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Mechanical properties of liquid-filled shellac composite capsules

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This paper describes the mechanical properties of thin-walled, liquid-filled composite capsules consisting of calcium pectinate and shellac. In a series of experiments we measured the deformation of these particles in a spinning drop apparatus. For different pH-values we studied the elastic properties of these particles and compared the obtained results with the mechanical response measured by squeezing capsule experiments. In analogy to these experiments, we also investigated liquid-filled unloaded calcium pectinate capsules without the addition of shellac. The deformation properties of these experiments and the surface Young moduli were in good agreement. Furthermore we investigated the liquid-filled calcium pectinate and the composite capsules by NMR microscopy. These experiments allowed investigations of the membrane thickness and the kinetics of membrane growing. Additional characterizations by stress controlled small amplitude surface shear experiments of similar composed gel layers provided coherent results for the surface Young modulus.

1. Introduction

Microcapsules are commonly used in pharmaceutical or medical processes for transporting drugs or encapsulation of organic cells.[1–3] Liquid-filled microcapsules consist of a liquid core surrounded by a thin, semi-permeable membrane.[1,3] The main functions of these membranes are the successful encapsulation, transportation and controlled release of the capsule content into the external environment. These properties depend crucially on the nature of the membrane structure.[4] Thereby, it is important that the thin-walled and therefore fragile capsules are not going to break up when it is not supposed to.

On grounds of the limited stability it is very interesting to study and characterize the deformation of different liquid-filled capsules under the onset of mechanical forces. In recent years different techniques have been proposed to measure the capsule deformability.[5–7] Large capsules, like in this case, can be investigated in a spinning-drop apparatus.[8–10]

The modification and the selective adjustment of the mechanical properties and therefore the capsule stability are required for each individual capsule system and depend on the desired application process. Thus, the creation of a composite system by adding further components to a common capsule system is a simple method to achieve different quality characteristics.

Based on these observations, we systematically studied the pH dependent deformational and elastic properties of single liquid-filled calcium pectinate and composite capsules under the action of centrifugal forces in a spinning-drop apparatus.

For comparison purpose, we also investigated these particles in squeezing-capsule experiments.[10–12] Whereas calcium pectinate beads have already been studied in detail,[13–16] investigations of liquid-filled calcium pectinate capsules are still not explored.

NMR imaging techniques were used to measure the size and the membrane thickness of the capsules in order to obtain information on the gelation process. In recent studies, NMR imaging was already used for measuring the membrane thickness of alginate microcapsules, as well as the relaxation times and structure of microbeads.[17–19]

In the last years, particularly in biological and biomedical fields, hydrogels have found many applications such as biomembranes, biosensors or carriers for controlled delivery of drugs, proteins and cells.[20,21] Hydrogels consist of three dimensional networks, containing hydrophilic polymers or monomers, which can absorb and retain aqueous fluids up to thousand times of their dry weight. In general, hydrogels which are originated from cross-linking polymer chains offer a better toxicological profile due to the absence of residual monomers.[22]

For this purpose, several polymers were used for their valuable specific characteristics, such as biocompatibility, biodegradability and a total lack of toxicity. All these outstanding properties are important because they can satisfy

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biomedical and biological requirements such as protection of active agents from extreme environments and temporal or site specific release of drugs.[23]

Owing to the fact that the gelation can be carried out under very mild conditions, we used pectin membranes. These polysaccharide materials, originating from plant cell walls, are natural, linear, heterogeneous and biodegradable.[16]

Because of its valuable properties, pectins have already been widely used in the food industry as thickening, stabilizing, gelling and film forming agent. Other applications appear in the pharmaceutical industry as a carrier material for different controlled-release systems.[15,24,25]

Pectin has a very complex structure that depends on both its source and the extraction process. This macromolecule contains predominantly linear chains of mainly 1 → 4 linked α-D-galacturonic acid residues.[13,14] These chains are regularly interrupted by some rhamnogalacturonan segments that combine galacturonic acid residues and α-L-rhamnopyranose by a 1 → 2 linkage.[26] The galacturonic acids of the backbone have carboxyl groups which are partially methyl-esterified in nature. Others groups have reacted with ammonia to produce carboxamide groups.[13,16,25] The degree of amidation (DA) and the degree of esterification (DE) are important parameters to classify pectins.

Rigid three-dimensional ionotropic gels can be formed with low methoxy pectins (with $DE < 50\%$) by ionic interactions with many divalent cations. These ions, acting as ionic bridges, can cross-link the galacturonic acid chains. This process is simplified and described in the so-called "egg-box-model".[24,25,27]

Amidated macromolecular compounds generally behave like low-ester pectins but need less calcium for gelling. This is caused by the introduction of amide groups into the pectin molecules, which tend to make the pectin less hydrophilic, increasing the tendency to form gels.[15]

As a stabilizing additive for the composite capsule system an aqueous shellac solution was used. Shellac is a natural, nontoxic, physiological harmless and biodegradable polymer that is obtained from the resinous secretion of the female insect *Kerria lacca*, a parasitic insect found on trees in Southeast Asia. The major components of shellac are aleuritic acid, shellolic acid and jalaric acid.[28,29]

Shellac, like other polymers with carboxyl groups, is practically insoluble in acidic and pH-neutral aqueous solutions. However, it is possible to prepare aqueous solutions of alkali salts.[30]

Due to its interesting properties, such as thermo plasticity, cohesiveness, insulating ability and pH dependent solubility, shellac is commonly used as an enteric coating material in pharmaceutical applications. It is also approved in the food industry as an additive for coatings of confectionaries and nutritional supplements.[31,32]

2. Experimental section

2.1 Materials

Amidated pectin (Pectin amid AU-L 027/09) was provided by Herbstreith & Fox KG, Germany. The aqueous ammoniacal shellac solution (SSB Aquagold, 25% solid content, pH ≈ 7.5) was provided by SSB Stroever Schellack Bremen, Germany. $CaCl_2 \cdot 2H_2O$ and anhydrous glycerol ($\geq 99\%$) were purchased from Merck Chemicals, Germany. All chemicals were used without further purification.

2.2 Capsule preparation

Liquid-filled calcium pectinate and shellac composite capsules were prepared by extrusion, using a simple one-step process.[33,34] An aqueous pectin solution of 0.8 %wt was used for the preparation of all different capsule types. The aqueous ammoniacal shellac solution was used as the second component for forming the composite membranes.

For preparing the cross-linking aqueous Ca^{2+}-solution, 2.0 g of $CaCl_2 \cdot 2H_2O$ salt was firstly dissolved in 100 ml double distilled water. Afterwards the obtained electrolyte solution was diluted with 100 ml of anhydrous glycerol, which was added to improve the mechanical properties and the density for facilitating the dropping in. In addition, this solution also served as the softening-agent for the shellac composite capsules. For comparing both systems, the same cross-linking solution was used, containing 50 %vol glycerol and a concentration of 1.0 %wt calcium chloride. In order to investigate the pH-dependence of the mechanical properties, cross-linking solutions with different pH values (pH 2, 3 and 4) were prepared from the stock solution by adding some drops of concentrated hydrochloric acid.

In the production process, droplets of the cross-linking solutions were added dropwise through a high-precision metering syringe into a cylindrical glass cell filled with 30 ml of an aqueous 0.8 %wt pectin solution. For preparing the composite capsules, the glass cell was filled with 30 ml of an aqueous 0.8 %wt pectin solution containing 20 %vol shellac.

A capsule membrane was formed instantly around each droplet as soon as the two liquids came into contact. The faster diffusion of the smaller sized calcium cations in comparison to the large charged macromolecules leads to cross-linking processes in which intermolecular junction zones are formed between the divalent calcium ions and the negatively charged carboxyl groups of the amidated pectin molecules.[14] Induced by these diffusion processes the gel membrane grows along the flux direction of the calcium ions.[35] In the case of the production of the composite capsules, the positively charged hydrogen ions induce the precipitation of the shellac and finally lead to the formation of a composite material composed of calcium pectinate and shellac.

In order to avoid the aggregation of the prepared capsules, the pectin solution was constantly moved by using a magnetic stirrer. A dropping height of 4 cm was used to ensure the formation of spherical capsules. After a gelation time of two minutes the capsules were separated, filtered and washed with double distilled water.

After isolating the capsules they were transferred into a 1.0 %wt $CaCl_2 \cdot 2H_2O$ solution with the aim of stabilizing the gel membranes and completing the polymerization process.[36]

The produced liquid-filled pectinate and composite capsules exhibit diameters of about 1–3 mm and membrane thicknesses in the range between 170 μm up to 320 μm.

2.3 Three dimensional gel layer preparation

Plane calcium pectinate and shellac composite gels were prepared in order to investigate the influence of shellac precipitation and the pH value on the gel strength and the degree of cross-linking. For establishing comparability between the capsule membranes and the flat gel layers, the concentrations were adjusted to obtain the same gel composition.

The plane gel layers were formed by adding 3.0 ml of an aqueous solution containing 0.8 %wt pectin or 0.8 %wt pectin and 20 %vol shellac into a small and flat plastic vessel. For initiating the polymerization 2.0 ml of an aqueous 1.0 %wt $CaCl_2{\cdot}2H_2O$ solution with the desired pH value was carefully poured over the already existing solution in the plastic vessels. After 15 min, the obtained gel layers were taken out of the plastic vessels and were kept in 1 %wt $CaCl_2{\cdot}2H_2O$ solution with the aim of stabilizing the gel layers and completing the gelation process.

The produced pectinate and composite gel layers had thicknesses of approximately 4 mm. After one day the gels were characterized by rheological measurements using dynamic strain sweep tests to determine the linear visco-elastic range. Dynamic frequency sweep tests provided detailed information on the gel strength and the degree of cross-linking in dependence of the pH value.

For these experiments we used a Rheometrics Fluid Spectrometer (RFS2) from Rheometrics Scientific with plate/plate geometry. The upper titanium-plate had a diameter of 25 mm.

2.4 Spinning capsule experiments

A commercial spinning drop video tensiometer SVT 20 from Dataphysics was used to study the deformation properties of calcium pectinate and composite capsules. A schematic drawing of such an apparatus is shown in Fig. 1. For this kind of measurements the capsule was assumed to be spherical in its quiescent state. The investigated particles were filled with an incompressible liquid with density ρ_i (aqueous $CaCl_2$ solution) and were enclosed by an infinitely thin-walled elastic membrane. First of all, the capsule had to be placed inside the cylindrical rotating tube, which was filled with the outer phase. For this fluid we used another incompressible liquid (FC 70: perfluorotripentylamine and isomers), with density ρ_e, whereas $\rho_e > \rho_i$.

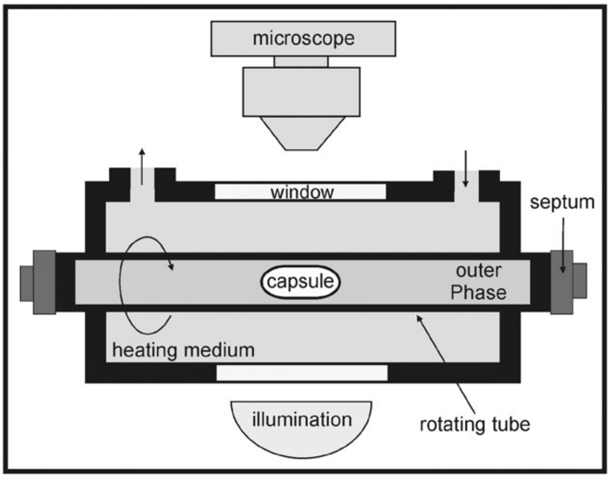

Fig. 1 Schematic drawing of the spinning-drop tensiometer.[9,10]

After closing and insertion of the tube in the measuring cell, the deformation experiment was started by rotating the cylindrical tube around the principal axis with steady angular velocity ω. Because of the high centrifugal forces, the capsule was centered on the tube axis. At experimental conditions an initially spherical capsule could be deformed by increasing the angular velocity of the glass tube. The shape and size of the capsules was recorded by means of a CCD-camera and the monitored deformation was calculated automatically. The deformation D of the capsules calculated by the results of the contour analysis was defined as:[8,9]

$$D = \frac{(l - b)}{(l + b)}, \tag{1}$$

where l and b denotes the length and width of the capsule profile. A convenient way to express the result is to compute the difference between the final (D) and initial (D_0) deformation of the capsules:

$$\Delta D = D - D_0. \tag{2}$$

A detailed description of the theory of spinning capsule experiments is represented in ref. 8 and 9. In the linear visco-elastic regime, the capsule deformation can be described by:

$$D = -\Delta\rho\omega^2 a^3 \frac{(5 + \nu_S)}{16E_S}. \tag{3}$$

In this equation, $\Delta\rho$ denotes the density difference between the internal and external liquid, a is the radius of the capsules in the quiescent state, ω describes the angular velocity of tube rotation, E_S is the surface Young modulus and ν_S the surface Poisson ratio.

Eqn (3) predicts that the capsule deformation depends on the ratio $(5 + \nu_S)/16E_S$ and that it is not possible to obtain the values of the surface Young modulus and the surface Poisson ratio from the spinning capsule experiments separately. However, D is not very sensitive to the exact value of the surface Poisson ratio when the latter varies between -1 and 1. On ground of this reason, eqn (3) can approximately be used to calculate membrane elastic properties from spinning capsule experiments.

A major advantage of the spinning capsule experiments is caused due to the fact that the single capsule is floating in another liquid and therefore it has no contact to solid surfaces. So the particles are investigated in a non-contacting manner.

2.5 NMR imaging measurements

The membrane thicknesses of liquid-filled calcium pectinate and shellac composite capsules, prepared at different pH values, were determined by NMR imaging. For this purpose, a common spin-warp sequence[37] was used on a 14.1 T Chemagnetics Infinity Plus 600 spectrometer, equipped with a microimaging accessory. The NMR images were obtained with a field of view (FOV) of 6 × 6 mm^2, a slice thickness of 100 μm and a spatial resolution of 23 × 23 μm^2. Echo-time and repetition-time were set to 100 ms and 2 s, respectively.

For each image acquisition, one capsule was placed in a 5.0 mm NMR tube at the interface between two liquids consisting of 1 %wt $CaCl_2$ aqueous solution at the top and tetrachloroethylene at the bottom. Since the highest point of the interface was located near the center of the tube, the capsule was pushed to a stable position at the edge of the tube. A small amount of $CuSO_4$ was added to the water solution. This allowed a short repetition time since the paramagnetic Cu^{2+} shortened the relaxation times of the surrounding water.

The thickness of the membranes was determined by measuring the distance between its inner and outer edge at several positions in a contour plot of the image. This was performed with images of five different capsules for each capsule type and the results were averaged.

2.6 Squeezing capsule experiments

In order to investigate the mechanical stability of liquid-filled capsules, we squeezed single calcium pectinate and shellac composite capsules between two parallel plates.[11,12] For these experiments we used an Advanced Rheometric Expansion System (ARES) from TA Instruments with plate/plate geometry. The upper titanium-plate had a diameter of 25 mm. The resulting normal force was measured by a Force Rebalance Transducer with Normal Force (FRTN 1) with a measuring range between 20 mN to 20 N.

We used a force gap test to compress the capsules from 2.5 mm to 0.05 mm during 360 s with a logarithmic decreasing compression rate. During the compression experiments we measured the gap and the normal force at the upper plate simultaneously. Each measurement was repeated three times. Then we evaluated the mean values and the standard derivation. The normal force (in mN) *versus* the gap distance (in mm) was plotted as compression curves.[38,39] From these data we obtained, first of all, qualitative differences of the mechanical capsule stability. The surface Young modulus could be calculated by a quantitative analysis of the obtained force–displacement curves using different methods of resolution.[12,40,41]

In earlier studies we applied this technique to investigate the mechanical stability of ionotropic alginate beads[42] as well as liquid filled calcium alginate capsules with different gelation times.[10]

3. Results and discussions

3.1 Influence of shellac on the capsule deformation in dependence of the pH value

On grounds of the limited stability of liquid-filled capsules it is very interesting to study and characterize their deformation properties under the onset of mechanical forces. Large capsules, as characterized in this study, can be investigated in a spinning-drop apparatus. For calcium pectinate and pectinate–shellac composite capsules, we measured the capsule deformation as a function of the centrifugal force in dependence of the pH value.

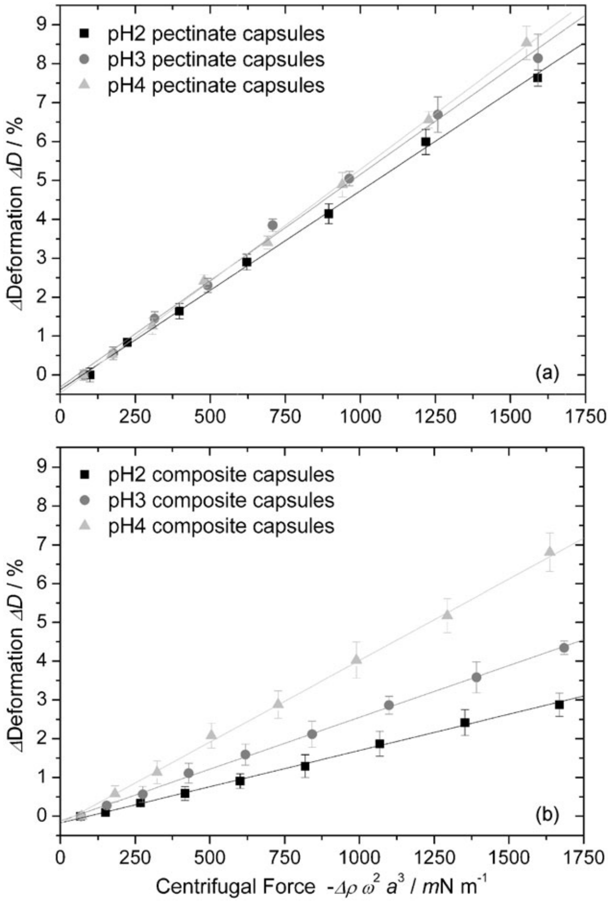

Fig. 2 Linear fitting of the deformability of liquid-filled calcium pectinate (a) and pectinate–shellac composite (b) capsules for different pH values.

As shown in Fig. 2, the capsule deformation increases linearly as a function of the centrifugal force for all capsules and each pH value. In a series of experiments we observed that liquid-filled calcium pectinate capsules are softer and therefore easier to deform than the composite capsules of the same composition, independent of the pH value.

At 1500 mN m^{-1} we obtained deformations of about 8% for capsules made of pure pectin. In comparison, pectinate capsules containing shellac showed only deformations between 2.5% to 6% depending on the pH value. By incorporation of the solid shellac particles in the calcium pectinate gel, the membrane became more solidified. Hence, we can conclude that these capsule membranes are stronger and stiffer than those formed from pure pectin solution.

It is interesting to note that for the composite capsules the pH value shows an effect on the deformation properties of the capsule membranes, whereas the capsule deformation as a function of the centrifugal force seems to be unaffected by the acid concentration for pure calcium pectinate capsules. This observation can be explained by the precipitation of shellac at low pH. The lower the pH value the higher the amount of embedded shellac particles in the capsule membrane. Contrary, the pH value plays a minor role for the deformation of capsules formed without shellac.

Eqn (3) makes it possible to calculate the surface Young moduli of all different capsule types by carrying out a linear regression, also shown in Fig. 2. Because it is not possible to obtain the surface Young modulus and the Surface Poisson

Table 1 The surface Young moduli E_S for the different gels measured with spinning and squeezing capsule technique, assuming a Poisson ratio of 2/3, in comparison to the two-dimensional shear modulus μ_S measured with rheological frequency sweep tests

Pectinate gel	pH 2	pH 3	pH 4
Spinning capsule	6.9 N m^{-1}	6.5 N m^{-1}	6.2 N m^{-1}
Capsule squeezing	8.8 N m^{-1}	7.9 N m^{-1}	7.4 N m^{-1}
Rheology	10.2 N m^{-1}	9.9 N m^{-1}	10.5 N m^{-1}
Composite gel	**pH 2**	**pH 3**	**pH 4**
Spinning capsule	18.9 N m^{-1}	13.3 N m^{-1}	8.9 N m^{-1}
Capsule squeezing	20.1 N m^{-1}	14.8 N m^{-1}	11.8 N m^{-1}
Rheology	20.8 N m^{-1}	15.4 N m^{-1}	13.3 N m^{-1}

ratio from the spinning capsule experiments separately, a value for the Poisson ratio has to be assumed.

In this study, two different methods are used for calculating the surface Young moduli which both depend on the Poisson ratio. If the Poisson ratio is cleverly selected, the deviation of the surface Young moduli of both methods can be minimized. In this case, a Poisson ratio of 2/3 affords the best consistence. By using this Poisson ratio, we obtained for the capsules formed by pectinate in the absence of shellac a surface Young modulus of about 6.5 N m^{-1}. For the pectinate capsules with added shellac we measured increasing values between 9 N m^{-1} and 19 N m^{-1} with decreasing pH (Table 1).

3.2 Membrane thicknesses measured by NMR microscopy

In order to investigate the membrane thicknesses of the different capsules, NMR microscopy was used. Fig. 3 shows the dependence of the membrane thickness as a function of the pH value for the pectinate and the pectinate–shellac composite capsules. We did not observe significant changes in the membrane thickness for the calcium pectinate capsules as a function of the acid concentration. This observation is in good agreement with the spinning capsule results.

In comparison to pure pectinate capsules, the composite capsules showed slight differences in the membrane thickness depending on the pH value. In the regime of low pH values the membrane was considerably thinner. This observation leads to the assumption that the precipitation of shellac particles reduces the membrane growth.

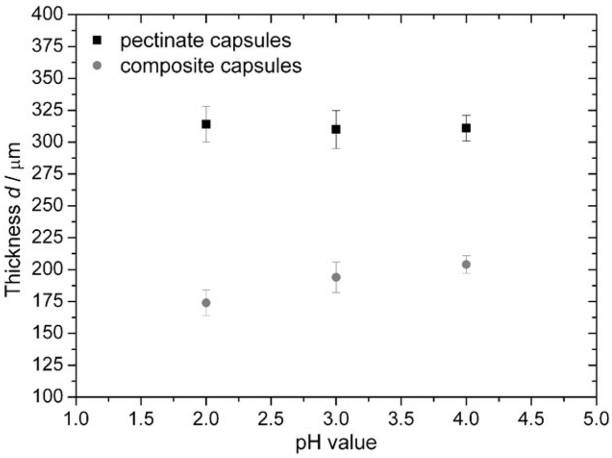

Fig. 3 Membrane thickness as a function of the pH value for calcium pectinate (black squares) and composite capsules (gray circles).

Additionally, the composite membranes showed lower membrane thicknesses than the pure pectinate capsules. For permitting a direct comparison between the two different capsule types in view of their membrane thickness, Fig. 4 shows two examples of NMR microscopy images. Both slices are 100 µm thick, perpendicular to the NMR sample tube, whose inner diameter is 4.24 mm. Fig. 4a shows a pure calcium pectinate capsule at pH 2 and a membrane thickness of 318 ± 9 µm. If 20 %vol shellac is added, the thickness decreases drastically to a value of 176 ± 11 µm.

It is interesting to note that the contrast of the pectinate shellac composite capsule in Fig. 4b is higher than the contrast of the pure pectinate capsule in Fig. 4a to the surrounding water phase. This might be caused by a shorter transverse relaxation time (T_2) due to a reduced amount of water or a higher fraction of bounded water in the composite gel membrane.

A possible explanation for the different thicknesses might be the inhibition of the calcium ion diffusion by the solid shellac particles. Fig. 5 tries to deliver insight into a feasible formation mechanism of the different capsule membranes. On the left hand side of Fig. 5 it is described that capsules formed without the addition of shellac are mainly formed by the diffusion of the calcium ions from the core of the droplet into the environmental pectinate solution. The hydrogen ions can

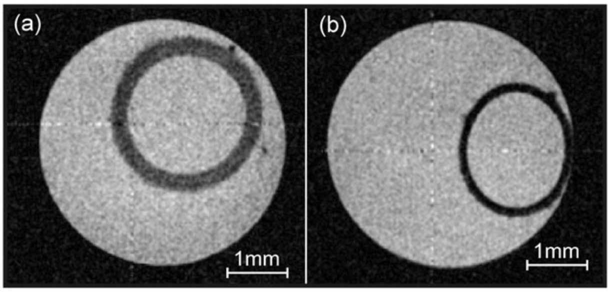

Fig. 4 NMR images of two capsules: (a) calcium pectinate capsule and (b) pectinate composite capsule at a pH value of 2.

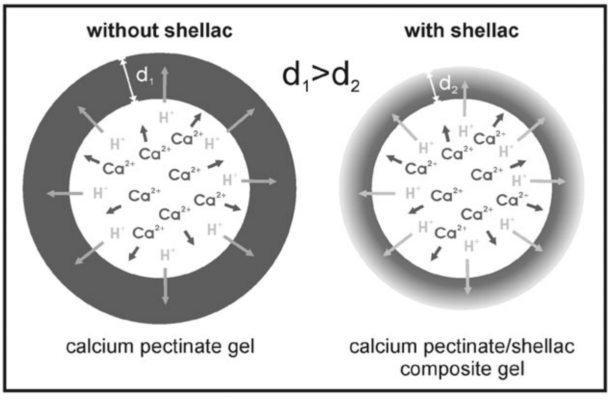

Fig. 5 Schematic drawing of the gel formation and diffusion disturbance mechanism of pure calcium pectinate and pectinate/shellac composite capsules (dark gray layer: cross-linked calcium pectinate gel; light gray: precipitated shellac).

also diffuse into the pectinate solution and favor the gel formation by increasing the gelling speed and additional cross-linking.

In the case of the capsules made of the pectinate–shellac mixture, the faster diffusion of the hydrogen ions as a consequence of their smaller size leads to the precipitation of shellac particles which reduce the flux of calcium ions. These diffusion obstacles might be the reason why the membrane thickness of the composite capsules was reduced.

Further processes, in addition to the inhibition of the diffusion, such as reduced reorientation of the pectinate chains or ionic interactions caused by positive charge preponderance might also have an effect on the calcium pectinate gel formation in the presence of additional shellac.

The observed membrane thicknesses coincide perfectly with the different capsule sizes. Capsules formed from pure pectin solutions showed diameters in the range between 2.6 mm and 2.8 mm while pectinate capsules containing shellac were considerably smaller with sizes between 1.9 mm and 2.1 mm.

Hence, we can conclude that the results for the pure pectinate capsules are in good agreement with the mechanical properties. Similar deformation values are explainable by similar membrane thicknesses. The dependence of the pH value for composite capsules on the deformation is also consistent with variations of the membrane thickness. Membranes prepared with additional shellac seem to be thinner but stiffer and the capsules become smaller in their diameter than capsules without shellac. Furthermore, at the lowest pH value the highest amount of precipitated shellac leads to the strongest inhibition of calcium ion diffusion and therefore to the thinnest membranes. In the regime of large pH values the amount of precipitated shellac is very small and the created membranes can grow without hindrance.

3.3 Mechanical properties of single capsules measured by squeezing-capsule experiments

A series of different capsules was also investigated in squeezing capsule experiments. This method is particularly useful to explore qualitative differences in the mechanical stability of the pectinate and the composite membranes. Typical results of such measurements are summarized in Fig. 6 in terms of force–displacement curves. In comparison, it is evident that the composite capsules are more stable than the pure pectinate capsules, because a higher external force is needed to obtain the same compression. These results are consistent with the data obtained from the spinning capsule measurements.

The earlier increase of the compression curves of the composite capsules can be traced back to the fact that these capsules are smaller in their diameter and therefore smaller displacements lead to higher deformations. However, the increase itself is still steeper and therefore the composite material shows stronger mechanical properties.

For obtaining quantitative results, an analysis of the force–displacement curves in Fig. 6 by eqn (4) provides the two-dimensional Young modulus E_S in the range of small deformations under point loading close to the pole by a simple linear fit, shown in the subplots with a magnification of the displacement range:[40]

$$F = \frac{4E_S d}{a\sqrt{3(1-\nu_S^2)}} d_D. \quad (4)$$

In this equation, d denotes the membrane thickness, a is the radius of the capsule, d_D is the displacement of the capsule pole, F is the measured force, E_S is the surface Young modulus and ν_S the surface Poisson ratio for which a value of 2/3 was assumed. Eqn (4) only holds in the regime of very small deformations. As mentioned before, other methods of resolution by dissolving numeric calculations are presented in further citations.[12,41]

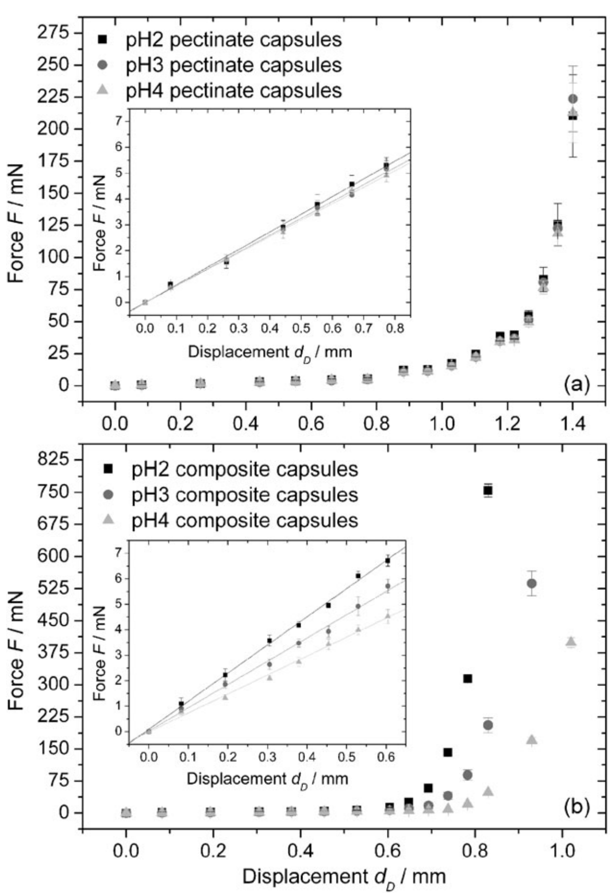

Fig. 6 Force–displacement curves of two different types of liquid-filled capsules: (a) calcium pectinate and (b) shellac composite capsules.

For the capsule squeezing experiments we obtained for the pectinate capsules surface Young moduli in the range between 7.4 N m^{-1} and 8.8 N m^{-1}. For the composite capsules we measured, depending on the pH-value, significantly higher moduli in the range between 11.8 N m^{-1} and 20.1 N m^{-1}. For comparison purposes, Table 1 shows the calculated two-dimensional Young moduli.

3.4 Mechanical properties of gel layers measured by rheological frequency sweep tests

In further experiments we performed rheological frequency sweep tests on three-dimensional gel layers. First, dynamic strain sweep tests were performed in order to investigate the

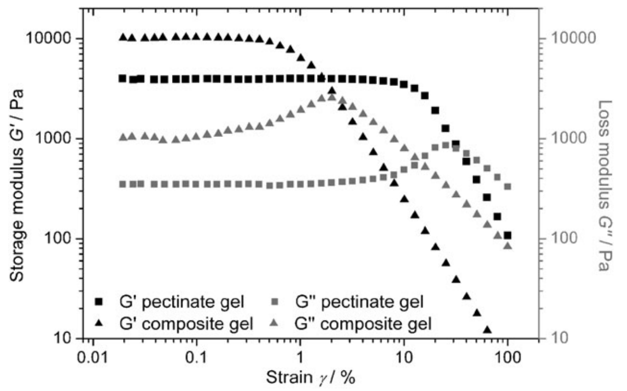

Fig. 7 Dynamic strain sweep tests of two different gel types at a pH value of 3 with the same composition as the comparable capsule membranes ($\omega = 2$ rad s^{-1}): pure pectinate gels (black symbols) and pectinate/shellac composite gels (gray symbols).

linear visco-elastic range. As shown in Fig. 7 a shear strain of 0.3% is still in the linear visco-elastic range for the pectinate and the composite capsules prepared at pH 3. This small deformation limit was, therefore, chosen as the parameter for the adjacent rheological frequency-sweep tests.

Relevant results of frequency tests are summarized in Fig. 8. It is easy to see that the storage modulus is much larger than the loss modulus for all measured gel types. The flat gel layers were mainly characterized by elastic properties. The slow increase of the storage modulus and the slow decrease of the loss modulus as a function of the angular frequency points to the existence of relaxation processes which can be induced by the release of entrapped entanglements or the opening of ionic junctions. These phenomena of temporary cross-linking are not very pronounced and the gels mainly exhibit rubber-elastic properties.

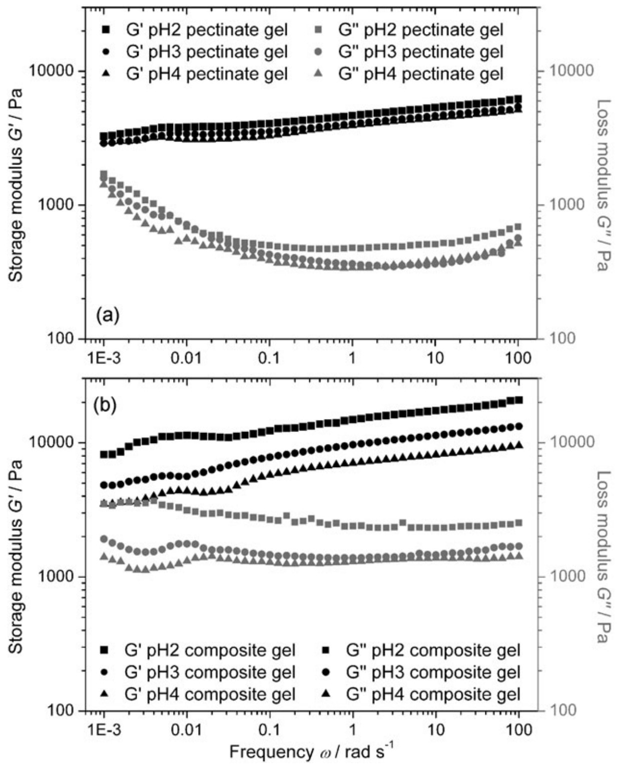

Fig. 8 Frequency sweep tests of two different pectinate gel types at different pH values with the same composition as the comparable capsule membranes (gap = 4.5 mm): (a) pectinate and (b) pectinate/shellac composite gels.

If the measured three-dimensional storage moduli are multiplied with the thickness of the gel layers, we obtain the two-dimensional shear moduli μ_S of these visco-elastic gels. For the different pectinate gels, surface shear moduli of about 10.0 N m^{-1} were calculated, while values in the range between 13.3 N m^{-1} and 20.8 N m^{-1} were obtained for the composite gels in dependence on the pH. A lower pH value results in stiffer and stronger gel layers with improved mechanical properties compared to the pure pectinate gels. Contrary, a higher pH value leads to the formation of softer gels (Table 1).

In general, the surface shear modulus should be lower than the Young modulus, as demonstrated in eqn (5).[9]

$$E_S = 2\mu_S(1 + \nu_S). \tag{5}$$

As in this case, the assumption of a surface Poisson ratio of 2/3 should lead to a more than three times higher Young modulus. It is evident that the results of the rheological measurements are in the same order of magnitude than the spinning as well as the squeezing capsule results. Therefore, they are a factor of three higher than expected in general.

Two different reasons should be named as possible causes for this observation. First of all, in spite of using gelling-solutions of the same concentration as used for the capsule preparation, in order to obtain gels with the same composition, three-dimensional gels with somewhat different gel structures and therefore different properties may be formed. If the gels are not completely identical in their structure and composition, this might be a possible explanation in comparison to the measured capsule membranes with spinning and squeezing capsule technique. In addition, spreading and wetting processes can occur at the metal surface of the plates so that the rheological results may be influenced by these processes.

4. Conclusion

In this paper we systematically studied the mechanical properties of thin-walled, liquid-filled pectinate capsules and the influence of the addition of shellac to the polymer solution. We measured the deformation of these different capsules in a commercial spinning drop video tensiometer. In a series of measurements we analyzed the elastic properties of these capsules by varying the pH value of the cross-linking calcium chloride solution.

The results of these measurements showed that the liquid-filled capsules made out of pure pectin were much softer and show higher deformations than capsules additionally prepared with shellac because of the precipitation of shellac under acidic conditions.

Furthermore, the experiments showed that changing the pH value of the cross-linking solution leads to considerably different deformation properties in the case of the composite capsules, while the deformational and elastic properties of the pure pectinate capsules are independent of the pH value. This observation can be explained by the quantity of incorporated shellac in the gel membrane of the capsule walls. A lower pH value leads to mechanically stronger gel shells.

In addition, NMR microscopy was used to measure the membrane thicknesses. These techniques also allowed the evaluation of the kinetics of membrane formation. We investigated the influence of pH values and the addition of shellac. In a series of experiments we noticed that the deformation properties were directly influenced by the membrane thicknesses.

The pure pectinate capsules showed similar deformation properties and this could be traced back to constant membrane thicknesses. The dependence of the pH value for composite capsules on the deformation was also consistent with the dimensions of the gel layers. At the lowest pH value the highest amount of precipitated shellac leads to the strongest inhibition of calcium ion diffusion and therefore to the thinnest membranes which were hindered in their growth. At the highest pH value the amount of precipitated shellac was very small. The diffusion of calcium ions was consequently not reduced and this leads to thicker membranes.

The diffusion of calcium and hydrogen ions into the environmental pectin or pectin/shellac solution seems to control the mechanical properties as well as the membrane thicknesses. Besides these phenomena more complicated cross-linking processes were presented.

The measured membrane thicknesses by NMR microscopy were used to calculate the surface Young moduli in combination with squeezing capsule experiments. The obtained results of the calculated Young moduli are in good agreement with the results of the spinning capsule experiments.

Moreover, dynamic frequency-sweep tests provided information on the gel strength and the two-dimensional shear moduli of different prepared three-dimensional gels with the same composition as the comparable capsule membranes. These gel rheological measurements approve the observations made by squeezing as well as spinning capsule experiments.

The surface Young moduli, which were measured by the spinning and squeezing capsule techniques, are of the same order of magnitude and therefore in good agreement. We can use these experimental methods in order to achieve comparable information on the elastic properties of cross-linked capsule membranes. Rheological experiments afford similar results, wherein minor changes of the calculated shear moduli, in comparison to the Young moduli may be caused by differences in the compositions and methodical influencing factors, as described before.

It was shown in the presented study that the addition of shellac to the pectin solution and a systematical selection of the pH value make it possible to adjust the mechanical properties of these capsule systems. This might be interesting for industrial applications but it is to keep in mind that pectin is a polymer from natural origin, which is quite inhomogeneous. Therefore the obtained results cannot be transferred to other natural polymers without restrictions.

The influence of the incorporation of these shellac particles into the gel membrane on diffusional delayed drug release is an interesting topic for further studies in our institute together with the evaluation of the mechanical properties of capsules with external shellac coatings.

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