Abstract. Osmotically induced deformations (invaginations) of polyelectrolyte capsules were observed in poly(styrene sulfonate, sodium salt) (PSS) solution since PSS of Mw 70 000 is excluded from the capsule interior. It was found that there is a critical osmotic pressure difference at which the initial spherical capsule shape becomes unstable and invaginations are formed. This critical osmotic pressure was obtained as a function of the wall thickness and the capsule size. A theoretical model is provided which describes the relationship between the critical osmotic pressure, the elasticity modulus, the capsule wall thickness, and the capsule radius. The model was verified by measuring the invagination onset as a function of particle radius and wall thickness. The elasticity modulus of the PSS/PAH (polyallylamine hydrochloride) polyelectrolyte multilayer was measured as a function of wall thickness and capsule diameter. The modulus ranges between 500 and 750 MPa, which indicates a relatively strongly interconnected polyelectrolyte multilayer structure. With higher molecular weight PAH the elasticity modulus of the PSS/PAH multilayer was slightly enhanced.

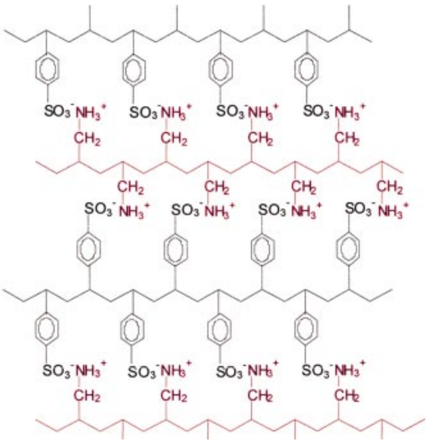
PACS. 46.32.+x Static buckling and instability – 68.60.Bs Mechanical and acoustical properties

1 Introduction

Nano- and micron-sized capsules are both of scientific and technological interest because of their potential applications [1,2]. For example, biopolymers such as proteins, enzymes or nuclear acid can be encapsulated, transported and released afterwards.

Recently a novel type of nano- and micrometer-sized hollow capsules has been prepared by the step-wise adsorption of polyelectrolytes (PE) onto charged colloidal templates, followed by decomposition of the templates [3]. The fabricated capsules have been characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), confocal laser scanning microscopy (CLSM), electrophoresis, electrorotation, and single particle light scattering [3–5]. These investigations have revealed some properties of capsules, *e.g.* the morphology both in the wet state and in the dry state, the capsule size, the surface charge, the capacity and the conductance etc. It has been shown that organic or inorganic materials can be precipitated inside the capsules [6]. Polymerization reactions were conducted to fabricate polymer filled capsules [7]. A solvent exchange protocol also yielded capsules filled with non-polar liquids [8].

Preliminary research has demonstrated that capsules composed of 10 layers of alternating PSS and PAH are stable in various chemical environments. They are permeable for small polar molecules, but exclude polymers [9–11].



Idealized structure model for the multilayer PSS/PAH complex.

---

[a] e-mail: `edwin.donath@mpikg-golm.mpg.de`

One promising feature of these capsules is that varying thickness and composition of the walls the mechanical properties can be tuned over a wide range. The elasticity and mechanical stability of the capsules are definitely important for a variety of practical applications. For example, deformation and rupture of PE multilayer capsules under shear stress may apparently limit the use of these novel structures. At present, however, the mechanical properties of the capsules are not known.

The mechanical properties of cells and liposomes have been successfully studied with the micropipette aspiration technique [12,13]. Recently, this method was used to investigate polymersomes, the crosslinked amphiphilic polymer vesicles [14]. Concerning the application of the micropipette aspiration technique for the investigation of PE capsules, it has to be considered that the aspiration force certainly depends on the hydraulic conductivity of capsules. The capsules are highly permeable for water and adhesive to charged substrates. Therefore, an osmotic technique was introduced to measure the deformation of a capsule population. Another advantage of the osmotic technique is that, for example, in contrast to anisotropic shear stress [15], isotropic osmotic pressure differences can be conveniently applied for inducing deformation in a controlled way. The capsule preparation is suspended into a solution of medium molecular weight PSS. Intact capsules (that means not permeable for PSS) deform as a result of the osmotic pressure difference created, broken capsules, *i.e.* capsules permeable for PSS keep their initial, mostly spherical shape. It is conceivable that this approach can be applied to other micro- and nanosized capsules as well.

2 Materials and methods

2.1 Materials

The source of chemicals are as follows: poly(styrene sulfonate, sodium salt) (PSS, Mw 70 000), and poly(allylamine hydrochloride) (PAH) with Mw 8–15 kD, and 50–65 kD, Aldrich; fluorescein isothiocyanate labeled albumin (FITC-albumin, FITC 12 mol/mol albumin), Sigma; weakly crosslinked melamine formaldehyde particles (MF-particles, different size), microparticles GmbH, Germany. All chemicals were used as received. The water was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity higher than 18.2 MΩ cm.

2.2 Methods

Capsule preparation

A membrane filtration technique was employed to consecutively adsorb PSS and PAH onto MF particles [16]. The adsorption of polyelectrolyte (1 mg/ml) was conducted in 0.5 M NaCl solution for 5 min, followed by 3 washings in H_2O. Then the respective oppositely charged polyelectrolyte species was adsorbed. After the desired number of layers was adsorbed the coated particles were treated in HCl solution, pH = 1.1, to decompose the MF cores. The produced MF oligomers and excess HCl were washed off until a neutral pH was established by filtration with gentle agitation. The outermost layer in this study is always the positively charged PAH.

FITC-albumin labeled capsules

Equal amounts of capsule solution and FITC-albumin solution (1 mg/ml) were mixed together, and stored at 4 °C at least for 2 hours. The suspension was centrifuged at 4 000 rpm (1145 g, Sigma 3K30 Laboratory Centrifuges) and washed 3 times in H_2O to remove the excess FITC-albumin.

Critical transition PSS concentration

The solution of FITC labeled capsules was mixed with an equal amount of PSS solution of different concentrations. Confocal laser scanning microscopy (CLSM) was employed to determine the number of deformed and undeformed capsules. The total number of capsules counted for each PSS concentration was at least 200. The deformation ratio was defined as the number of deformed capsules divided by the total number of capsules. The critical PSS concentration was defined as the concentration necessary to induce the invagination of 50% of the intact capsules.

Confocal Laser Scanning Microscopy (CLSM)

Confocal micrographs were taken with an inverted confocal laser scanning microscope from Leica, equipped with a 100× oil immersion objective. The samples were mounted with nail lacquer. This prevented the evaporation of water. Thus the PSS concentration remained constant during the counting procedure.

Osmotic pressure

The osmotic pressure of the PSS solutions was measured by means of vapor pressure reduction with a Vapor Pressure Osmometer, No. A0280, Knauer. Thus, the osmotic pressure for a given PSS concentration is read from the calibration curve (Fig. 1).

3 Theory

A general model describing the deformation of polyelectrolyte capsules is reasonably complicated since it includes elastic as well as plastic deformations. But the images of the deformed polyelectrolyte capsules provided further below show that in many cases the capsules change their shape without a prior microscopically detectable stretching. Especially, at the initial moment, the deformations

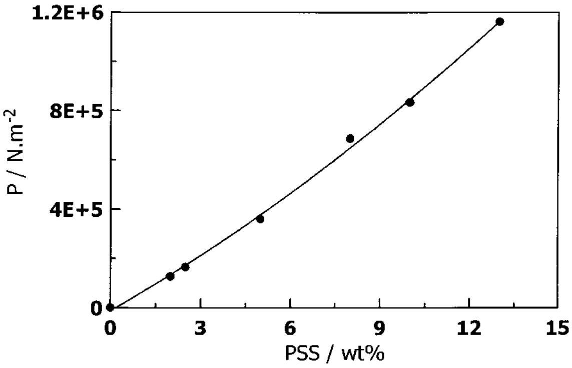


Fig. 1. Osmotic pressure calibration curve.

may be considered as elastic. The experiments have shown that there is a rather well defined threshold pressure (critical pressure) difference above which the capsules loose their spherical shapes. A shape transformation from a convex spherical shape to a concave cup-like shape takes place. The problem of relating the critical pressure to the mechanical properties of this curved thin layer was solved in [17,18]. Following the deformation of elastic bodies is given by two constants, K-the compression modulus, and μ-the elasticity modulus.

The capsules loose their stability and, hence, spontaneously change the shape when the work performed by the external pressure

$$A = \iint_G p h_n \mathrm{d}S \tag{1}$$

is equal to the deformation energy

$$U = \int_\gamma \frac{E\delta^2 h'}{R\sqrt{3(1-\sigma^2)}} \mathrm{d}l \tag{2}$$

where p is the external pressure, h_n is the component of the bending field perpendicular to the surface of the capsule, G is the area of deformation, γ is the meridian curve along the area of deformation, $h_\perp$ is the component of the bending field perpendicular to γ on the surface,

$$E = \frac{9K\mu}{3K+\mu}$$

is Young's modulus,

$$\sigma = \frac{3K-2\mu}{2(3K+\mu)}$$

is Poisson's ratio, δ is the thickness of capsule wall, and R is the radius of the capsule. The geometrical equality (3) for the deformation volume transforms the area integral into a contour integral

$$V = \iint_G h_n \mathrm{d}S = \frac{R}{2}\int_\gamma h_\perp \mathrm{d}l. \tag{3}$$

Finally, comparing (1) and (2) by using (3), the critical pressure is found

$$P_\mathrm{c} = \frac{2E}{\sqrt{3(1-\sigma^2)}}\left(\frac{\delta}{R}\right)^2 \cdot \tag{4}$$

Thus, the critical pressure difference between the capsule interior and the bulk required for deformation induction is proportional to the square of thickness of the capsule wall δ and is inversely proportional to the square of the capsule radius (for more details, see [18]). As far as the capsule wall stretching can be considered small, it follows that $K \gg \mu$, and (4) can be rewritten in terms of the elasticity modulus

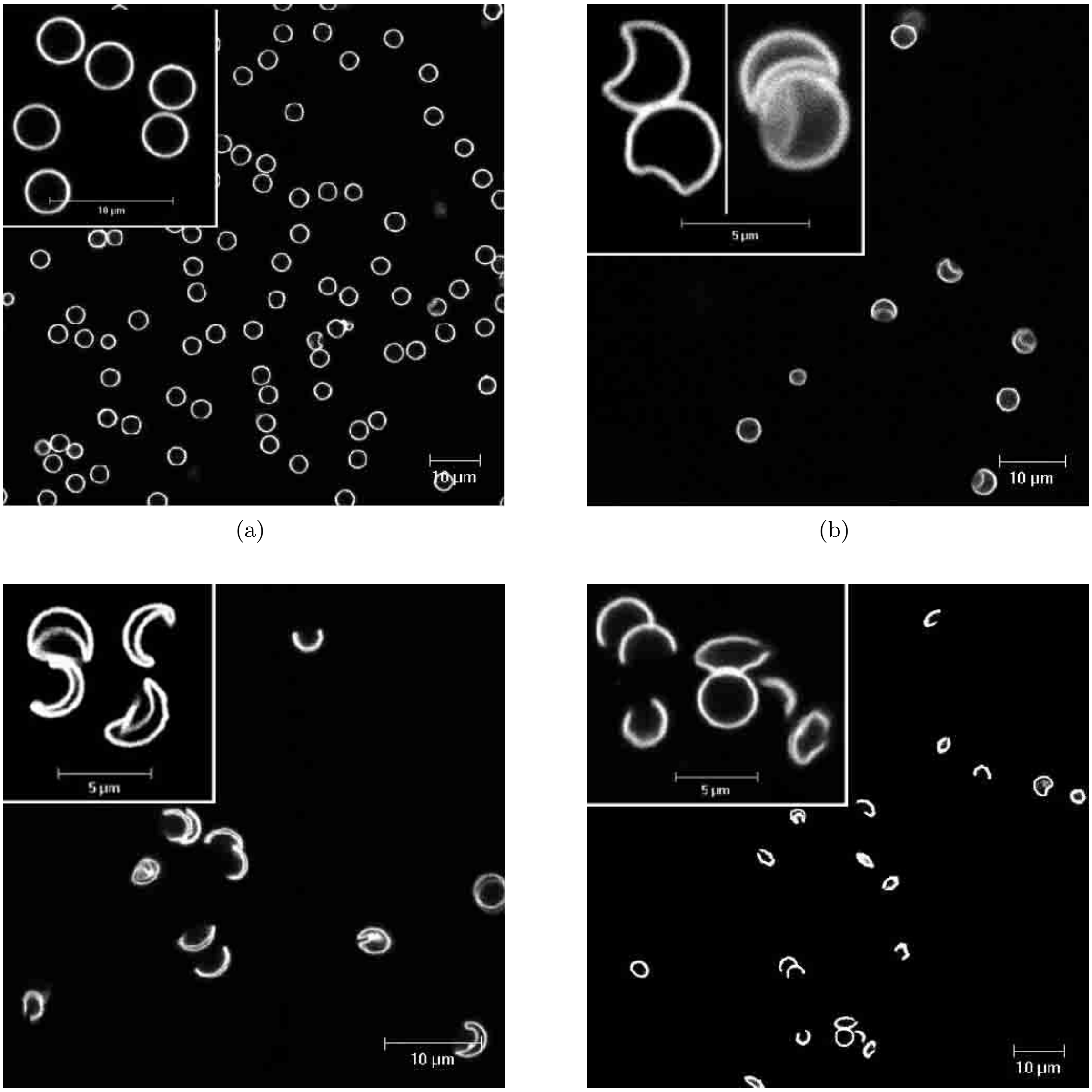
$$P_\mathrm{c} = 4\mu\left(\frac{\delta}{R}\right)^2 \cdot \tag{5}$$

Equation (5) will be used below for obtaining the elasticity of the capsule walls from the experimental data of capsule deformation.

4 Results and discussion

FITC-albumin was selected as a fluorescence label, since, as shown in Figure 2a, it adsorbed on capsules with either PAH (Fig. 2a) or PSS (images are not shown) as the top layer. This occurred regardless of the presence of bulk polyelectrolytes, because of the zwitterionic nature of albumin. Low molecular weight fluorescent polar dyes, such as 6-carboxyfluorescein (6-CF), showed a different behavior. 6-CF adsorbed only on positively charged capsules. After PSS was added to the bulk solution containing these capsules, 6-CF desorbed and the capsule fluorescence largely decreased. The visualization of capsules is then very difficult. Another important advantage of albumin is that it may prevent PSS adsorption to occur. The thickness of the capsule wall as well as the polyelectrolyte concentration remain constant. The disadvantage of FITC-albumin could be that it might have some effect on the elasticity of the capsule wall.

The capsule wall is permeable for the solvent H_2O, but impermeable for polymers of a higher molecular weight [11]. When the osmotic pressure in the bulk is larger than in the interior, the solvent is squeezed out provided the elastic restoring forces do not compensate the arising hydrostatic pressure difference. Indeed, Figure 2b shows that unbroken capsules undergo a shape transition from spherical into a cup shape at a certain critical PSS concentration range. At still higher PSS concentration, the capsules shrink further (Fig. 2c), and at very high PSS concentration the capsules do not have a noticeable internal volume (Fig. 2d). Broken capsules are easily distinguished by the absence of shrinking. In such capsules PSS can equilibrate through sufficiently large pores. Hence, osmotic shrinkage is also a powerful method to distinguish unbroken capsules from broken ones. It is worthwhile to note that it is largely the PSS counterion concentration, which is responsible for the created osmotic pressure difference. The contribution of the polymer itself is very small due to the colligative nature of the osmotic pressure. For example, a 7 wt% PSS solution would correspond to 1 mM. This, according to the van't Hoff's law yields a pressure of $\Pi = RTC = 2.5$ kPa. Hence, only polyelectrolytes are suitable for inducing large enough osmotic pressure



(a) (b) (c) (d)

Fig. 2. The deformation of polyelectrolyte capsules consisting of 10 layers of PSS/PAH as a function of the PSS (Mw 70 000) bulk concentration. The insets are higher magnification of the corresponding images. (a) Control, (b) 2.5 wt% PSS, (c) 5 wt% PSS, and (d) 10 wt% PSS. Capsule radius 2 μm.

differences. They combine exclusion with a high concentration of osmotically active species, *e.g.* counterions. As indicated in the theory part, the critical pressure depends on the wall material, the thickness of the capsule wall and the size of the capsules.

The mechanical properties of the capsules may be slightly different due to some inhomogeneity of the preparation. The onset of deformation itself is an instability phenomenon and, hence, subject to some arbitrariness. Therefore, instead of a sharp transition point one would expect a concentration region, where the invagination starts. Hence, to obtain the mean critical osmotic pressure for a defined capsule preparation, the percentage of deformed capsules was measured as a function of the PSS concentrations. The critical pressure can then be obtained from the 50% transition point, as shown in Figure 3.

To qualitatively verify the validity of equation (5) for the capsules under consideration, first, the number of adsorbed polyelectrolyte layers was varied while keeping the radius constant. It was shown earlier that the thickness of the wall increases proportionally with the layer number [4,5]. Figure 3 shows clearly that along with the increase of the capsule wall thickness the critical deformation pressure (PSS concentration) also increased. A typical sigmoidal shape of the deformation *vs.* PSS concentration curve is obtained. Most capsules do not invaginate at low PSS concentrations. At lower polyelectrolyte concentrations the osmotic pressure is not large enough to

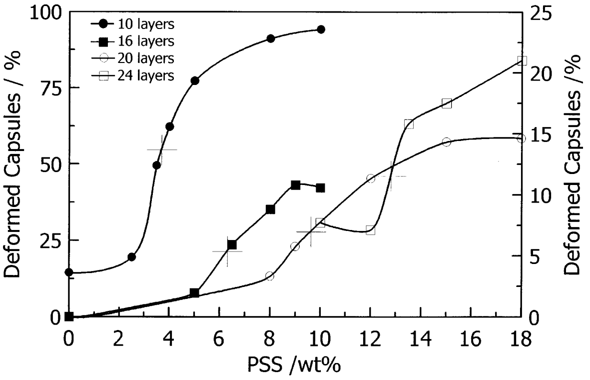


Fig. 3. Percentage of deformed capsules as a function of the PSS concentration. Capsule radius 2 μm. Number of layers given in the inset. The left axis is employed for the filled symbols (● and ■), and the right axis, the open symbols (○ and □). The crosses indicate the critical transition points.

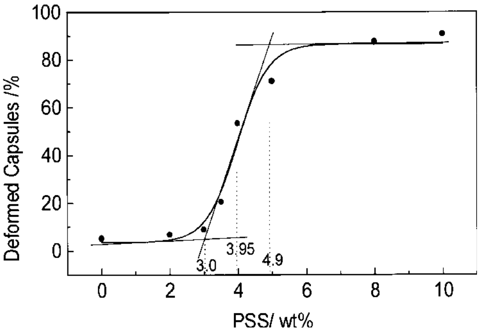


Fig. 4. Percentage of deformed capsules as a function of the PSS concentration. 10 layer PSSPAH, PAH Mw 50–65 kD, capsule radius 2 μm. The straight lines illustrate how the critical PSS concentration was obtained. It was defined as the 50% increase of the second straight line corresponding to the deformation of 50% of the PSS excluding capsule population.

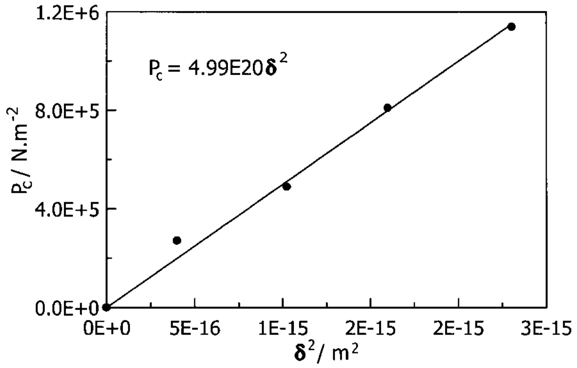


Fig. 5. Critical osmotic pressure as a function of the square of the thickness of the capsule wall. Capsule radius 2 μm.

overcome the elastic restoring force of the capsule walls. At high PSS concentrations all capsules, except broken ones, are deformed. Therefore the deformation-PSS concentration curves observe two plateaus. An exception was capsules with only 6 layers. Their deformation ratio saturated at 25%. This is explained by the fact that the thin capsule wall consisting of only 6 layers is probably permeable for PSS, Mw 70 000.

It has to be mentioned that increasing the capsule wall thickness, it becomes more and more difficult to prepare intact capsules, because the products of core decomposition cannot leave fast enough through the capsule walls. The resulting osmotic pressure difference breaks the capsules. For this reason with increasing layer thickness a smaller and smaller percentage of potentially deformable capsules is found. For example, when the layer number increases from 10 to 16 the content of capsules responding to the osmotic pressure decreases from 80% to 40%, and decreases even further to 15% and 13% for 20 and 24 layers, respectively. It should be noted that some capsules in the control were already deformed, *e.g.* in the cases of 10 and 24 layers. This deformation percentage should not contribute to the osmotic pressure induced capsule deformation. Therefore, a three tangent evaluation technique was used to estimate the critical PSS concentration (CPC). The procedure is schematically illustrated in Figure 4. One can deduce that the midpoint can be determined with an accuracy of 10% giving the accuracy of P_c. The following CPCs were found: 3.7, 6.25, 9.6 and 12.75 wt% for 10, 16, 20 and 24 PSS/PAH layers (PAH Mw 8–15 kD), respectively. From AFM measurements and single particle light scattering it is known that the thickness of a double layer of PSS/PAH is approximately 4 nm [4,5]. According to the osmotic pressure calibration curve P_c is found. Theoretically, it should depend linearly on the square of layer thickness, δ^2 (Eq. (5)). This prediction is indeed confirmed by the experiment (Fig. 5) demonstrating that the continuum mechanics approach is also applicable to polyelectrolyte multilayers of a thickness of the order of only 10 nm. The slope in Figure 4 is 4.99×10^{20} N m^{-4}. The radius R was measured by CLSM. It equals 2×10^{-6} m. Therefore the elasticity modulus of the PSS/PAH capsule wall was estimated as $\mu = 4.99 \times 10^{20} R^2/4 \approx 500$ MPa.

Equation (5) predicts an inverse dependence of the critical pressure difference on the square of the particle radius. To further verify the applicability of the macroscopic continuum approach the radius was varied keeping layer thickness and layer composition constant. Figure 6 shows the percentage of deformed capsules as a function of the PSS concentration for three different capsule radii. It is obvious that with decreasing radius higher osmotic pressure differences are necessary to induce capsule deformation. The CPCs were found as 0.71, 2.4 and 3.05 wt% for capsules with a radius of 4.3, 2.35 and 2.0 μm, respectively. Figure 7 shows that the critical osmotic pressure depended linearly on the inverse of the capsule radius square. This further proved equation (5). It follows that $4\mu\delta^2 = 8.76 \times 10^{-7}$ N. So another estimate for the elasticity modulus μ of 550 MPa is obtained for the PSS/PAH multilayer. This value is close to 500 MPa independently estimated above.

When a higher molecular weight PAH (Mw 50–65 kD) was used, the elasticity modulus estimated from the

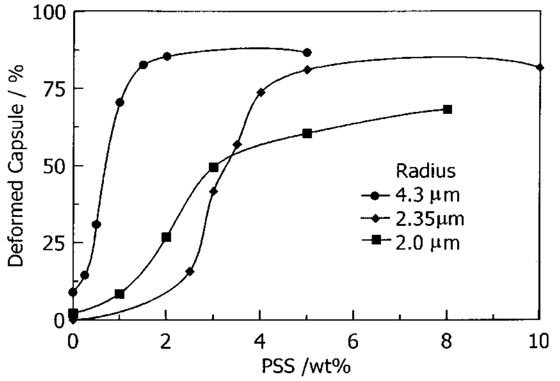


Fig. 6. Percentage of deformed capsules in dependence on the capsule radius. 10 layers PSS/PAH.

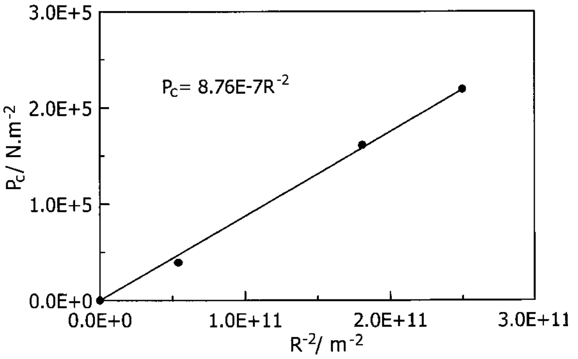


Fig. 7. Critical osmotic pressure in dependence on the inverse of the capsule radius square. 10 layers PSS/PAH.

critical pressure increased to 750 MPa (Fig. 4). It was concluded that the elasticity modulus slightly increased with increasing molecular weight of at least one of the polyelectrolyte layer components. At the present state of knowledge one can only speculate that with increasing molecular weight of PAH a more symmetric situation with regard to the PSS molecular weight is achieved. This could lead to a small increase of the elasticity modulus.

The results demonstrated that the PSS/PAH capsule walls represent a quite rigid material comparable to other plastic bulk materials. For instance, polycarbonate, chlorinated polyvinyl chloride, medium impact acrylonitrile-butadiene-styrene copolymer and cast rigid epoxy resin have an elasticity modulus of 490, 560, 500–580 and 650–780 Mpa [19], respectively. The numerous interactions between the polyanionic and polycationic groups SO_3^- and NH_3^+ are presumably responsible for the stiffness of the polyelectrolyte multilayer structure.

5 Conclusions

In this work we used the fact that polyelectrolyte capsules with walls as thin as a few nm can be made impermeable for polyelectrolytes and that that wall thickness and capsule diameter can be varied systematically. Thus, osmotic pressure differences between the capsule interior and the bulk can be established and deformations observed. It was found that there is a critical pressure difference which induce a shape transition from spherical shape to a cup shape and this transition occurs at a well-defined pressure difference P_c.

A theoretical model is provided which describes the dependence of this critical osmotic pressure P_c on the elasticity modulus of the multilayer and the geometric parameters of the capsule. The validity of the model is experimentally verified. This demonstrates the applicability of the macroscopic continuum mechanics approach to micron sized polyelectrolyte multilayer capsules. The elasticity modulus for the two-dimensional PSS/PAH polyelectrolyte complex obtained in this study was 500–750 MPa. It slightly depends on the molecular weight of PAH. This value is close to the elasticity of other bulk plastics. It is concluded that this reflects a high degree of local interactions between the polyanion and the polycation. Hence, the PE multilayer formed by means of electrostatic interactions of strong polyelectrolyte resembles a polymer glass rather than a rubber material. The observation of a defined critical pressure also indicates a narrow distribution of elasticity moduli between different capsules. We expect that the elastic properties depend on preparation parameters and on materials which can vary from other polymers to composites and inorganic materials, thus yielding large area to apply the technique. Studies are under way to explore other non-linear mechanical properties such as the rupture strength and the ability for plastic deformation of PE capsules.

We thank Dr. K.-H. Lerche, microparticles GmbH, Berlin, Germany, for the continuous supply of monodisperse soluble MF particles. C.G. thanks the DAAD and the Max Planck Society for the financial support. The work was partially supported by a grant from BMBF No. 03C0293A1.

References

1. D.D. Lewis, in *Biodegradable Polymers and Drug Delivery Systems*, edited by M. Chasin, R. Langer (Marcel Decker, New York, 1990).
2. J.P. McGee, S.S. Davis, D.T. O'Hagan, J. Control Release **34**, 77 (1995).
3. E. Donath, G. Sukhorukov, F. Caruso, S. Davis, H. Möhwald, Angew. Chem. Int. Ed. **37**, 2201 (1998).
4. G. Sukhorukov, E. Donath, H. Lichtenfeld, E. Knippel, M. Knippel, A. Budde, H. Möhwald, Col. Surf. A **137**, 253 (1998).
5. G. Sukhorukov, E. Donath, S. Davis, H. Lichtenfeld, F. Caruso, V. Popov, H. Möhwald, Poly. Adv. Tech. **9**, 759 (1998).
6. G. Sukhorukov, L. Dähne, J. Hartmann, E. Donath, H. Möhwald, Adv. Mater. **12**, 112 (2000).
7. L. Dähne, E. Donath, H. Möhwald, J. Am. Chem. Soc. (submitted, 2001).

8. S. Moya, G. Sukhorukov, M. Auch, E. Donath, H. Möhwald, J. Colloid Interf. Sci. **216**, 297 (1999).
9. F. Caruso, E. Donath, H. Möhwald, J. Phys. Chem. B **102**, 2011 (1998).
10. R. von Klitzing, H. Möhwald, Macromolecules **29**, 6901 (1996).
11. G. Sukhorukov, M. Brumen, E. Donath, H. Möhwald, J. Phys. Chem. B **31**, 6434 (1999).
12. R.P. Rand, A.C. Burton, Biophys. J. **4**, 115 (1964).
13. A. Yeung, E. Evans, Biophys. J. **56**, 139 (1989).
14. B.M. Dishcer, Y.-Y. Won, D.S. Ege, J.C.-M. Lee, F.S. Bates, E.E. Discher, D.A. Hammer, Science **284**, 1143 (1999).
15. E.A. Evans, Biophys. J. **13**, 941 (1973).
16. A. Voigt, H. Lichtenfeld, G. Sukhorukov, H. Zastrow, E. Donath, H. Bäumler, H. Möhwald, Ind. Eng. Chem. Res. **38**, 4037 (1999).
17. L.D. Landau, E.M. Lifshitz, *Course of Theoretical Physics*, Vol. 7, *Theory of Elasticity*, 3rd edn. (Butterworth-Heinemann, Oxford, 1997), p. 187.
18. A.V. Pogorelov, *Bending of Surface and Stability of Capsules* (American Mathematical Society, 1988), p. 77.
19. J.F. Shackelford, A. William, P. Juns, *Materials Science and Engineering Handbook*, 2nd edn. (CRC press, 1994), p. 521.