Melting of PDADMAC/PSS Capsules Investigated with AFM Force Spectroscopy

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ABSTRACT: We investigate the temperature dependency of the elastic constants of polyelectrolyte multilayers made from poly(diallyldimethylammonium chloride) (PDADMAC) and poly(styrenesulfonate) (PSS) by measuring the stiffness of individual hollow polyelectrolyte multilayer capsules in water using AFM force spectroscopy. Statistical analysis of the deformation data of the capsule ensemble combined with continuum mechanical modeling allows quantifying changes in the deformation characteristics and respective changes in the Young's modulus of the wall material. Our results show that the Young's modulus of the wall material decreases from the regime of 100 MPa to the order of MPa above 35 °C. This transition is reversible when returning to room temperature. The modulus becomes dependent on the deformation rate for high temperature, while it is not rate-dependent for low temperature. Therefore, we conclude that the wall material undergoes a melting process from a glassy to a viscoelastic fluid state. At the same time, a shrinking of the capsules is observed, which we explain qualitatively with surface tension effects. We discuss the implications of this finding in comparison with other multilayer systems and discuss novel strategies for shape control in PE multilayer systems based on these effects.

Introduction

Artificial capsule systems of colloidal dimensions have caught considerable attention during the past years: Microcapsules can be used to protect sensitive agents or to achieve control of their release and are therefore used in various applications, especially in life sciences (drug delivery, cosmetics, food design). From a basic science point of view, microcapsules of micron dimensions and submicron wall thickness can serve as model systems for their more complex biological counterparts like virus capsids, bacterial shells, or cell walls. For both aspects, mechanical properties of the capsules are of key importance since they govern stability under external forces (compression, shear, etc.), compliance, and indirectly also the adhesion behavior. Therefore, an understanding of shell mechanics and the underlying physicochemical mechanisms, which is in the center of this paper, is essential for optimizing capsule properties.

Within artificial capsule systems, polyelectrolyte multilayer capsules (PEMs) are widely used due to their versatility in terms of composition and shape. PEMs are prepared by template-assisted self-assembly: Colloidal particles are in a first step coated with a polyelectrolyte multilayer by alternating adsorption of positively and negatively charged polyelectrolytes from aqueous solution, also known as electrostatic layer-by-layer self-assembly[1] (see ref 2 for an overview of this technique). Subsequently, the particles are dissolved under conditions that do not dissolve the multilayer. The resulting hollow capsule's shape is determined by the template particle, while the wall is formed by the multilayer and thus can be tuned in its thickness and composition on the molecular scale.[3] The mechanical properties of PEMs have been in the center of several studies using micropipet,[4] osmotic pressure induced shape changes,[5,6] or force spectroscopy using atomic force microscopy (AFM),[7,8] which we also use in this study. Typically, regarding the fact that the polyelectrolyte multilayers contain a significant amount of water, surprisingly high Young's moduli larger than 100 MPa are found for the most widely used systems, poly(allylamine) (PAH)/poly(styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC)/PSS. This suggests, together with the slow self-diffusion[9] and the high degree of plasticity in the deformations,[4,5] a glassy nature of the wall material at room temperature. Therefore, one expects that temperature can have a pronounced effect on the mechanical properties of the multilayers, which we investigate here for the system PSS/PDADMAC. For this system, previous studies of some of the authors have shown that incubation at temperatures higher than or equal to 35 °C results in drastic changes in the capsule morphology.[10,11] Similar, although less pronounced, effects were previously found also for the PAH/PSS system by Leporatti and coworkers.[12] Upon heating, the capsules are reducing their diameter and increase their wall thickness. These changes are irreversible when returning to room temperature. Temperature-dependent studies on solid supported multilayers were performed by Helm and coworkers, who have found an increase in film thickness and roughness upon increasing the temperature during the buildup of multilayers made from PAH/PSS.[13]

We have investigated here the changes in the mechanical properties accompanying this shrinking. Our strategy is to perform statistical analysis of the defor-

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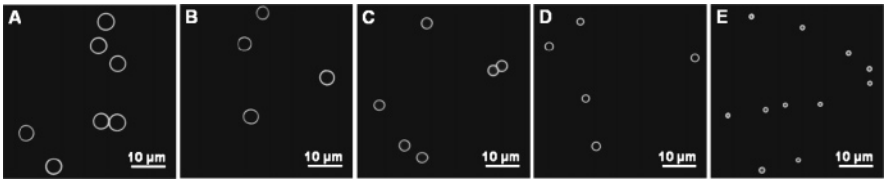

Figure 1. Confocal laser scanning microscopy images of $(PDADMAC/PSS)_4$ polyelectrolyte capsules made on 4.55 μm silica cores before (A) and after incubation for 20 min at 45 (B), 50 (C), 55 (D), and 70 °C (E).[10]

mation data obtained from many single-capsule deformation experiments which yields statistically relevant data. We use continuum mechanical modeling to derive information on the elastic constants of the wall material from the deformation data. This is especially important here, since geometric effects on the capsule stiffness due to the capsule shrinking have to be separated from effects of changes in the material constants. We find that indeed the Young's modulus of the material decreases by 2 orders of magnitude above 35 °C and shows a dependency on the rate of deformation, which is absent in the room temperature state. We discuss this finding in terms of a melting process of the wall material and offer a semiquantitative explanation for the observed shrinking effect. Further, we discuss implications of this finding for novel approaches to control shape and mechanics in these systems. We believe that, although obtained for a capsule system, our findings are relevant as well for solid supported multilayers of the same or structurally similar types as described below.

Experimental Section

Materials. Capsule Preparation. Poly(diallyldimethylammonium chloride) (PDADMAC, $M_w \sim 200-350$ kDa), sodium poly(styrenesulfonate) (PSS, $M_w \sim 70$ kDa), Rhodamine 6G, hydrofluoric acid, and sodium chloride were purchased from Sigma-Aldrich (Germany). All chemicals were used without further purification except for PSS, which was dialyzed against Milli-Q water (M_w cutoff 20 kDa) and lyophilized. Monodisperse silica particles with a diameter of 4.55 μm were obtained from Microparticles GmbH (Berlin, Germany).

The water used in all experiments was prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity higher than 18 MΩ·cm.

Hollow polyelectrolyte capsules were fabricated using the layer-by-layer (LbL) technique as described previously;[3] see ref 14 for details on the process. The alternating adsorption of PDADMAC and PSS onto the surface of silica particles was carried out from 2 mg/mL polyelectrolyte solutions containing 0.5 M NaCl, starting with PDADMAC since silica particles are negatively charged within the used pH range of 4−6. After 15 min of adsorption, the particles were washed three times with water in order to remove nonadsorbed polyelectrolyte molecules using centrifugation. After deposition of eight layers, the silica cores were dissolved in 0.1 M hydrofluoric acid. The resulting hollow capsules were washed again twice with 0.1 M HF to remove the remaining SiF_6^{2-} ions. Afterward, the hollow shells were thoroughly washed with water until the pH reached a value of 6.

For the temperature treatment 100 μL of the aqueous capsule suspensions were incubated at the respective temperature for a certain time in a Lauda Ecoline RE 112 thermostat. In the case of stiffness measurements at variable temperature, the heating was carried out in situ.

Experimental Methods. a. Confocal Laser Scanning Microscopy (CLSM). Optical images of polyelectrolyte capsules in water were obtained using a Leica TCS SP confocal scanning system (Leica, Germany) equipped with a 100×/1.4−0.7 oil immersion objective. To visualize the polyelectrolyte shells, Rhodamine 6G was used as fluorescent label for the capsules by mixing the sample suspension with the dye. For the determination of the capsule diameter the fluorescence profiles of at least 50 capsules were analyzed and their diameters averaged.

b. Scanning Force Microscopy (SFM). SFM measurements were performed in air at room temperature using a Nanoscope III Multimode SFM (Digital Instruments Inc.) operating in tapping mode. The samples were prepared by placing a drop of the sample solution onto a freshly cleaved and with poly(ethylene imine) (PEI) precoated mica substrate. Afterward, they were dried at room temperature. The wall thickness of the shells was measured from the flat regions in the capsule profiles. At least 20 profiles of different capsules were analyzed, and the average thickness difference between the mica surface and the lowest region of the shells was averaged.[12]

c. Atomic Force Microscope (AFM): Force Spectroscopy. Force spectroscopy measurements were carried out under water using commercial AFM setups: A MFP3d (Asylum Research) was used for the room temperature measurements of untreated and annealed capsules and a Nanowizard setup (JPK Instruments, Germany) was used for the measurements at variable temperature. In both setups, the AFMs were placed on top of inverted optical microscopes (Olympus IX71 for the first and Zeiss Axiovert 200 for the second setup) such that fluorescence microscopy could be used to locate and monitor the capsules during the experiment. For the measurements, the colloidal probe technique was used:[15,16] colloidal particles (glass beads, diameter ≈ 30−50 μm, Polyscience Inc.) were attached to tipless cantilevers (MicroMash, Spain) with two component epoxy glue (UHU Plus endfest 300, UHU GmbH & Co.KG, Germany) using a micromanipulator (Suttner Instrument Co.). The spring constants of the cantilevers were determined using the thermal noise method[17] or the Sader method.[18] Both methods agreed within 10%, and values of the spring constants were in the range reported by the manufacturer. During the experiment, individual capsules were compressed, and both the force and the deformation of the capsule were measured, as described in more detail in ref 7. We limited ourselves to capsule deformations on the order of the capsule wall thickness to avoid plasticity and effects due to the permeation of the solvent through the capsule membrane as discussed in ref 19.

Results and Discussion

First, we have investigated previously heated capsules at room temperature and compared them to nonheated capsules with respect to their morphology and their mechanical properties. Capsules were annealed for 20 min at 45, 50, and 55 °C. Figure 1 shows the morphological changes before and after the heating process. The diameter of the capsules could be determined by confocal microscopy, and the wall thickness could be determined for a part of the samples by SFM of dried capsules. This was only possible for capsules that collapsed as a result of the drying process, which was not the case for capsules that were annealed at $T > 55$ °C, which did not completely collapse upon drying. The respective values for diameter and wall thickness are listed in Table 1. In agreement with previous findings which are discussed in detail elsewhere,[10] the shrinking of the capsule diameter is accompanied by an increase of the wall thickness, such that the total volume of the wall only shows a minor reduction. Thus,

Table 1. Diameter, Wall Thicknesses, and Stiffness of the Untreated Capsules and the Capsules Incubated at 45, 50, and 55 °C, Measured at Room Temperature

capsule	diameter [μm]	wall thickness [nm]	stiffness [pN/nm]
initial	4.57 ± 0.22	21.21 ± 1.03	223.6 ± 121.3
45 °C, 20 min	3.8 ± 0.19	29.33 ± 1.21	586.9 ± 163.2
50 °C, 20 min	2.99 ± 0.18	44.6 ± 2.33	874.9 ± 150.78
55 °C, 20 min	2.23 ± 0.18		2603.0 ± 707.7

the material is mainly changing molecular conformation and dissolution effects are not responsible for the shrinking.

Figure 2a shows typical force deformation curves of individual capsules from the different batches: After heating, the capsule mechanics is drastically altered at room temperature. Figure 2b shows statistical results on the initial slope (further denoted as capsule stiffness) of the force deformation characteristics for deformations on the order of the wall thickness. For each batch at least 35 capsules were investigated. The mean values of capsule stiffness are listed in Table 1. The stiffness of the capsules was found to increase by more than a factor of 10 as a result of the heat treatment. In previous work, we have investigated the influence of capsule radius and diameter on the capsule stiffness, and we have found that the analytical Reissner[20,21] solution of shell deformation can be used to describe the scaling of the capsule stiffness c with these parameters and derive quantitative data on the shells mechanical parameters.[22,23] The stiffness c (the ratio of deformation force

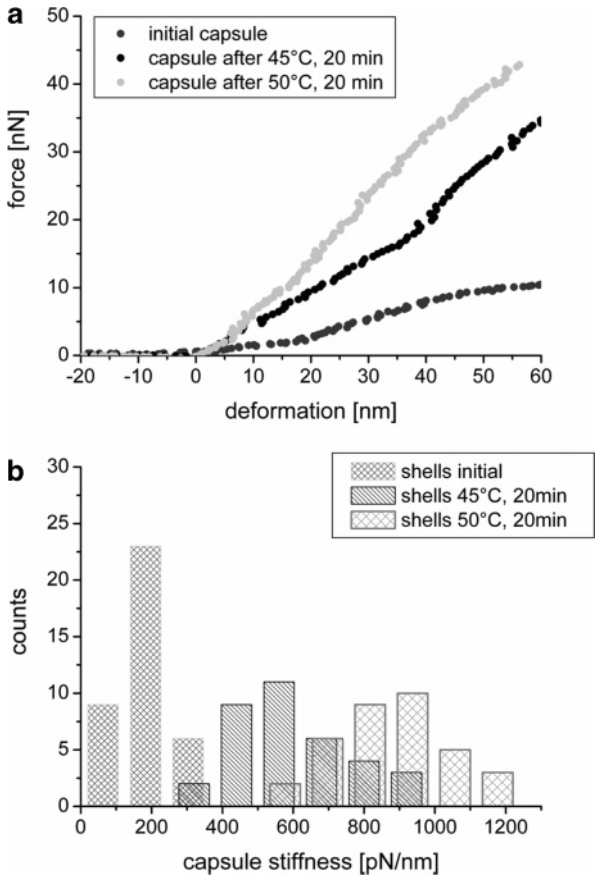

Figure 2. (a) Force deformation curves of an initial capsule and incubated capsules (45 and 50 °C for 20 min), probed at room temperature. (b) Histogram of the spring constants of initial capsules and incubated capsules (20 min at 45 and 50 °C).

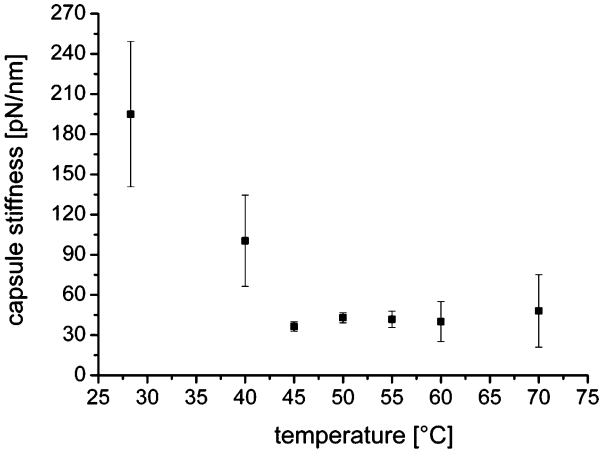

Figure 3. In situ experiment shows during the heating process the stiffness of the shells (spring constant) is dramatically decreasing with the temperature. For each data point five individual microcapsules were probed.

F and deformation d in the linear deformation regime) scales with the shell wall thickness h, radius R, Young's modulus E, and Poisson ratio ν like

$$c = \frac{F}{d} = \frac{4}{\sqrt{3(1-\nu^2)}} \frac{Eh^2}{R} \tag{1}$$

Therefore, the rescaled stiffness c^* is proportional to the material properties E and ν by rescaling with a factor R/h^2.

$$c^* = cR/h^2 \tag{2}$$

One finds a rescaled stiffness c^* of 1.1 GPa for untreated capsules and 0.6 GPa for capsules treated at 50 °C (the thickest ones for which h and R are available). Therefore, the main reason for the increase in stiffness by a factor of 4 between these batches is not a change of the materials deformation properties, but rather a pure geometry effect. Indeed, the material properties show a slight decrease of the Young's modulus around 30% for the annealed capsules, which is however close to the accuracy of the measurement as discussed below. Assuming a Poisson ratio of 1/3 and taking into account the capsule wall thicknesses measured in dry state as well as the independently measured swelling ratio upon transfer from dry state to water, the capsule Young's modulus is 45.5−102.4 MPa. The large uncertainty stems here from the thickness increase of the multilayers in water as compared to the dry state, which was found to scatter between a factor of 2−3. These values are in between those reported in the literature from Gao[5] for capsules and for solid supported multilayers from Salomäkki.[24]

The situation is completely different when measurements are not carried out at room temperature, but *during* the annealing process. For the stiffness measurements shown in Figure 3, the temperature of a batch of capsules in water was increased stepwise, and at each temperature at least five individual capsules were measured to get a statistically relevant overview of the development of capsule stiffness as a function of temperature. One observes a marked reduction of capsule stiffness for temperatures above 35 °C which plateaus off at higher temperatures, showing slight stiffening for the highest temperatures. As described

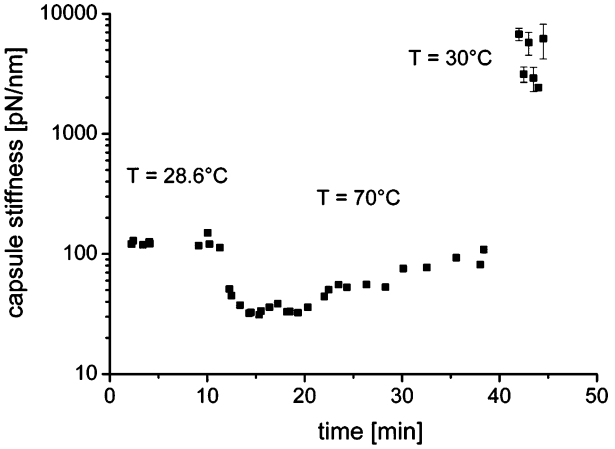

Figure 4. Development of the spring constant under temperature treatment. Starting at room temperature (28.6 °C) one single microcapsule is probed over 30 min at 70 °C. Afterward, the capsules were cooled to 30 °C. There are shown the average spring constants of six individual capsules.

above, c can only be related to material properties if one takes into account the geometry. Therefore, in the measurement shown in Figure 3, two counteracting effects are superimposed: On one hand, the capsules are shrinking and increasing their wall thickness which increases their stiffness; on the other hand, the material properties (mainly the Young's modulus E, since the Poisson ratio only has a minor impact on c) are changing such that the total stiffness decreases. While it is difficult to separate the two opposing effects during temperature increase, it is simple to do so for the case of temperature reduction, since here the geometry is fixed and only the material parameters change. Therefore, we have monitored a full temperature cycle (heating and cooling) for an individual capsule. The stiffness data are shown in Figure 4 as a function of time for a temperature increase from room temperature to 70 °C and subsequent cooling back to room temperature. Upon heating, one can clearly identify the drop in c, which is however followed by reentrant increase of c. This is expected since the geometrical changes have not reached their final state on that time scale but rather the capsules are progressively shrinking at 70 °C, which explains this reentrant stiffness increase. Upon cooling, a drastic increase in c by almost 2 orders of magnitude is observed. Since the geometry does not change in this step, the stiffness change can directly be translated into changes in the Young's modulus E, assuming that the Poisson ratio remains unchanged. This yields an increase of the Young's modulus from 1 to 102 MPa upon cooling. This result is well compatible with a transition from a highly viscoelastic polymeric melt to a glassy state. As well, if the experiment is carried out such that the temperature is cycled several times between room temperature and a temperature above the transition temperature, one finds that the stiffness changes are reversible (data not shown).

Another important aspect of the deformation properties of the material is the deformation rate dependency of the elastic constants. To probe this aspect, we have varied the rate of the deformation and its impact on the capsule stiffness. Figure 5 shows the dependency of c normalized to the stiffness value at the slowest speed of deformation for several capsules at RT and above the transition temperature. The normalized stiffnesses are collapsing onto two master curves: At room temperature, the elastic constants are not depending on deformation rate; in contrast, above the transition temperature, the elastic constants become rate dependent, showing an increase with speed by a factor of 7 (suggesting a square root dependency). The material becomes viscoelastic.

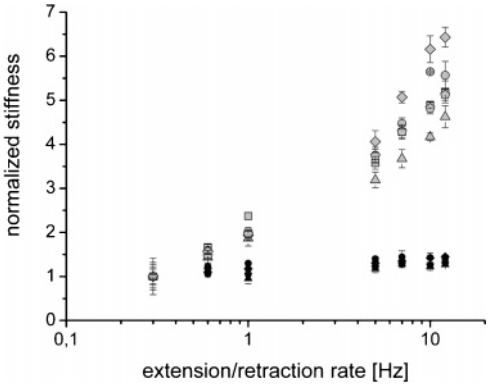

Figure 5. Normalized stiffness of capsules at room temperature (dark spots) and at 70 °C (empty spots) depended on the extension and retraction rate of the piezo.

Regarding these changes in the mechanical properties, the rearrangements that are observed upon annealing could be driven by surface tension effects: If capsules can rearrange their shape due to a sufficiently high mobility of the polyelectrolytes forming the multilayers, one would expect that the system can minimize its surface tension contribution to the total energy $E = 4\pi\sigma R^2$ by shrinking. The speed with which this rearrangement can take place should in the overdamped system depend on the viscosity of the multilayer. The viscosity can be dominated either by the activation energy ΔE to break bonds between the complex forming polyelectrolytes or by entanglements between the polyelectrolytes. We believe that the first scenario is more realistic since the changes are taking place above a characteristic temperature, which is in favor of an activation energy dominated phenomenon. Another indirect hint in this direction is the fact that very similar effects (correlation of shrinking and softening) were found for PAH/PSS upon increase of salt concentration at room temperature.[22] Indeed, these findings could in light of our novel results be interpreted as signs of a lowering of the energy barrier ΔE for this system upon increase of salt concentration and thus a salt-induced lowering of the transition temperature, which was previously predicted by Cohen-Stuart and co-workers.[25] Salomäkki and co-workers have found similar effects for salt during the layer buildup.[24] Looking at flat layer systems, it is remarkable that several solid supported multilayers show a much lower Young's modulus on the order of MPa or even below[26,27] and much higher self-diffusion,[27] typical for a viscoelastic polymeric melt. In contrast, all systems for which capsule formation was so far successful are in the range of elastic constants reported here.[5,22,24] It seems that glassiness of the material is a prerequisite for the multilayer to survive the dissolution process which is accompanied by transient osmotic stresses and for the success of this concept of capsule formation.

So far, there does not exist a simple rule to predict the melting temperature of a polyelectrolyte multilayer, based on a single parameter like for example the linear charge density of the involved polyelectrolytes. The examples of nonglassy multilayers mentioned above

have linear charge densities comparable to the ones that are nonglassy; however, the fact that they are less hydrophobic could play a role in making the systems nonglassy. In any case this requires more deep investigations in which the molecular structure of the multilayer forming polyelectrolytes is varied in a systematic fashion to obtain structure−property relationships for these systems. Heuristically, the growth mode of the multilayers can be used to get a hint of the state of the material: Polyelectrolyte multilayers can show linear or exponential thickness as a function of the number of deposited layers. The glassy examples are all showing a linear growth characteristic. For the exponential growth, a high mobility of the polyelectrolytes forming the multilayers is necessary and was also experimentally found.[28,29] This suggests that these materials are nonglassy. Indeed, in a recent study of Salomäkki and co-workers,[24] it was demonstrated that the type of salt present during the multilayer assembly could lead to a switching from glassy to molten state, which was accompanied by a change in the growth characteristic from linear to exponential.[30] Similar observations concerning the correlation of growth mode and mobility of the polyelectrolytes forming the multilayer were made by Hübsch and co-workers[29] and by von Klitzing.[31] Therefore, the selection of materials can be simplified by using the massive amount of data on the growth characteristics which is available in the literature.

This finding offers interesting perspectives for shape control of polyelectrolyte membranes and capsules, since they are highly deformable and viscoelastic at high temperatures and can be frozen by cooling back to room temperature. As well, when incubated at high temperature, they will change their shape such that it is minimizing their surface energy, which means symmetric shrinking in the case of spherical objects, but in the case of nonspherical objects (e.g., cylindrical shapes), more complex shape changes are expected. As the time scale of these rearrangements is such that it can be experimentally well controlled, various shapes can be achieved by freezing the system at intermediate stages, as it was previously demonstrated for the spheres by Köhler and co-workers.[10,11] Rather than plain annealing, the effects of shear or osmotic pressure in the high temperature state could offer novel perspectives to generate capsule systems with variable and also anisotropic shape. Both strategies are currently explored and will be published separately.

Conclusion

In this paper, we show evidence that the wall material of hollow polyelectrolyte multilayer capsules made from PSS and PDADMAC undergoes a glass−melt transition around 35 °C as measured by AFM force spectroscopy. We conclude this from the fact that the stiffness of polyelectrolyte multilayer capsules undergoes a drastic decrease above this temperature which is reversible upon cooling. Using analytical models on the deformation mechanism of the capsules, we derive a change of the Young's modulus of the material from the 100 MPa regime to the MPa regime from the measured stiffness data, which is consistent with expectations on a glassy or viscoelastic molten material. In the high-temperature regime, the elastic constants become speed dependent, while they are independent of deformation speed for a temperature below 35 °C.

The change of the elastic constants of the material is accompanied by a shrinking of the capsules and a simultaneous increase of their wall thickness. While this phenomenon was already previously reported, the mechanics measurements give a hint on the possible mechanisms: While in the glassy state the system is frozen and cannot shrink to minimize its surface energy, it can do so above the glass transition temperature. Upon returning to room temperature, these shape changes are irreversible because the material freezes again. This result suggests that other shape changes could be achieved in the nonglassy state, e.g., by osmotic pressure or shear, which could be frozen in by returning to room temperature. From the discussion of our findings in comparison with other capsule and flat multilayer systems, we propose that the growth characteristic can serve as a heuristic criterion to distinguish glassy from nonglassy multilayers.

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