Young’s modulus of polyelectrolyte multilayers from microcapsule swelling

O. I. Vinogradova,1,2 D. Andrienko,1 V. V. Lulevich,1,2 S. Nordschild,3 and G. B. Sukhorukov3

1Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
2Laboratory of Physical Chemistry of Modified Surfaces, Institute of Physical Chemistry, Russian Academy of Sciences, 31 Lenskis Prospect, 119991 Moscow, Russia
3Max Planck Institute for Colloid and Interface Research, Golm 14424, Potsdam, Germany

(Dated: March 22, 2022)

We measure Young’s modulus of a free polyelectrolyte multilayer film by studying osmotically induced swelling of polyelectrolyte multilayer microcapsules filled with the polyelectrolyte solution. Different filling techniques and core templates were used for the capsule preparation. Varying the concentration of the polyelectrolyte inside the capsule, its radius and the shell thickness yielded an estimate of an upper limit for Young’s modulus of the order of 100 MPa. This corresponds to an elastomer and reflects strong interactions between polyanions and polycations in the multilayer.

PACS numbers: 46.70.De, 68.37.Ps, 81.05.Lg

I. INTRODUCTION

Molecularly thin polyelectrolyte multilayer films are composed of alternating layers of oppositely charged polyelectrolytes and are important for a variety of potential applications.1,2 Supported multilayer films are normally produced via layer-by-layer (LbL) adsorption of polyelectrolytes on a charged solid substrate. In the later case, the colloidal template can be dissolved to give so-called polyelectrolyte microcapsules.3 The shell of such microcapsules is nothing more than a free standing multilayer film. The free thin film geometry allows investigation of properties not accessible in the bulk or in supported films and helps to gain a better understanding of polyelectrolytes in general.

There have been a number of recent experimental studies of mechanical properties of thin multilayer films. First, by studying osmotically induced buckling of “hollow” (water inside) capsules immersed in a polyelectrolyte solution, the Young’s modulus was found to be above 1000 MPa, close to the plasticity of the bulk plastics.4 The second, more recent, approach is based on measuring the deformation of microcapsules under applied load using an atomic force microscope (AFM)10,11,12. This method yielded an estimate of the lower limit for Young’s modulus of the order of 1-10 MPa which corresponds to an elastomer.6 The reason for such a discrepancy between two approaches might be hidden in the assumptions of the models used to fit experimental data. The first model assumes that the shell is highly permeable for water, even on short timescales of the relaxation of buckling deformation. The second approach treats the shell as impermeable for water on short timescales, relying on the conservation of capsule volume for small deformations. The accuracy of existing experimental results does not allow to conclude which approach is more realistic.

In this paper we propose an alternative way to probe the elastic properties of a polyelectrolyte multilayer. The method is based on studying the swelling of microcapsules filled with a solution of a strong polyelectrolyte. The size of a swollen capsule depends on the Young’s modulus of the capsule shell. Fitting the experimental data to the prediction of a simple model yields Young’s modulus of the order of 100 MPa. We argue that our results give the upper limit of Young’s modulus. Taken together with recent AFM observations, this result leads to the conclusion that the mechanical behavior of a polyelectrolyte multilayer is that of an elastomer.

II. THEORETICAL MODEL

We consider a “filled” (polyelectrolyte solution inside) capsule immersed in a low molecular weight solvent (water in our case). The capsule swells due to excess osmotic pressure of the inner solution. The osmotic pressure of polyelectrolyte solutions is the sum of polymer and counterion contributions. However, in a salt-free solution the latter exceeds the osmotic pressure due to polymer itself by several orders of magnitude.10,11,12. The capsule shell is permeable to the solvent (on time scales larger than the characteristic diffusion time), but impermeable to the encapsulated polymer of high molecular weight. Then the solvent diffuses into the capsule until the elastic force of the stretched shell balances the osmotic pressure. We assume that the inner polyelectrolyte solution remains electroneutral, i.e. all counter ions due to polyelectrolyte dissociation remain in the capsule interior. A similar assumption was used in Ref.6.

We also assume that, for small relative deformations, the response of the capsule shell is elastic. If the capsule swells from the initial radius r0 to a final radius r the energy of stretching of the shell is given by the elastic...
theory of membranes \[13\]

\[
G = 4\pi \frac{E}{1 - \nu} h (r - r_0)^2 ,
\]

(1)

where \(E\) is Young’s modulus, \(\nu\) is Poisson’s ratio \((\nu \approx 1/2)\), and \(h\) is the shell thickness \((h \ll r_0)\).

For a dilute solution of the inner polyelectrolyte, or, alternatively, small concentration \(n = N/V\) of counterions in the capsule, the osmotic pressure induced by the counterions reads

\[
\Pi = \varphi \frac{N}{V} k_B T.
\]

(2)

where \(N\) is the number of counterions and \(\varphi \leq 1\) is the osmotic coefficient, defined as the ratio of experimentally measured osmotic pressure \(\Pi\) to the ideal osmotic pressure of all counterions. The difference between these two values is due to a fraction of condensed counterions being bound to the polyelectrolyte chain and not contributing to the osmotic pressure \[14, 15, 16\].

The work done by the osmotic pressure \(\Pi\) to swell the capsule from radius \(r_0\) to \(r\) then reads

\[
A = \int_{V_0}^V \Pi dV = -3\varphi N k_B T \ln \frac{r}{r_0}.
\]

(3)

The equilibrium radius of the capsule is given by the minimum of the total energy \(F = G + A\), where \(\partial F/\partial r = 0\), giving

\[
r = \frac{1}{2} r_0 \left(1 + \sqrt{1 + \frac{3(1 - \nu)\varphi N k_B T}{4Eh r_0^2}}\right).
\]

(4)

To relate the number of counterions to the concentration of the polymer solution in the capsule before it swells, \(N_A\) is the Avogadro number. For a strong polyelectrolyte this number could be taken as 1, i.e. one counterion per monomer. Then

\[
N = N_A c V_0 = \frac{4}{3} \pi r_0^3 c N_A ,
\]

(5)

where \(c\) is the concentration of the polymer solution in the capsule before it swells, \(N_A\) is the Avogadro number. Substituting Eq. (5) into Eq. (4) one obtains

\[
r = \frac{1}{2} r_0 \left(1 + \sqrt{1 + \frac{2\pi r_0 (1 - \nu) c R}{h c E} \varphi RT}\right),
\]

(6)

where \(R = k_B T N_A\) is the universal gas constant. Equation (6) relates the size of the swollen capsule to the concentration of the inner solution, thickness of the capsule shell, and Young’s modulus.

Our model allows design of a swelling experiment. To determine the Young’s modulus, one can measure the deformation of the capsule as a function of concentration \(c\) and the shell thickness \(h\) and then fit the experimental data to Eq. (6).

III. EXPERIMENTAL

For an initial application of our approach we have chosen to study two types of capsules, characterized by different methods of encapsulation and templated on different cores. The first type are “filled” capsules prepared on manganese carbonate templates by a controlled precipitation \[8, 17\], i.e. by an assembly of the inner layer of polyelectrolyte shell by means of multivalent ions with the subsequent extraction of these ions and polymer release into the capsule interior. The second type of “filled” capsules were made from the “hollow” ones, templated on melamine formaldehyde particles, by regulating their permeability for high molecular weight polymers \[14, 15\].

As a polyelectrolyte for encapsulation we have chosen sodium polystyrene sulfonate (PSS). The behavior of this highly charged flexible polyanion in salt-free conditions has been studied both theoretically \[15\] and experimentally \[10, 11, 19, 20\]. The value of \(\varphi\) for PSS was found to range from 0.2 to 1 and suggests some condensation of counter-ions \[12, 17\].

A. Materials and Methods

1. Materials

The fluorescent dye Rhodamine B isothiocyanate (RBITC), monomers allylamine and 4-styrenesulfonic acid sodium salt hydrate (SS), shell-forming polyelectrolytes poly(sodium 4-styrenesulfonate) (PSS; \(M_W \sim 70,000\) g/mol) and poly(allylamine hydrochloride) (PAH; \(M_W \sim 70,000\) g/mol), and ethylenediaminetetraacetic acid (EDTA) were purchased from Sigma-Aldrich Chemie GmbH, Germany. Hydrochloric acid (HCl), acetone and sodium chloride (NaCl) were purchased from Riedel-de-Haën; Germany. The ionic initiator potassium persulphate (K\(_2\)S\(_2\)O\(_8\)) for the radical polymerisation and Y(NO\(_3\))\(_3\) were obtained from Merck GmbH; Germany. All chemicals were of analytical purity or higher quality and were used without further purification.

To produce labelled PSS for encapsulation we used a modification of a method published in Ref. \[21\]. First, labelled allylamine was made which was afterwards mixed with 4-styrenesulfonic acid sodium salt hydrate and then copolymerised radically. The allylamine was mixed with RBITC solved in ethanol. The mixture was stirred for four hours at room temperature. Afterwards SS was added in an amount corresponding to a label grade of about 200 monomer units each. Then K\(_2\)S\(_2\)O\(_8\) was added.
to this solution as an ionic initiator for the radical polymerization. The mixture was heated up to 80°C and was stirred for four hours in a nitrogen atmosphere. Afterwards it was centrifuged with a membrane which filters molecules with a molecular weight of 100,000 g/mol or more, and polydispersity was found to be $M_W/M_N \sim 1.8$. The remaining PSS was chipped into small parts and washed with ethanol until no more colour could be observed in the filtrate.

Suspensions of monodispersed weakly cross-linked melamine formaldehyde particles (MF-particles) with a radius of $r_0 = 2.0 \pm 0.1 \mu m$ were purchased from Micro particles GmbH (Berlin, Germany).

The manganese carbonate template (MnCO$_3$) was prepared by a mixing method described in Ref. [22]. Briefly, acidic manganese sulfate solution ($9 \times 10^{-3}$ M, pH=4.2 adjusted by sulfuric acid) was added at 1:1 volume ratio to $2.25 \times 10^{-3}$ M NH$_4$HCO$_3$. Then the stirred mixture was aged at 50°C for 16 hours. The resulting MnCO$_3$ particles had a spherical shape with a radius of $1.85 \pm 0.2 \mu m$ and $2.5 \pm 0.2 \mu m$.

Water used for all experiments was purified by a commercial Milli-Q Gradient A10 system containing ion exchange and charcoal stages, and had a resistivity higher than 18MΩ/cm.

2. Methods

Capsule Preparation

Two different approaches have been exploited for preparation of filled capsules.

FIG. 1: Scheme illustrating the preparation of “filled” microcapsules of the first type.

The preparation of filled capsules of the first type consisted of several steps (Fig.1). The first step (Fig.1a) was surface controlled precipitation of labeled PSS (by complex formation with Y$^{3+}$ ions) on the surface of MnCO$_3$. By varying the number of precipitated layers we were able to tune the surface density for adsorbed layers, and, therefore, the number of PSS molecules precipitated on MnCO$_3$ particles. In our experiments we prepared samples with 20-80 layers of adsorbed labeled PSS, which should lead to a surface density, $\rho$, in the range from $5 \times 10^{-5}$ to $2 \times 10^{-4}$mol/m$^2$. These values were calculated by assuming that the surface density for a monolayer is constant, and that the amount of adsorbed PSS grows linearly with the number of deposited layers [15, 24]. As a result, each capsule contained up to a few pg of PSS, depending on the template size and amount of assembled layers. With such a method, the concentration of encapsulated polyelectrolyte is approximately equal to $c = 3\rho/r_0$. The MnCO$_3$ particles were dissolved in $\sim 1$mol/L HCl after assembling of 7 layers in order to facilitate the process of core removal since shells with a thickness of more than 10 layers prevent ion penetration [25]. Core dissolution led to the formation of “double shell” structured capsules (Fig.1c). The inner shell formed by the PSS/Y$^{3+}$ complex was not stable and was decomposed either by metal ion complex agents (EDTA) or in salt solution. Yttrium ions were gradually expelled out of the outer stable shell formed by PSS/PAH while PSS molecules were released into the capsule interior (Fig.1d). Then the polyelectrolyte capsules were covered additionally with a number of layers varied in the interval from 1 to 13 to tune the final shell thickness, which, as a result, varied from 4 to 10 PSS/PAH bilayers.

The “filled” capsules of the second type were made from pre-formed “hollow” capsules [26]. The original “hollow” capsules were produced by a standard LbL assembly of 4 PSS/PAH bilayers on MF particles. MF-particles coated with PSS/PAH multilayers were dissolved in $\sim 1$mol/L HCl and MF-oligomers were removed by washing, as described in [27]. Then the encapsulation of polymer included several steps. (Fig.2). The original “hollow” capsules (Fig.2a) were exposed to acetone/water mixture (1:1) to make the polyelectrolyte multilayer permeable for high molecular weight polymer [8], and the PSS molecules were added to the mixture. The permeable state of the capsule shell allows the polymers to penetrate inside (Fig.2b). During the encapsulation process the PSS concentration was increased gradually to avoid an osmotic collapse of the microcapsules [8]. The initial concentration was 1g/L, and was doubled every hour. When the required concentration was reached, the mixture was diluted with water and the multilayer shells were assumed to return to an impermeable state (Fig.2c). After washing in pure water the capsules contain polymer solution (Fig.2d). With such a method, the concentration of encapsulated polyelectrolyte (before swelling) is approximately equal to the final concentration in the bulk.
3. Confocal Laser Scanning Microscopy.

To scan the capsule shape and to measure the concentration of PSS inside the capsules we used a commercial confocal microscope manufactured by Olympus (Japan) consisting of the confocal laser scanning-unit Olympus FV 300 in combination with an inverted microscope Olympus IX70 equipped with a high resolution 100-oil immersion objective. The excitation wavelength was chosen according to the label Rhodamine (543 nm). The z-position scanning was done in steps of 0.2 µm. The diameters of the swollen capsules were determined optically with an accuracy of 0.4 µm. Concentration measurements were performed via the fluorescence intensity coming from the interior of the PSS containing capsules. In this case we assumed that fluorescence is directly proportional to PSS concentration and used a calibration curve of fluorescence intensity of free polymer in the bulk solution. The measured concentration was then recalculated to the initial concentration inside unswollen capsules.

IV. RESULTS AND DISCUSSION

The 3D confocal scanning showed that the capsules filled with PSS have spherical form. It should be noted that immediately after the preparation the capsule sizes were close to the size of the templates used for their preparation. The capsules swell for at least several days before reaching their equilibrium size, so that all the measurements of the radius of the swollen capsules were performed 2 weeks after filling with PSS. Fig. 3 (top) shows a typical confocal fluorescence image of the swollen capsules. The fluorescence intensity suggests a uniform concentration in the capsule’s interior. The bright interior of the capsules did not change with time, and there was no fluorescence signal from water. This proves that the capsules are in the impermeable state. Typical fluorescence intensity profiles along the diameter of the capsules are presented in Fig. 3 (bottom). We note that the level of fluorescence from the wall is higher than from the interior, which could be connected with some adsorption of the inner polyelectrolyte [17].

The size of the swollen capsules was determined as an average of 6-10 capsules. The variability in size of the similarly prepared capsules was always within the error of optical measurements. We found that the “filled” capsules are always larger than the original colloidal template, and that their radius depends on the size of the original template, the number of the bilayers in the shell, and the amount of encapsulated polyelectrolyte. These observations are consistent with our theoretical model.

Fig. 4 illustrates the typical dependence of equilibrium radius on the shell thickness. Here, the results for the first type of “filled” capsules (MnCO₃ template) filled with PSS solutions of different concentrations, and made on the particles of the same size $r_0 = 1.85 \pm 0.2$ µm are given. It was previously found [3, 28] that the thickness of a PSS/PAH bilayer is in the range of 3-5 nm. Here to evaluate the thickness of the shell with a known number of PSS/PAH bilayers we use the average value of 4 nm, as before [5, 7]. The radius of the swollen capsules decreases with the shell thickness and is larger for the capsules with higher concentration of the inner polyelectrolyte solution. We fitted these experimental results to Eq. (6) taking the combination of Young’s modulus and the osmotic coefficient $E/\varphi$ as a fitting parameter and obtained the value of $E/\varphi \sim 200$ MPa for both curves presented in Fig. 4. One can see that the predictions of the model are indeed confirmed by experiment, and the continuum mechanics approach is applicable for a molecularly thin multilayer film.

The dependence of the equilibrium radius on the concentration of the inner polyelectrolyte, both the fitting curves and the experimental data, are shown in Fig. 5. Here we present data both for the capsules of the first (MnCO₃ template) and the second (MF template) types. The capsules are made on the templates of different size $r_0 = 2.5 \pm 0.2$ µm and $r_0 = 2.0 \pm 0.1$ µm, correspondingly. The shell was always composed by four PSS/PAH bilayers. From the fit of experimental data we have ob-
FIG. 4: Radius of the swollen capsule made on the MnCO$_3$ template of radius 1.85 µm as a function of the shell thickness. Two concentrations are shown: 0.16 mol/L (squares) and 0.32 mol/L (circles). Fitting (solid curves) corresponds to $E/\varphi \sim 200$ MPa.

One reason for such a decrease could be connected with a partial dissociation of the PSS, while our model assumed that it is fully dissociated. One also cannot exclude that some of the counter-ions might condense on the polyelectrolyte shell. Besides that, a portion of counter-ions could escape from the inner polyelectrolyte solution to the outer solvent, reducing the osmotic pressure difference. Such a possibility was not included in our model. All these effects (also ignored in Ref. [5]) will effectively lead to smaller values of the Young’s modulus.

Thus, our results strongly support the results of previous AFM studies implying that we are dealing with an elastomer. In other words, the value of Young’s modulus of the polyelectrolyte multilayer falls in the range characteristic for cross-linked rubbers. Such a mechanical behavior is probably due to strong interaction between polyanions and polycations in the multilayer. Our model also shows that the final permeability of the shell to water is very important for the stabilization of the microcapsules, increasing the threshold of the buckling transition.

V. CONCLUSION

We have provided a theoretical model, which relates Young’s modulus, shell thickness, capsule radius and concentration of the inner polyelectrolyte solution. The validity of the model was experimentally verified, and confirms the applicability of the macroscopic continuum mechanics approach to polyelectrolyte multilayer microcapsules. Young’s modulus of the molecularly thin polyelectrolyte multilayer was found to be of the order of 100 MPa. This represents the upper possible value for Young’s modulus and is close to the elasticity of an elastomer. Such a value reflects a high degree of local interactions between polyanions and polycations. Hence, mechanically at small deformations the polyelectrolyte multilayer resembles a cross-linked rubber material.

One can conclude that, taking into account realistic values of the osmotic coefficients for PSS solutions, Young’s modulus $E$ found in our swelling experiment is of the order of 100 Mpa. This value is confined between the values found in the osmotic buckling experiment and recent AFM results and requires further comments.

We remark and stress that current study gives the upper possible value of Young’s modulus. In reality, the excess osmotic pressure could be smaller than estimated from the known concentration of polyelectrolyte chains.

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VI. ACKNOWLEDGEMENTS

We acknowledge the support of the Alexander von Humboldt Foundation through a research fellowship (DA) and a Sofja Kovalevskaja award (GBS). We are grateful to I.L. Radtchenko for help with polyelectrolyte encapsulation, and to Y. Fedutik for MnCO$_3$ synthesis. M. Deserno, C. Holm, and V. Khrenov are thanked for helpful discussions. We also thank R. G. Horn for valuable remarks on the manuscript.

[1] Decher, G. Science 1997, 277, 1232-1237.
[2] Yoo, D.; Shiratori, S.; Rubner, M. Macromolecules 1998, 31, 4309-4318.
[3] Sukhorukov, G. B.; Donath, E.; Lichtenfeld, H.; Knippel, E.; Budde, A.; Mohwald, H. Colloids Surfaces A 1998, 137, 253-266.
[4] Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S.; M"ohwald, H. Angew. Chem. 1998, 37, 2202-2205.
[5] Gao, C.; Donath, E.; Moya, S.; Dudnik, V.; Mohwald, H. Eur. Phys. J. E 2001, 5, 21-27.
[6] Shackelford, J. F.; William, A.; Juns, P. Materials Science and Engineering Handbook, 2nd ed.; CRC press, 1994.
[7] Lulevich, V. V.; Andrienko, D.; Vinogradova, O. I., submitted (cond-mat/0306737).
[8] Lulevich, V. V.; Radtchenko, I. L.; Sukhorukov, G. B.; Vinogradova, O. I. J. Phys. Chem. B 2003, 107, 2735-2740.
[9] Lulevich, V. V.; Radtchenko, I. L.; Sukhorukov, G. B.; Vinogradova, O. I. Macromolecules 2003, 36, 2832-2837.
[10] Takahashi, A.; Kato, N.; Nagasawa, M. J. Phys. Chem. 1970, 74, 944-946.
[11] Wang, L.; Bloomfield, V. A. Macromolecules 1990, 23, 804-809.
[12] Barrat, J. L.; Joanny, J. F. Adv. Chem. Phys. 1996, 94, 1-66.
[13] Landau, L. D.; Lifshitz. Theory of elasticity. Course of theoretical physics; Butterworth-Heinemann: Oxford, 1995; Vol. 7.
[14] Stevens, M. J.; Kremer, K. J. Chem. Phys. 1995, 103, 1669-1690.
[15] Micka, U.; Holm, C.; Kremer, K. Langmuir 1999, 15, 4033-4044.
[16] Liao, Q.; Dobrynin, A. V.; Rubinstein, M. Macromolecules 2003, 36, 3399-3410.
[17] Radtchenko, I. L.; Sukhorukov, G. B.; Leporatti, S.; Khomutov, G. B.; Donath, E.; Mohwald, H. J. Colloid Interface Sci. 2000, 230, 272-280.
[18] Sukhorukov, G. B.; Antipov, A. A.; Voigt, A.; Donath, E.; Mohwald, H. Macromol. Rapid Commun. 2001, 22, 44-46.
[19] Essafi, W.; Lafrun, F.; Williams, C. E. J. Phys. II France 1995, 5, 1267-1275.
[20] Essafi, W.; Lafrun, F.; Williams, C. E. Eur. Phys. J. B 1999, 9, 261-266.
[21] D"ahne, L.; Leporatti, S.; Donath, E.; M"ohwald, H. J. Am. Chem. Soc. 2001, 123, 5431-5436.
[22] Gaponik, N.; Radtchenko, I. L.; Gerstenberger, M. R.; Fedutik, Y. A.; Sukhorukov, G. B.; Rogach, A. L. Nano Letters 2003, 3, 369-371.
[23] Dudnik, V.; Sukhorukov, G. B.; Radtchenko, I. L.; M"ohwald, H. Macromolecules 2001, 34, 2329-2334.
[24] Radtchenko, I. L.; Sukhorukov, G. B.; M"ohwald, H. Colloids Surfaces A 2002, 202, 127-133.
[25] Petrov, A. I.; Gavryushkin, A. V.; Sukhorukov, G. B. J. Phys. Chem. B 2003, 107, 868-875.
[26] Lvov, Y.; Antipov, A. A.; Mamedov, A.; M"ohwald, H.; Sukhorukov, G. B. Nano Letters 2001, 1, 125-128.
[27] Sukhorukov, G. B.; Donath, E.; Davis, S.; Lichtenfeld, H.; Caruso, F.; Popov, V. I.; M"ohwald, H. Polym. Adv. Tech. 1998, 9, 759-767.
[28] Estrela-Lopis, I.; Leporatti, S.; Moya, S.; Brandt, A.; Donath, E.; Mohwald, H. Langmuir 2002, 18, 7861-7866.