Interplay of Hydrogen Bonding and Hydrophobic Interactions to Control the Mechanical Properties of Polymer Multilayers at the Oil–Water Interface

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ⓢ *Supporting Information*

ABSTRACT: We probe the mechanical shear and compression properties of hydrogen-bonded polymer multilayers directly assembled at the oil–water interface using interfacial rheology techniques. We show that the polymer multilayers behave mechanically like a transient network, with elastic moduli that can be varied over 2 orders of magnitude by controlling the type and strength of physical interactions involved in the multilayers, which are controlled by the pH and the hydrophobicity of the polymer. Indeed, the interplay of hydrogen and hydrophobic interactions enables one to obtain a tighter and stronger network at the interface. Moreover, we show how a simple LBL process applied directly on emulsion droplets leads to encapsulation of a model oil, dodecane, as well as perfume molecules.
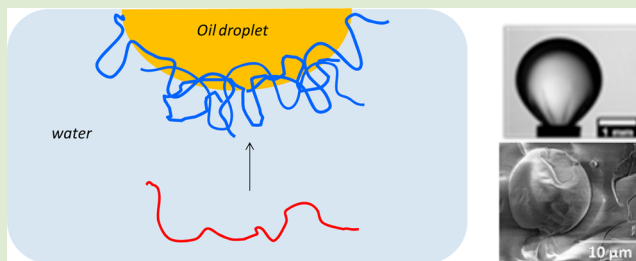
Polymer capsules are used in a wide range of applications such as cosmetics, pesticides, food and detergency, where protection, transport and delivery of active species are needed.[1] Capsules prepared by the layer-by-layer assembly (LBL)[2] of polymer multilayers onto a colloidal template is a powerful method to produce polymer membranes with controlled thickness, porosity, and permeability.[3−6] Such capsules are a good alternative to other technologies based on cross-linking reactions at the interface of oil droplets[7] that may raise concerns about potential residuals in suspensions of capsules. However, in this LBL process, the core has to be dissolved to obtain a hollow capsule that then needs to be filled with active species. Recently, to circumvent these issues, stable O/W emulsions were prepared using a polymer surfactant and then the LBL method was used to build in situ a polymer membrane on the oil droplets.[8−10] In addition to stability and encapsulation properties, most applications require precise control of the mechanical properties of the capsules to resist environmental stresses and achieve suitable encapsulation/release properties with respect to the desired application. For example, in detergency applications, fragrance capsules need to remain stable during storage in end-use products like liquid detergents, but the perfume molecules should be delivered to clothes at some key stages of the whole washing/drying process. This example can be extended to other fields of capsule application and shows the importance of an appropriate control of the mechanical properties of the capsules membrane. To the best of our knowledge there are no rules to guide the capsule design, mainly because of a lack of experimental methods available to easily measure the mechanical properties of capsules.[11−14]

In this letter, we probe the shear and compression mechanical properties of hydrogen-bonded polymer multilayers directly assembled on a single millimetric oil droplet in water and at a flat oil–water interface. We show that the elastic moduli of the multilayers can be varied over orders of magnitude by using an interplay of hydrogen and hydrophobic interactions between the layers. Moreover, we show how a simple LBL process allows the assembly of polymer multilayers directly onto model oil and perfume droplets to produce capsules.

As hydrogen bonds have recently emerged as a good way to produce polymer assemblies,[6,15] we built polymer multilayers made from polyvinylpyrrolidone (PVP) as a hydrogen-acceptor and two poly(carboxylic acid)s with different hydrophobicities as hydrogen-donors, poly(acrylic acid) (PAA) and polymethacrylic acid (PMAA) (Figure 1a). Hydrophobicity is a parameter
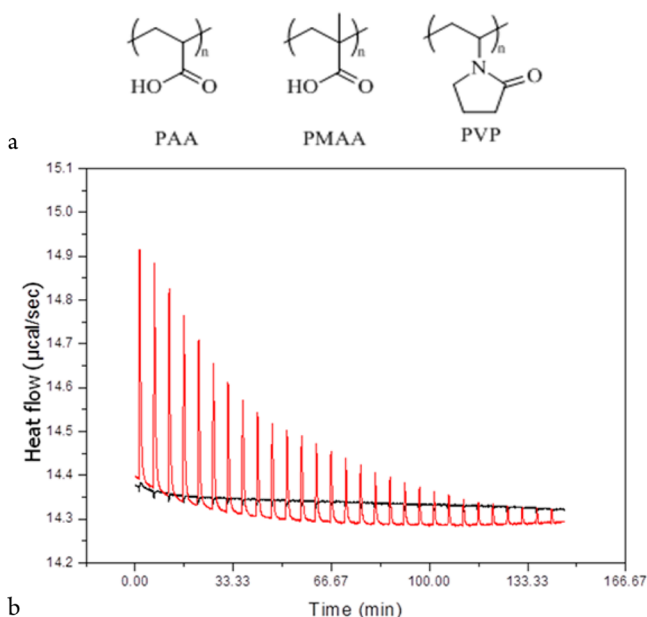
Figure 1. (a) Proton donors PAA and PMAA and proton acceptor, PVP, used for the assembly of polymer multilayers at the oil−water interface. (b) ITC experiment showing the heat effect produced by injecting 10 μL aliquots of a 10 mM PVP solution in water (pH 4) to a 1 mM PMAA solution (red curve) and by injecting 10 μL aliquots of a 10 mM PVP solution in water (pH 4; T = 25 °C) to pure water (pH 4; black curve; T = 25 °C). Peaks directed upward correspond to an endothermic interaction.

that is known to control the stability of hydrogen-bonded complexes via the existence of hydrophobic interactions between the molecules.[16−18] In bulk solutions, for both polyacids, we find that PAA/PVP and PMAA/PVP complexes form in the range of pH = 2−4 as solutions become turbid. Using isothermal titration calorimetry of the polymer complexes in solution, we measured a strong endothermic interaction upon addition of PVP in a PMAA solution, showing that the PMAA/PVP complexes interact through strong hydrophobic interactions (Figure 1b). In the same conditions, the interaction between PAA and PVP is weakly exothermic. We note that, for technical reasons, these measurements were performed at pH = 4, where the hydrogen bonds between the polyacids and PVP are weak because this pH is close to the pK_a of the polyacids. Therefore, our ITC measurements are mostly sensitive to the hydrophobic interaction between the polyacids and PVP. At pH = 3, we expect that the hydrogen bonds between PAA and PVP are stronger, which is confirmed by the fact that PAA/PVP solutions become turbid at this pH. We conclude that, at pH = 3, PMAA/PVP interact through strong hydrophobic interactions and hydrogen bonds, while PAA/PVP interact mostly with hydrogen bonds.

Multilayers composed of 1−5 PMAA/PVP bilayers were assembled directly on perfume and dodecane emulsion droplets. To obtain a large quantity of capsules, we prepared a direct emulsion using PMAA as an emulsifier (see details in Supporting Information, SI1). The drops were then left to cream and the polymer solution was replaced by water at pH = 3 to remove the excess of PMAA in the solution. A PVP solution was then added to adsorb the PVP chains on the oil droplets primarily coated with PMAA. This process was repeated between one and five times to obtain up to five bilayers. For both oils, we obtained capsules (Figure 1a,b),

which remain stable for several months in solution and can also be dried successfully. We did not observe any coalescence of the droplets, therefore, most of the oil was successfully encapsulated. Using granulometry, we find that the size distribution of the drops is centered around 20 μm and remains unchanged during the LBL assembly process (Figure 2b,d). The LBL process is, hence, robust with respect to the preparation method and time stability of the capsules batch without any reticulation.
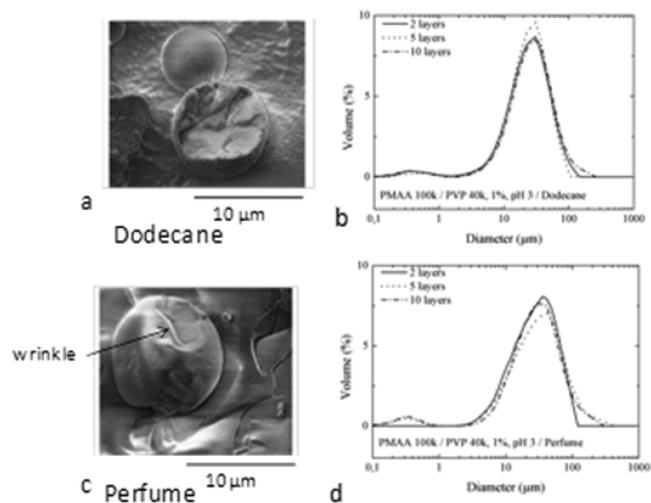

Figure 2. Cryo-SEM image of (a) dodecane and (c) perfume capsules made with 2 and 5 bilayers of PMAA/PVP assembled at pH = 3. Size distribution of the (b) dodecane and (d) perfume capsules assembled with PMAA/PVP multilayers for 2, 5, and 10 layers. The distribution of capsule diameters is similar for dodecane and perfume droplets.

Distinct odors associated with entrapped perfume were emitted after applying a mechanical friction onto dried capsules, indicating that perfume molecules remained trapped in the capsules even after several months in solution. Although highly stable, the capsules built at pH 3 can be stimulated through environmental control. As a matter of fact, the polymer multilayer can be destabilized and perfume is quickly released by increasing pH to 8, as the PMAA/PVP complex is not stable at that pH. This new LBL process is therefore robust with respect to the type of oil and time stability and can be used to prepare large quantities of capsules.

We probe the compression properties of PMAA/PVP and PAA/PVP hydrogen-bonded multilayers in a model geometry by assembling them on a single millimetric dodecane droplet in water and performing droplet compression and oscillatory dilatation/compression experiments.[19] We also screen the resistance to shear of the polymer layers adsorbed at the flat dodecane−water interface using the double wall Du Noüy ring shear rheometer (TA Instrument, ARG2).[20] Both set-ups are described in Methods and Supporting Information, SI2. For the PAA/PVP system, the compression/dilatation elastic modulus, E', increases from 2 to 78 mN/m as the number of layers varies from one (PAA monolayer) to five (PAA/PVP/PAA/PVP/PAA) layers (Figure 3a). Compared with the PAA/PVP bilayer, the PMAA/PVP bilayer is clearly a different type of 2D material at the oil−water interface as these droplets buckle upon compression for the largest compression rate (Figure 3b) while no buckling is observed for the PAA/PVP bilayer at any compression velocity.
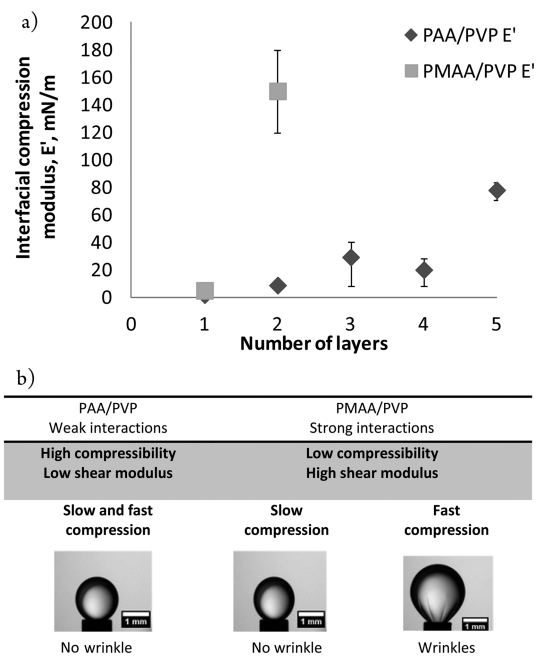
Figure 3. (a) Interfacial compression modulus, E' of the PMAA/PVP and PAA/PVP multilayers at the dodecane−water interface (pH = 3) for a frequency of 0.6 rad·s^{-1}. (b) Photographs of drop compression experiments at compression rate either 2 mm^2/s or 0.2 mm^2/s. For the largest compression rate, the PMAA/PVP bilayer forms wrinkles close to the tip of the needle, while the PAA/PVP bilayer does not buckle for any compression rate.

The folds appear close to the tip of the needle, showing that the surface stress is not homogeneous and that the droplet sustains a high surface stress without flowing, which is a consequence of low compressibility and high shear elasticity.[21,22] For PMAA/PVP above two layers, the compression modulus cannot be determined from the classical fit of the drop profile to the Laplace equation as the interfacial tension becomes anisotropic even at low deformations. Studies from Carvajal et al.[23] and Knoche et al.[24] describe methods to fit the shape of the drops taking into account both the meridional and hoop tensions to obtain the Young's modulus of the interface. Taking Carvajal's method, in the linear regime, we find a 2D Young's modulus of the order of 250 mN/m for five layers.

These observations are confirmed by very large values of the interfacial shear modulus, G', that increases from about 1 to 200 mN/m as one transitions from the PMAA monolayer to the PMAA/PVP/PMAA layer. Furthermore, the moduli of the PMAA/PVP/PMAA layer are 2 orders of magnitude higher than the PAA/PVP/PAA layer. Figure 4 also shows a maximum in G' when the number of layers exceeds three for the PMAA/PVP system. This result is surprising given the fact that the compressibility of the layer remains weak and wrinkles are observed for a number of layer above three. This can be explained by the brittleness of the polymer membrane as revealed from the Brewster angle microscopy image of the four (PMAA/PVP) layered interface at the surface of water. This was accomplished using an ellipsometer set to the Brewster condition (Figure S5).

To summarize, we find that the PAA and PMAA monolayers present the same static properties, interfacial tension and thickness, and have similar dynamic properties, that is, low compressibility and weak shear modulus. When turning to the
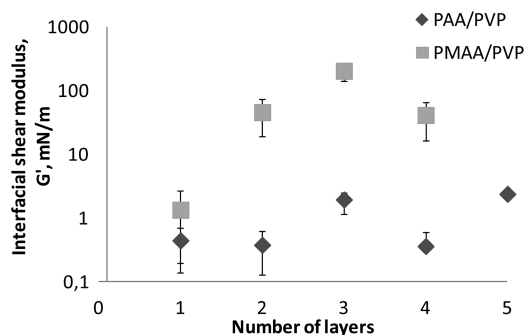

Figure 4. Interfacial shear elastic modulus, G', of the PMAA/PVP and PAA/PVP multilayers (pH = 3) as a function of the number of layers obtained for a frequency of 0.6 rad·s^{-1}.

PAA/PVP and PMAA/PVP multilayers, both systems present similar static properties while their mechanical behaviors are very different. The PMAA/PVP system presents a large shear modulus and buckles upon compression, while the PAA/PVP system presents a weak shear modulus and no buckling. This striking difference appears for a low number of layers, i.e. even for a bilayer. We suggest that the difference in the behavior of the PAA/PVP and PMAA/PVP bilayers is related to the dynamics of the polymer chains in the polymer membranes. Similar to solutions of associative polymers[25] and polyelectrolyte complexes,[26] where the shear elastic modulus and the mobility of the chains[27] can be controlled by the strength of the intermolecular interaction, our interfacial multilayers can be viewed as 2D physical network involving hydrogen and hydrophobic interactions that can be used to adjust the strength and number of the linkages between connecting chains. Coupling hydrogen and hydrophobic interactions leads to a tighter and stronger network at the interface with a larger shear modulus. The dynamical response of the chains also influences the compression properties. Upon large area compression, adsorbed monomer units, known as the "trains", can desorb from the interface and be expelled from the layer to form loops[28] (Figure 5).
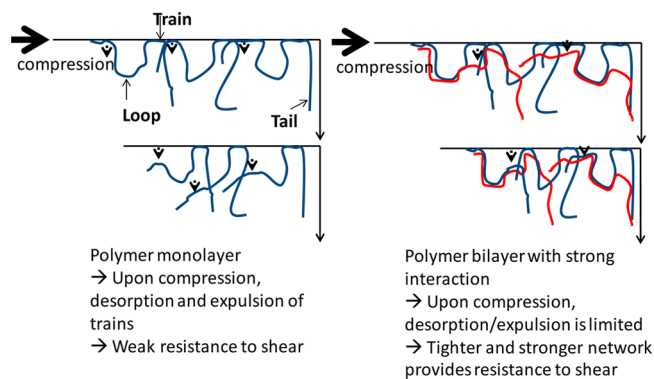

Figure 5. Schematic drawing of the dynamics of polymer monolayers and bilayers adsorbed at the air−water or oil−water interface.

The resistance to compression depends on how fast the desorption/expulsion occurs in comparison to the rate of compression. We expect that strong hydrophobic interactions between the PMAA and PVP molecules slow down the expulsion of monomer units from of the layer upon compression and hence, decrease the compressibility of the layer. In fact, when the compression rate is decreased by a

factor 10, from 2 mm^2/s to 0.2 mm^2/s, the PMAA/PVP bilayer does not buckle, as it has more time to rearrange.

To tune the strength of the hydrogen-bonded network, we vary the pH from 2 to 4 (Figure 6) causing the shear modulus
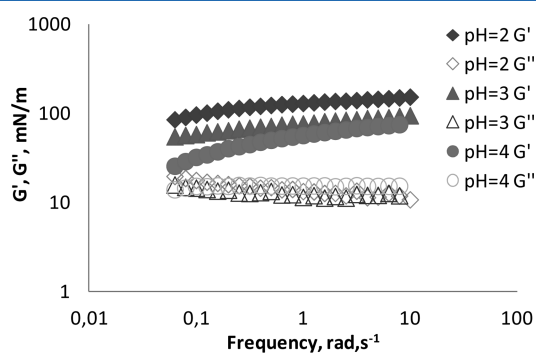

Figure 6. Influence of the pH on the shear properties of a bilayer of PMAA/PVP.

to drop by a factor two. Furthermore, the characteristic frequency, defined as the crossover between the interfacial shear elastic modulus, G', and the interfacial shear loss modulus, G'', is well below the range of investigated frequencies for pH = 2, which is consistent with a rubbery plateau of a transient network. This crossover frequency appears to increase to value slightly lower than 0.06 rad·s^{-1} at pH = 4. This result confirms that both the number of physical links and relaxation time can be tuned by varying the pH.

In conclusion, we show these polymer multilayers behave mechanically like a viscoelastic transient network whose shear and compression elastic moduli can be varied over orders of magnitude by tuning the type and strength of interactions existing in the multilayers. Varying the pH is a means of tuning the relaxation time and elastic modulus of the hydrogen-bonded network, whereas using a hydrophobic polymer leads to an interplay of hydrogen and hydrophobic interactions to obtain a tighter and stronger network at the interface. We have encapsulated large quantities of oil droplets, either a model oil or perfume molecules, over long periods of time using a process that enables assembling the polymer multilayers directly at the surface of emulsion droplets. LBL is indeed a robust process even in the case of a perfume batch, which are known to be challenging molecules to encapsulate as they consist of a complex mixture of up to tens of small molecules with different polarities and water solubilities. The capsules can be stimulated by adjusting pH since stabilization/destabilization of the polymer complex forming the membrane is very sensitive to this variable. Overall, our work provides new routes for the design of ecofriendly capsules with tunable mechanical properties adapted to encapsulation/release applications.

■ METHODS

Materials. PAA (M_n = 50 kg/mol) and PMAA (M_n = 100 kg/mol) were obtained from Polysciences, PVP (M_w = 40 kg/mol) from Fluka Analytical and dodecane from VWR (GPR Rectapur). Perfume was supplied by Givaudan. For most experiments, we worked at pH = 3, where both poly(carboxylic acid)/PVP systems form complexes in bulk solutions.

Rinsing Process and LBL Assembly. For the rinsing drop experiment, we use the same method as the one in ref 19, where a drop of dodecane is formed at the tip of a syringe in a polymer aqueous solution, to let the first polymer layer adsorb at the oil–water interface. After equilibrium tensions are reached, the polymer in excess

is removed by injecting water (at the complexation pH) into the dish using a peristaltic pump. The second polymer solution is then injected and the polymer is left to adsorb on the first layer for 30 min. This process is repeated to build the polymer multilayers at the oil–water interface. A similar rinsing process is used to build the multilayers at a flat water–air interface for the ellipsometric measurements (Nanofilm, Germany) and at a flat oil–water interface for the measurement of the shear interfacial elasticity.

Compression and Shear Properties. To probe the compression properties of the adsorbed multilayers, the interfacial area of the droplets is decreased by changing the volume of the oil droplets using the Tracker from IT Concept (France). The interfacial compression modulus, E, writes $E = d\gamma/d \ln A = E' + iE''$, where γ is the interfacial tension, A is the area of the drop, and E' and E'' are, respectively, the elastic and loss compression moduli. The interfacial tension is obtained by fitting the profile of the drop to the Laplace equation. The shear properties of the multilayers are measured with a setup consisting in a Du Noüy ring fixed on a rheometer in a double wall ring cup (TA Instrument).[21] The ring is positioned at the oil–water interface and then oscillated. The rheometer records the interfacial stress and strain caused by the deformation of the multilayer at the interface from which we obtain the interfacial shear elastic modulus, G' and the interfacial shear viscous molulus G'' in mN/m.

■ ASSOCIATED CONTENT

ⓢ Supporting Information
Experimental setup to produce the capsules (SI1), setup to assemble the polymer multilayers at the oil–water interface (SI2), and ellipsometry and interfacial tension measurements during the assembly of the polymer multilayers (SI3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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