

Dual Xanthan Gum/Poly(vinyl acetate) or Alkyl-Functionalized Poly(vinyl alcohol) Films as Models for Advanced Coatings

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ABSTRACT: Double-layer films, prepared by casting films of xanthan gum (XG), and subsequently poly(vinyl acetate) (PVAc) onto the former, are reported. The resulting XG/PVAc films provide high protection as coatings to a bleaching agent, 6-(phthalimido)peroxyhexanoic acid, in liquid detergents, due to the combined roles of the outer PVAc layer as water-barrier and the inner XG layer as water-sink. PVAc films cast from either homogeneous solutions in acetone or aqueous dispersions were used; the stabilities exerted by the former were markedly superior. For comparison, poly(vinyl alcohol) (PVA) was also used as outer wall material, resulting in much lower protection due to its hydrophilicity. Functionalization (silylation or acetylation) of PVA films is also suggested as a means to decrease the surface hydrophilicity of the material. The dual hydrophilic–hydrophobic films presented herein serve as models for advanced coatings in (micro)encapsulation processes, owing to the straightforward study of their morphology and transport phenomena. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40870.

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INTRODUCTION

Encapsulation technology is currently a field of major innovation in pharmaceutical, food or consumer product industries. By enclosing certain high-performance ingredients (benefit agents) within conveniently selected wall materials, two main advantages may be achieved: (1) the protection of such benefit agents during shelf-life and (2) their controlled release during use.¹ The desired performance of the benefit agent would be thus enhanced by increasing its stability until the appropriate “in-time” release. The latter process would be ideally triggered by stimuli capable of disrupting the wall. Polymeric materials are, due to their versatility, the wall components of choice for many demanding encapsulation processes sought by industry.

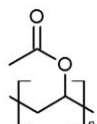
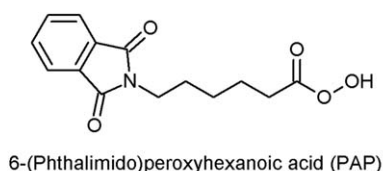
Frequently, long-term stability during storage is compromised in cases where such benefit agents are prone to degrade and/or to react with other ingredients in the formulation. In detergents, bleaching agents represent a paradigmatic case of such stability challenge.² Bleaching agents are extremely efficient stain-removing substances, but unfortunately, their high reactivity may cause product decay at time spans dramatically shorter than the

lapse between production and household use (shelf-life). This is even more critical for liquid detergent formulations, as compared to powdered products, due to faster diffusion phenomena.² Bleaching agents for laundering applications are strongly oxidizing substances, often containing peroxide groups.^{3,4} Among such materials, 6-(phthalimido)peroxyhexanoic acid (PAP, see structure in Chart 1) is one of the most frequently used, due to its considerably higher stability as compared to other peroxyacids,⁵ while being its bleaching properties maintained. Therefore, industry has focused its attention to PAP as a bleaching ingredient for detergents,^{5–7} cosmetics,^{8,9} or personal care products, such as toothpastes.⁸ The use of appropriate polymeric wall materials for encapsulation of PAP is certainly one of the most promising, albeit challenging, strategies to achieve high stability, and long shelf-life for liquid detergents containing such bleaching agent.

Polymeric capsules are being widely investigated within the sector of liquid detergents. This is illustrated by the increasing number of reports which can be found in the patent literature regarding their use to encapsulate, *inter alia*, fragrances,^{10,11} enzymes,¹² or bleaching agents.^{12–14} Recently, it has been claimed that

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Poly(vinyl acetate) (PVAc)



Poly(vinyl alcohol) (PVA)

Chart 1. Structures of the bleaching agent (PAP) and the polymeric materials (PVAc and PVA) used in this work.

double-layer coatings in capsules provide high stability to a bleaching agent as encapsulate.¹⁵ In particular, by encapsulating a material based on PAP as an active bleach, firstly with a layer of a gel-forming hydrophilic polymeric material, such as xanthan gum (XG), and then with a layer of a more hydrophobic polymeric material, such as poly(vinyl acetate) (PVAc), long-term storage can be achieved (see structures of the involved materials in Chart 1). This was hypothesized as the result of the combined effect of the outer PVAc wall acting as water-barrier, and the inner XG layer acting as water-sink in the event of accidental diffusion in through the outer layer. In fact, the role of XG as a gel-forming material in aqueous environments has been shown to slow down the transport of active materials in pharmaceuticals such as tablets,^{16–18} thus enabling a controlled and sustained release. Kinetic studies revealed that caffeine is released at a constant zero-order rate from XG matrices in water.¹⁸ More recently, the mechanism of drug release from XG tablets has been investigated by magnetic resonance imaging,¹⁹ confirming previous studies¹⁷ which suggested three main steps in the process: (1) swelling of the outer layers of the tablet by water uptake, (2) decrease of diffusion rates by gel formation, and (3) slow dissolution or erosion of the surface. Furthermore, XG has been reported as a suitable stabilizer in formulations containing PAP.^{7,20} All the aforementioned properties thus support the choice of XG as the inner layer material for double-layer coatings of PAP in liquid detergents.

The preparation of double-layer coatings for microcapsules has been reported for melamine-formaldehyde/calcium carbonate²¹ or polyurea/polyurethane²² systems, both by interfacial polymerization on oil-in-water microemulsion surfaces, a method for which only a limited set of polymeric materials can be used. The choice of polymers can be widened by implementation of spray-coating techniques, as described in our previous patent, wherein a method for coating PAP particles with XG/PVAc double-layers by sequential wall deposition was reported.¹⁵ Nevertheless, studying the morphology of the walls and the transport phenomena across them in microcapsules prepared by either method is extremely challenging, due to their small dimensions.

In this work, film and membrane technologies were used to prepare flat, two-dimensional analogs of such multilayer capsules. The objective was to study wall-forming processes and sta-

bility at a macroscopic scale, thus providing support for previous encapsulation studies, and setting principles for future developments. A systematic comparison of different wall materials is enabled by such a straightforward methodology. The beneficial effects of dual hydrophilic–hydrophobic films are herein assessed by means of the study of transport phenomena in diffusion modules. Moreover, the functionalization of hydrophilic polymeric film surfaces, aiming at decreasing their hydrophilicity, is also presented.

EXPERIMENTAL

Materials

XG powders were supplied by either Sigma–Aldrich (from *Xanthomonas campestris*, designated herein as ^SXG) or CPKelco (Kelzan[®] ASX-T, designated herein as ^KXG). PVAc of two different M_w values (10^5 or 5×10^5 g mol⁻¹, hereinafter referred to as ¹PVAc or ⁵PVAc, respectively) were supplied by Sigma–Aldrich as beads or granules, respectively. Aqueous PVAc dispersions [Vinavil[®] 2160 L, solid content = 60 wt %, dispersing agent: poly(vinyl alcohol) (PVA)] were kindly provided by Vinavil (Milano, Italy) and further diluted as described below; solid materials obtained from Vinavil[®] 2160 L are referred to as ^VPVAc in the text. PVA was used as dispersed in water (solid content \approx 20 wt %). Ethanol (absolute, synthesis grade), acetone (reagent grade), heptane (99%, reagent grade), ethyl acetate (reagent grade), potassium iodide (reagent grade), glacial acetic acid (HPLC grade), aqueous sodium thiosulfate (0.1 M), and aqueous starch solutions (1%, w/v) were provided by Scharlau. Triethoxymethylsilane, trimethoxyoctylsilane (96%), hexadecyltrimethoxysilane (\geq 85%), and nonanol (95%) were supplied by Sigma–Aldrich. PAP (ca. 71%, Eureco[™] WM1) was supplied by Solvay Chemicals. Silicone oil (246 fluid) was supplied by Dow Corning. Sulfuric acid (95–97%) was supplied by J.T. Baker. All chemicals were used as received unless otherwise stated. The liquid detergent used in stability studies was the commercially available Ariel Actilift[™], manufactured by The Procter & Gamble Company.

Instruments and Methods

Film thicknesses were measured with a Starrett[®] (436.2 Series) outside micrometer. Additional measurements were done on cross-sectioned samples by microscopy measurements (SEM, see details below). Reported figures were averaged over a minimum of five micrometer measurements and three microscopy measurements, performed on different regions of the film (standard deviations = \pm 5–10 μ m on measurements done by either method, depending on film surface roughness). Scanning electron microscopy (SEM) observations and measurements were performed on a JEOL JSM-6400 scanning microscope. Samples were mounted on appropriate holders and coated with a gold layer on an Emitech K575X gold coater at a 30 mA current during 2.5 min. Samples of PVAc films were observed by adjusting the electron beam to a 20 kV accelerating voltage. In contrast, XG and PVA films were too sensitive: they often underwent cracking or surface disruption under such conditions; therefore, accelerating voltages were reduced to 10–15 kV. Multilayer membranes containing PAP powders and silicone oils as binder (see details below) sandwiched between polymeric films were not robust

Table I. Details for the Preparation of XG Films^a

| | Polymer | Polymer concentration (wt %) | Film thickness ^b (μm) | Film roughness ^c |
|-------------------|-----------------|------------------------------|----------------------------------|-----------------------------|
| ^S XG-1 | ^S XG | 1 | 25 | 72.7 |
| ^K XG-1 | ^K XG | 1 | 19 | 14.7 |
| ^K XG-3 | ^K XG | 3 | 82 | |

^aFilms were obtained by slow water evaporation from aqueous XG gels spread by means of a casting knife and a K-Paint applicator; cast parameters: cast thickness = 4 mm, cast temperature = 50 °C, time = 5 h; see Materials section for details on the polymeric materials.

^bMeasured by both a micrometer and SEM, as detailed in the text (Instruments and Methods section).

^cMeasured by AFM, using the WSxM software.

enough for high vacuum operation: the different layers disassembled apart from each other. Therefore, low vacuum operation on an environmental and variable pressure scanning electron microscope (ESEM, FEI-Quanta 600 instrument) was performed instead. Micrographs of single-layer film cross-sections were obtained after cooling down in liquid nitrogen and snapping the films; the sectioned films were then mounted on appropriate holders for microscopic observations. In the case of multilayer films, such a procedure could not be used as freezing led to unwanted layer separation. Therefore, multilayer film cross-sections were studied after carefully cutting with scissors and mounting the sectioned specimens in appropriate holders. By proceeding in this manner, the morphology of the film layer assemblies could be observed, although at the expense of a slight damage to film edges. Atomic force microscopy (AFM) observations were performed on an Agilent Technologies AC Mode III Module instrument equipped with a Hunt CCTV-Navitar Highlight 2001 Olympus Europe CCD camera and a Pico PlusTM laser molecular imaging device, at a 1 line per second scanning rate using a 20 nm diameter silicon tip; the scanning area was a 20 × 20 μm square; surface roughness analyses were performed by means of the WSxM software. Contact angles were measured using a Neurtec Instruments OCA 15 EC video-based system as follows: a sessile Milli-QTM water drop (3 μL) was dispensed from a Hamilton syringe on a flat horizontal polymeric film surface, the drop allowed to settle on the surface for about 5 s and the contact angle measured by fitting the drop contour to a circle by means of the SCA20 software.

Table II. Details for the Preparation of Double-Layer XG/PVAc and XG/PVA Films^a

| | Polymer | Solvent | Polymer concentration (wt %) | Cast thickness (μm) | Cast temperature (°C) | Time (h) | Film thickness ^b (μm) | |
|----------------------------|-------------------|---------|------------------------------|---------------------|-----------------------|----------|----------------------------------|----------|
| | | | | | | | PVAc or PVA layer | XG layer |
| XG/¹PVAc | ¹ PVAc | Acetone | 30 | 300 | 40 | 3 | 47 | 20 |
| XG/⁵PVAc | ⁵ PVAc | Acetone | 30 | 300 | 40 | 3 | 60 | 25 |
| XG/^VPVAc | ^V PVAc | Water | 40 | 200 | 40 | 5 | 72 | 25 |
| XG/PVA | PVA | Water | 20 | 300 | 40 | 5 | 48 | 24 |

^aFilms were obtained by slow solvent evaporation from PVAc or PVA solutions (or suspensions) spread by means of a casting knife and a K-Paint applicator onto the surface of XG films, prepared as ^KXG-1 (see Table I); see Materials section for details on the polymeric materials. ^b Measured by both a micrometer and SEM, as detailed in the text (Instruments and Methods section).

Preparation of Polymer Gels and Solutions

Aqueous XG gels (solid content = 1 or 3 wt %) were prepared by mixing appropriate amounts of the solid polymeric material in deionized water and then heating the mixture under stirring at 90 °C for 1 h; after cooling down to room temperature, the XG gels thus prepared were free of air bubbles. Solutions of PVAc (either 10⁵ or 5 × 10⁵ g mol⁻¹, ¹PVAc or ⁵PVAc, respectively, solid content = 30 wt %) in acetone were prepared by slowly adding appropriate amounts of the solid polymeric material into the solvent under stirring at room temperature. Gels of ¹PVAc (solid content = 30 wt %) in ethanol were prepared by slowly adding appropriate amounts of the solid polymeric material in the solvent under stirring and reflux conditions; such gels were immediately used after cooling down to 40–50 °C under vigorous stirring, as they showed a strong tendency to splitting into a lower swollen polymer phase (solid content ≈ 65 wt % based on ¹H-NMR analysis) and an upper solvent phase (polymer content below the limit of detection of ¹H-NMR). Dispersions of PVAc in water (^VPVAc, solid content = 40 wt %) were prepared by adding the corresponding amount of water to Vinavil[®] 2160 L under stirring.

Casting of Single-Layer XG Films

XG films were prepared by casting the corresponding gel on a glass plate covered with a poly(vinyl chloride) adhesive sheet using a casting knife (area ≈ 20 × 13 cm²) and a K-Paint applicator. Casting conditions and film codes are reported in Table I.

Casting of Double-Layer Films

Either PVAc or PVA films were cast directly onto XG films using a similar procedure as that described above; after removing the solvent, the adhesive sheets were detached from the glass plate; then, the resulting translucent, free-standing, double-layer XG/PVAc or XG/PVA films were peeled off the poly(vinyl chloride) sheet. Film casting data are listed in Table II.

Fabrication of Multilayer Sandwich Membranes and Stability Studies

XG/PVAc or XG/PVA films were used as the outer coatings for sandwich membranes enclosing EurecoTM WM1/silicone oil (2 : 1 by weight) blends as follows: Two square pieces (5 × 5 cm²) of the appropriate double-layer films were cut; then, a certain amount of EurecoTM WM1/silicone oil blend was spread on the XG side of one of the double-layer films covering a *ca.* 4 cm diameter circular area on the center of the film square; finally, the second film square

was placed on top of the Eureco™ WM1/silicone oil blend, being the XG surface always facing the interior, that is, the PAP blend side. The multilayer membranes thus prepared are designated as *polymer/XG/PAP/XG/polymer* (*polymer* = ¹PVAc, ⁵PVAc, ^VPVAc, or PVA, as appropriate). For stability experiments, such membranes were placed in the membrane compartment (tightly sealed by two rubber O-rings) of a diffusion module consisting of two 200 cm³ cells (see photographs in Supporting Information Figure S1); the module was tightened with four threaded rods and bolts. Identical liquids were placed in either cell and then stirred at 500 min⁻¹ for the desired length of time. At the end of the experiment, the module was emptied, disassembled, and the membranes were inspected and analyzed by iodometric titration (where appropriate) as follows: the multilayer membrane was either cut into small pieces or frozen in liquid nitrogen and subsequently ground on a mortar (this latter method providing a better recovery of active material), and then added into a mixture of a 2% (w/v) aqueous potassium iodide solution (100 mL), a 10% (w/v) aqueous acetic acid solution (100 mL), and ethyl acetate (50 mL); the resulting mixture was stirred at 45 °C for 1 h; then, two or three drops of a 1% (w/v) aqueous starch solution were added and the resulting brownish liquid mixture titrated under vigorous stirring by slowly adding a 0.01 M (prepared by 10-fold diluting a commercial 0.1 M solution) aqueous sodium thiosulfate solution until color disappearance. The amount of PAP was quantified as $n(\text{PAP}) = (0.01 V)/2$, where $n(\text{PAP})$ stands for the amount of PAP in mols, and V is the volume of sodium thiosulfate solution in liters. Because of possible mechanical losses of the bleaching agent material during sample preparation for titration, deviations up to $\pm 10\%$ for the stabilities are estimated.

PVA Surface Functionalization

Square-shaped ($2.5 \times 2.5 \text{ cm}^2$) samples of PVA films (cast from 20 wt % aqueous dispersions, cast thickness = 300 μm , solvent evaporated at 40 °C for 5 h; film thickness $\approx 50 \mu\text{m}$) were cut and functionalized by following two different procedures:

1. Silylation. PVA films were suspended in solutions containing either triethoxymethylsilane (1 mL, 5.02 mmol), trimethoxyoctylsilane (1.5 mL, 5.80 mmol), or hexadecyltrimethoxysilane (2 mL, 5.14 mmol) in heptane (20 mL) and the solutions gently stirred at room temperature for 24 h and then at 60 °C for 3 h; then, the films were removed from the solutions, washed by immersing in hexane, and dried in air for 1 day; the resulting films were named **C₁SiO-PVA**, **C₈SiO-PVA**, and **C₁₆SiO-PVA**, respectively.
2. Acetalization. A PVA film was suspended in a solution containing heptane (22 mL), sulfuric acid (8 mg, 0.08 mmol), and nonanal (1.5 mL, 8.72 mmol) and the solution gently stirred at room temperature for 24 h and then at 60 °C for 3 h; the film was treated as described for the silylated films and named **C₈CHO-PVA**.

RESULTS AND DISCUSSION

Single-Layer Films

Flat and dense XG films were prepared by solvent evaporation at 50 °C from aqueous gels containing either 1 or 3 wt % solid

XG materials (Table I) by conventional casting methods.²³ Gels containing 1 wt % XG, although viscous, were suitable for film casting as they did not contain air bubbles. More concentrated XG gels were noticeably more viscous and tended to retain bubbles, thus giving films with large pores or surface defects. Film thicknesses were 20–25 or 70–85 μm for 1% or 3% gels, respectively (cast thickness = 4 mm, see data in Table I). Two different XG powders, either ^SXG (from *Xanthomonas campestris* provided by Sigma–Aldrich) or ^KXG (Kelzan® ASX-T provided by CPKelco), were used as starting materials and compared. The appearances of their respective aqueous gels were significantly different depending on the starting XG material: for 1 wt % concentrations, colorless transparent gels were obtained from ^KXG, whereas analogous gels from ^SXG were white, cloudy, and translucent [see pictures of the gels in Figure 1(A)]. This indicates a better miscibility of the ^KXG material with water (i.e., more homogeneous gels could be produced from this material). In accordance with this, films resulting from ^KXG or ^SXG were also transparent or translucent, respectively, and the surface of the former appeared to be considerably more even [see pictures for representative films ^KXG-1 and ^SXG-1 in Figure 1(B)]. Observations by SEM confirmed that ^KXG films have denser interior and more even surface than ^SXG analogs; this is clearly seen in the micrographs shown in Figure 1(C), wherein the morphology of the cross-section of a ^KXG film appears to be layered and dense, whereas that of a ^SXG analog is rather granular and uneven, probably due to the presence of aggregated polymeric particles. This was further confirmed by AFM measurements [see Figure 1(D)], which indicated that the surface of ^SXG films was uneven with noticeable protrusions, probably due to the presence of polymeric particles, whereas those of ^KXG analogous films was even and devoid of aggregates or particles, consistent with the observed complete miscibility of the ^KXG material. This was quantified by means of film roughnesses as calculated with the WSxM software, 14.7 and 72.7 for ^KXG-1 and ^SXG-1, respectively.

Based on the more suitable characteristics of ^KXG films as compared to ^SXG, that is, surface evenness and interior uniformity and compactness (as discussed above), the former material was used as the hydrophilic part of double-layer films. Thus, in a typical experiment, a second polymeric film was directly cast on the external surface of a previously prepared ^KXG film, resulting in **XG/polymer** double-layer films (where *polymer* stands for the second cast material, and XG is in this case the preformed ^KXG film, see Table II). In most cases in this study, the second polymer of choice was PVAc. The resulting hydrophilic–hydrophobic double-layer films (XG/PVAc) can be considered as two-dimensional macroscopic models for doubly coated core/XG/PVAc capsules, such as those described in our companion patent.¹⁵ Different PVAc materials were tested. Furthermore, PVA, a water-soluble polymeric material, was also used, resulting in XG/PVA films, and tested for comparison.

Parameters for PVAc or PVA film casting were optimized by a series of experiments, as summarized in this paragraph (complete set of actual data not shown). ¹PVAc or ⁵PVAc films were cast by solvent evaporation at 40 °C from either solutions in acetone or ethanolic gels. This is a more convenient method as compared to

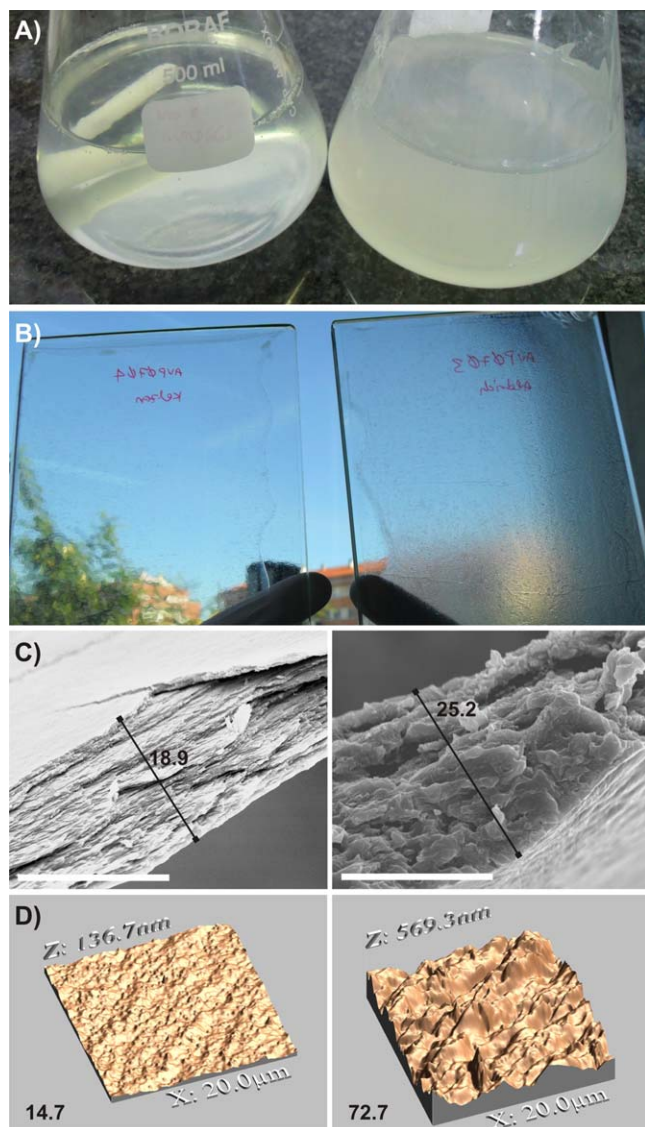


Figure 1. Comparison of XG gels, and films derived thereof, prepared from either K XG (left images) or S XG (right images, see Materials section for details on the polymeric materials); (A) pictures of 1 wt % aqueous gels; (B) pictures of as prepared K XG-1 and S XG-1 films on glass plates; (C) SEM cross-sectional micrographs of the films, where black lines indicate measured film thicknesses (values [μm] indicated next to the lines, white scale bars = 20 μm); (D) AFM micrographs of the films; X and Z indicate the in-plane and orthogonal scales; film roughness figures are shown in black. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

similar ones which report the casting on mercury surfaces²⁴ or at high temperatures.²⁵ As in the case of XG, the viscosity of the casting fluid was a crucial factor for the quality of the resulting films. For polymer weights above 30%, solutions or gels were too viscous and large bubbles remained trapped in the films during solvent evaporation. For polymer weights of around (or below) 30%, flat, flexible, dense, transparent films of even surfaces were obtained. Typically, by casting 300 μm thick layers of polymer solutions, film thicknesses in the order of tens of micrometers (40–70 μm) were obtained, a range which was considered as appropri-

ate for the fabrication and subsequent stability studies of multi-layer membranes as models for microcapsule wall materials. A different approach to PVAc film preparation was the use of commercial dispersions of the polymer in water (Vinavil[®] 2160 L). In this case, the solid content of the dispersions was adjusted to 40%; the viscosities of the resulting dispersions were appropriate for film casting. To achieve film thicknesses comparable to those of the 1 PVAc or 5 PVAc films described above, the cast thickness was adjusted to 200 μm . The resulting V PVAc films were brittle and translucent and their surfaces were flat, but slightly rough. The flexibility of the films did not improve upon addition of glycerol as plasticizer. Observation of cross-sections of the films by SEM revealed that the interior of the V PVAc films was formed by aggregated spherical particles (diameter \approx 1–2 μm). Moreover, PVA films could be cast from 20 wt % dispersions in water. The resulting films were flat, flexible, dense, and transparent, and exhibited even surfaces.

Double-Layer Films

Dual hydrophilic–hydrophobic double-layer films consisting of a XG layer and a PVAc layer (XG/PVAc) were prepared by first casting a K XG film (20–25 μm thick, see Table II) and then casting a PVAc film on its surface. Typically, 30 wt % PVAc (either 1 PVAc or 5 PVAc, $M_w = 10^5$ or 5×10^5 g mol⁻¹, respectively) solutions in acetone were spread (300 μm cast thicknesses) using a casting knife and a K-Paint applicator. After removing the solvent by slow evaporation at 40 °C, the resulting films (XG/ 1 PVAc or XG/ 5 PVAc) were peeled off; they were transparent and flexible, and the adherence of the layers onto each other was acceptable, although they could be separated if some mechanical stress was applied. Depending on the molecular weight of the polymeric material, PVAc layer thicknesses were slightly different: 47 for XG/ 1 PVAc, 60 μm for XG/ 5 PVAc.

Similarly to the preparation of XG/ 1 PVAc and XG/ 5 PVAc double-layer films, aqueous dispersions of PVAc (Vinavil[®] 2160 L diluted to 40%) were cast on K XG films as detailed in Table II (200 μm cast thicknesses, solvent evaporation at 40 °C for 5 h). The resulting translucent films were robust and could be easily peeled off (albeit the V PVAc films showed somewhat stiff and brittle behavior, see above). Such a material may be advantageous in the perspective of encapsulation processes as only water (no flammable organic solvents) is used. Furthermore, the XG layers of the films maintained their shape and did not undergo significant dissolution in the aqueous PVAc dispersion cast onto it (no diffusion zone observed by SEM, see below). This can be ascribed to slow diffusion in the viscous liquids involved, which impairs mixing of the polymers to take place during the relatively short cast times. The PVAc layer of the XG/ V PVAc film reported in Table II had a thickness of 72 μm , slightly thicker than those of analogous XG/ 1 PVAc or XG/ 5 PVAc. Nevertheless, thinner V PVAc films were too brittle for successful comparative membrane studies to be performed.

Figure 2 shows SEM micrographs of the cross-sections of XG/ 1 PVAc and XG/ V PVAc. In the images, the adherence of the PVAc and XG layers onto each other is clearly observed. Furthermore, as discussed above, the interior of the 1 PVAc layer is dense and a continuous polymeric phase is observed, whereas

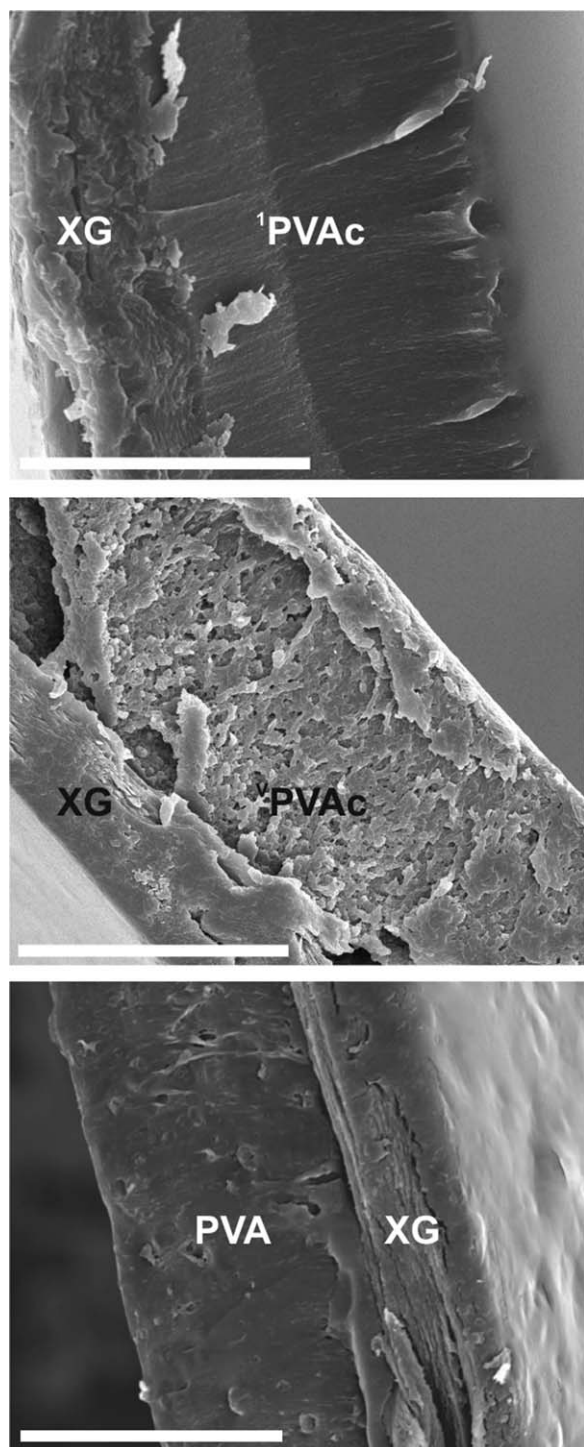


Figure 2. Comparison of SEM cross-sectional micrographs of XG/^IPVAc (top, scale bar = 30 μm), XG/^VPVAc (middle, scale bar = 60 μm), and XG/PVA (bottom, scale bar = 80 μm) films; the composition of each layer is indicated by the corresponding label; XG = ^KXG.

the ^VPVAc layer is composed of aggregated spherical particles. This is not surprising, as the latter was prepared from aqueous dispersions of the polymer. Such textures exert significant differences in the performance of the resulting double-layer coatings in liquid detergent media, as discussed below.

By casting aqueous PVA dispersions on preformed ^KXG films, double-layer XG/PVA films were obtained. The resulting dual films are flexible, transparent, and robust (good layer adherence). In a typical preparation (see Table II), the resulting XG/PVA film consists of 48 and 24 μm thick PVA and XG layers, respectively. As observed by SEM (see Figure 2), the interior of the PVA layer in XG/PVA is dense, indicating that, similarly to XG/^IPVAc and XG/^SPVAc, the polymeric material was dissolved in the casting dispersion. Similarly to XG/^VPVAc films (see above), both XG and PVA layers are clearly distinguishable, that is, no inter-penetration into each other was observed by SEM (Figure 2) due to the high viscosity of the polymer solution, as discussed for XG/PVA above. XG/PVA films can be regarded as analogs to XG/PVAc films, but having a second layer of a highly hydrophilic material, that is, the former are hydrophilic-hydrophilic films, whereas the latter are dual hydrophilic-hydrophobic films.

Sandwich Multilayer Membranes

A double-coating encapsulation process has been reported in a recently published (and closely related to this work) patent application.¹⁵ In a particular example therein, granules of PAP (a bleaching agent) were first coated with a XG layer, and subsequently with a layer of PVAc. According to previous results, each one of the different layers has a dedicated function: the outer PVAc acts as a water-barrier, whereas the inner XG layer acts as a water-sink absorbing any water which may penetrate the outer layer accidentally through any surface defects, causing gelling and slowing down the diffusion of water into the PAP core. Such combined roles are called to protect the bleaching agent inside the capsule, preventing the contact with the ingredients of the formulations where the capsules should be stored in, and minimizing the diffusion of PAP outwards into the liquid detergent. Therefore, the ultimate goal of the double-coating design for such capsules is the protection and stability of both PAP and liquid detergent components by preventing the contact between them during product shelf-life. Finally, the capsules would be broken during washing, thus releasing the bleaching agent.

Here, XG/PVAc films were used to enclose PAP, in a manner analogous to the double-layer encapsulation described above, that is, the bleaching agent is covered with an internal coating of XG and an external coating of PVAc. This was done by simply placing XG/PVAc films on either side of a central PAP layer (a small amount of silicone oil was used as binding agent for PAP and the internal XG surface). The result is a sandwich-type multilayer membrane (PVAc/XG/PAP/XG/PVAc), a two-dimensional, flat model for the doubly coated particles claimed in the mentioned patent application. This is illustrated in Figure 3, where the correspondence of both the core and the multiple coatings in spherical microcapsules to the different layers in a PVAc/XG/PAP/XG/PVAc membrane is schematically shown; the internal PAP layer and the coatings (XG and PVAc) can be clearly distinguished in the ESEM micrograph shown therein. For comparison, analogous sandwich membranes where the outer wall is composed of PVA (PVA/XG/

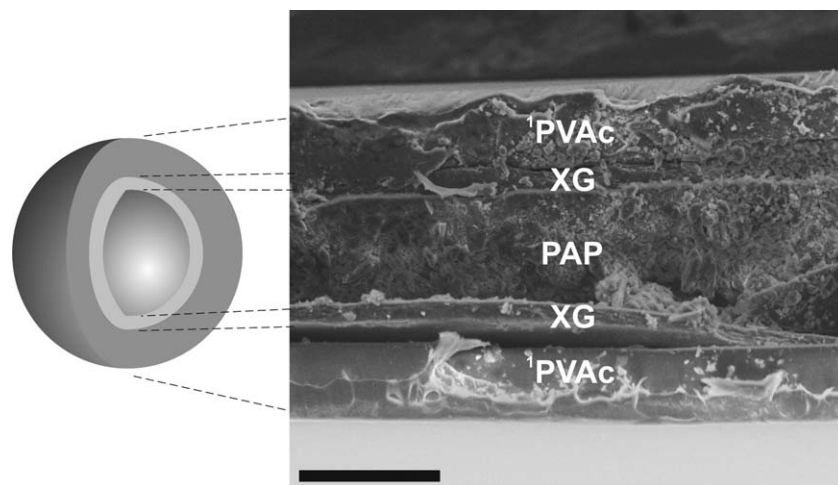


Figure 3. Schematic representation of a doubly coated capsule and correspondence of its different parts (core and multiple coatings) with a sandwich multilayer membrane, exemplified by an ESEM micrograph of the cross-section of the ${}^1\text{PVAc}/\text{XG}/\text{PAP}/\text{XG}/{}^1\text{PVAc}$ membrane; black scale bar = 100 μm ; the composition of each layer is indicated by the corresponding label; XG = ${}^k\text{XG}$.

PAP/XG/PVA) were also prepared and tested for stability, as discussed below.

Stability of PAP Entrapped Within Sandwich Membranes Towards Either Liquid Detergent Media or Water

Sandwich multilayer membranes with different outer polymeric coatings, that is, using $\text{XG}/{}^1\text{PVAc}$, $\text{XG}/{}^5\text{PVAc}$, $\text{XG}/{}^V\text{PVAc}$, or XG/PVA double-layer films, were prepared. The stability of the resulting membranes towards a liquid detergent was tested in diffusion modules (see Experimental section) and quantified as the amount of PAP remaining after 1 week (see data in Table III). In the cases where the outer layer was composed of ${}^1\text{PVAc}$ or ${}^5\text{PVAc}$, the membranes recovered after contact with the liquid detergent remained visually unaltered and no sign of transport of either the detergent inside or PAP outside was observed. Indeed, iodometric titration data revealed that PAP remained stable inside the sandwich membranes at essentially quantitative levels; 97 and 92% of initial PAP were measured for ${}^1\text{PVAc}/\text{XG}/\text{PAP}/\text{XG}/{}^1\text{PVAc}$ and ${}^5\text{PVAc}/\text{XG}/\text{PAP}/\text{XG}/{}^5\text{PVAc}$, respectively. It should be noted that small amounts of PAP may be lost during membrane disassembly or sample preparation, thus generating quantification errors, and then it may be concluded that either $\text{XG}/{}^1\text{PVAc}$ or $\text{XG}/{}^5\text{PVAc}$ confer a very high or complete protection to PAP in the liquid detergent medium. In contrast, when using $\text{XG}/{}^V\text{PVAc}$ films as PAP coatings, the outer surfaces of the membranes showed some cracks and the interior looked swollen to a certain extent, indicating disruption of the wall. Quantification of the PAP remaining inside the membrane showed that only around two thirds (67%) of the initial still remained. Therefore, the use of ${}^V\text{PVAc}$ instead of ${}^1\text{PVAc}$ or ${}^5\text{PVAc}$ resulted in a decreased stability. This may be due to the dense texture of the latter materials when forming films, as opposed to the granular texture of ${}^V\text{PVAc}$, which may allow water diffusion inwards. Finally, if PVA is used as outer wall material, the recovered membranes after experiments in liquid detergent medium show gel-like, soft textures, clearly indicating the diffusion of water through the PVA film, but not complete dissolution of such film. The loss of bleaching agent is also obvious (PAP

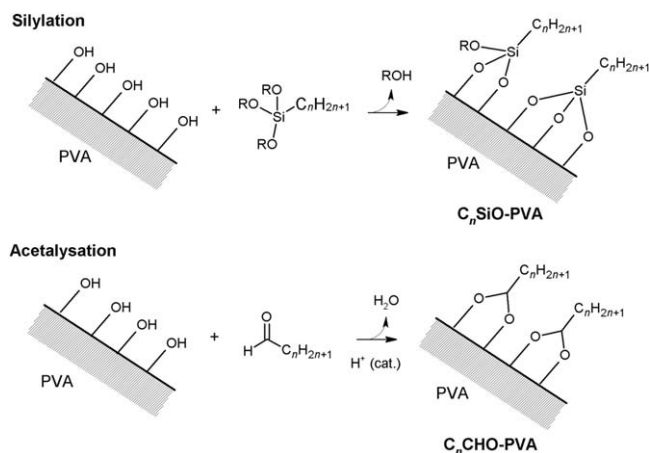
stability = 20%, see Table III), thus confirming that XG/PVA films are not appropriate as coatings for PAP. This is consistent with the high solubility of PVA in water and consequently, low stability in water-based formulations, as previously demonstrated for analogous capsules.¹⁵

Stability experiments were also done with water as liquid media. In the case of ${}^1\text{PVAc}/\text{XG}/\text{PAP}/\text{XG}/{}^1\text{PVAc}$, the membrane experienced little changes (if any) after an exposure time of 1 week, and 94% of the entrapped PAP remained stable, as revealed by iodometric analysis (see Table III). In sharp contrast, neither ${}^V\text{PVAc}/\text{XG}/\text{PAP}/\text{XG}/{}^V\text{PVAc}$ nor $\text{PVA}/\text{XG}/\text{PAP}/\text{XG}/\text{PVA}$ succeeded in maintaining PAP stable; quite the opposite was observed, as the coating films and the interior were completely dissolved or dispersed in the liquid, releasing the entire amount of bleaching agent. In the first case (${}^V\text{PVAc}$ as outer layer), the solid coating had dispersed into a suspension in the water medium within less than 2 days. In the PVA case, not surprisingly, the polymeric material had completely dissolved within the first day of experiment. Therefore, PVAc films cast from solutions in acetone, and thus consisting of a continuous phase of dense polymeric material (e.g., ${}^1\text{PVAc}$), showed a high resistance

Table III. Stability of PAP (%)^a in polymer/XG/PAP/XG/polymer Sandwich Multilayer Membranes

| Polymer | Liquid medium | |
|-------------------|------------------|-------|
| | Liquid detergent | Water |
| ${}^1\text{PVAc}$ | 97 | 94 |
| ${}^5\text{PVAc}$ | 92 | - |
| ${}^V\text{PVAc}$ | 67 | 0 |
| PVA | 20 | 0 |

^a The stability is reported as the amount of PAP remaining after 1 week experiments, measured by dismantling the membrane from the diffusion module and analyzing the whole membrane (or only the interior, where feasible) by iodometric titration; deviations up to $\pm 10\%$ for the stabilities are estimated.



Scheme 1. Suggested surface functionalization of PVA films by treatment with either trialkoxysilanes (silylation) or aldehydes (acetalization). Three different silanes were used, yielding C_1SiO -PVA ($n = 1$, $R = Et$), C_8SiO -PVA ($n = 8$, $R = Me$), and $C_{16}SiO$ -PVA ($n = 16$, $R = Me$), whereas nonanal ($n = 8$) yielded C_8CHO -PVA.

to aqueous environments, whereas those cast from aqueous dispersions, and thus formed by aggregated particles (e.g., ∇ PVAc), were readily dispersed in water. Finally, PVA films quickly disintegrated in aqueous media, as expected.

The above results confirm that PVAc performs efficiently as a water-barrier wall material when its consistency is that of a dense layer, as expected from its hydrophobicity. In contrast, if the texture of the PVAc layer is not completely dense, as is the case for the granular ∇ PVAc, water permeates through it. However, even in the event of water penetration in liquid detergent media, the swelling of the inner XG layer slows down the release of PAP, thus maintaining a moderately high stability (i.e., 67% remaining after 1 week, see Table III). It is therefore demonstrated here that flat multilayer membrane designs are valid for stability assessments for bleach stability tests, as the trends (PVA protects less than PVAc) are consistent with those found for analogous double-layer capsules prepared by fluid bed coating PAP particles consecutively with XG and finally (after drying the so-formed single-coating capsules) with PVAc.¹⁵ It should be noted that, whereas these experiments in liquid detergent confirm the stability exerted by the XG/PVAc double-layer coatings to PAP, experiments in water

should not be directly related to the release behavior under washing conditions, where several other factors such as mechanical stress are expected to be of importance.

Functionalization of PVA Film Surfaces for Decreased Hydrophilicity

A completely different approach to the double-layer films described above was also considered here to obtain dual hydrophilic–hydrophobic coatings. In this new approach, films of PVA, a highly hydrophilic and even water-soluble material (leading to poor coating efficiency in aqueous environments, see above), are functionalized with organic moieties, aiming at decreasing the hydrophilicity of their surfaces, while keeping the chemical and physical characteristics of the bulk material. Two different functionalization procedures were performed. Contact angles were measured for the resulting films, as indications for their surface hydrophilic or hydrophobic character.

PVA films were treated with different trialkoxysilanes or aldehydes (in the presence of sulfuric acid as a catalyst in the latter case) in heptane, yielding the corresponding silylated or acetylated films, respectively. The structures of the grafting reagents and the suggested reaction pathways between them and PVA films are depicted in Scheme 1. Three silylating agents with alkylic side-chains of different lengths (methyl, octyl, or hexadecyl), and one aldehyde (nonanal, containing octyl as side-chain) were used. The thereby modified PVA films are abbreviated as C_1SiO -PVA, C_8SiO -PVA, and $C_{16}SiO$ -PVA (silylated) or C_8CHO -PVA (acetylated), respectively (see Scheme 1). After treatment, the films did not show significant changes as compared to the pristine PVA films, based on SEM observations (not shown).

The hydrophilic or hydrophobic character of the modified PVA film surfaces was estimated by measuring the contact angles of water on them. It should be noted that contact angles depend on roughness, topography, and chemistry of the surface. Herein, films were prepared by identical procedures and treated under similar functionalization conditions, and therefore, surface roughness and topography are not expected to differ significantly among specimens. Thus, contact angle data can be used as a qualitative indication of film surface chemistry (and of hydrophilic or hydrophobic properties). The photographs of the contacted water droplet–film pairs and data measured for each one are presented in Figure 4. Water droplets on unmodified

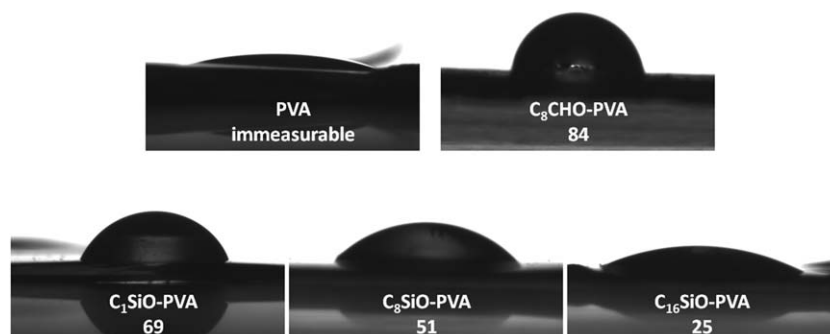


Figure 4. Photographs of water droplet–film pairs, where the films were pristine PVA, acetylated PVA (C_8CHO -PVA) or silylated PVA (C_1SiO -PVA, C_8SiO -PVA, and $C_{16}SiO$ -PVA); the figures below each film name represent the contact angle in degrees, except in the case of the pristine film (PVA), where the water droplet immediately collapsed by dissolving the film and, therefore, the contact angle could not be measured.

PVA films did not stand for the sufficient amount of time for a contact angle to be measured; instead, the droplets collapsed and dissolved the films in around or less than 2 s. In contrast, all the functionalized PVA films could bear water droplets for tens of seconds on their surfaces, which allowed the contact angles to be measured. It can be thus concluded that functionalization of PVA films with alkylic moieties (by either silylation or acetalization) leads to a clear decrease in their surface hydrophilicities.

According to the actual contact angles, hydrophilicity decreases in the following order: $\text{PVA} > \text{C}_{16}\text{SiO-PVA} > \text{C}_8\text{SiO-PVA} > \text{C}_1\text{SiO-PVA} > \text{C}_8\text{CHO-PVA}$. Acetalization is, in this case, more efficient than silylation, as for identical alkyl chain lengths, the contact angle exhibited by $\text{C}_8\text{CHO-PVA}$ (84°) is clearly larger than that found for $\text{C}_8\text{SiO-PVA}$ (51°). This may be due to a more favorable reaction and/or to the use of an acidic catalyst (H_2SO_4) for aldehyde grafting. Finally, by comparing the silylated films, it was clearly observed that hydrophilicity decreases with decreasing alkyl chain length (contact angles for $\text{C}_{16}\text{SiO-PVA}$, $\text{C}_8\text{SiO-PVA}$, and $\text{C}_1\text{SiO-PVA}$: 25° , 51° , and 69° , respectively). Such a trend does not match the expected order of hydrophobic character of the side-chains (it is in fact opposite to it), and thus, might be explained by slower grafting rates of the bulkier silanes bearing longer alkyl groups. A similarly anomalous trend has been reported for paper samples treated with alkyltrichlorosilanes in the vapor phase, where methyl-functionalization results in higher contact angles as compared to decyl-functionalization.²⁶ This apparent higher grafting density of the shorter methyl siloxanes was there ascribed to phenomena such as cross-linking over the paper surface in the short range.

The functionalization of PVA with silanes was claimed in a patent as long back as the 1970s.²⁷ However, the process described therein involved grafting the organic moieties on the bulk of the polymer in solution, and subsequently casting films of the modified polymeric material. The process presented here is rather simpler, more straightforward and only involves functionalization of the film surfaces. Furthermore, bulk functionalization of PVA in solution with trimethylsilyl groups has also been reported.^{28,29}

It has been here demonstrated that a highly hydrophilic polymer (PVA), which forms readily water-soluble films, can be surface functionalized by grafting alkyl chains. Both acetalization and silylation induced decreases in the hydrophilicity of PVA film surfaces, the former process being more efficient under the grafting conditions studied here. Moreover, shorter chain lengths (methyl) exert larger effects in the case of silylation, although the (currently unknown) different degrees of functionalization might be responsible for such a phenomenon; this could be the basis for further investigations in this context. These successful results may still be optimized by further adjusting the type of reagent used and/or the grafting conditions, and as in the case of silylated paper,²⁶ films modified in this way may be even able to repel water. Thus, it is expected that the functionalization procedure reported here might be applied to the hydroxyl-rich surfaces of hydrophilic (or even water-soluble) polymeric coatings for improved stability of encapsulated active ingredients in aqueous environments.

CONCLUSIONS

Dual hydrophilic–hydrophobic films, as those prepared by first casting one layer of XG, and subsequently a second layer of PVAc onto it, served as flat, two-dimensional models for double coatings in capsules. The resulting XG/PVAc double-layer films were used to contain a bleaching agent (PAP), yielding sandwich multilayer membranes where the inner coating is hydrophilic whereas the outer one is hydrophobic. The source of PVAc material and the type of casting fluid influenced the performance of the coatings. Highest stabilities of the bleaching material were observed both in detergent and in water for PVAc films cast from homogeneous solutions in acetone ($^1\text{PVAc}$ and $^5\text{PVAc}$), as the PVAc layers thus obtained were dense and devoid of pores or defects; therefore, they effectively act as water-barrier coatings. In contrast, PVAc films cast from aqueous dispersions ($^V\text{PVAc}$) of the polymeric material were granular in texture, formed by aggregated particles; in consequence, the stability of enclosed PAP was lower in liquid detergents, due to (slow) water diffusion into the membranes, whereas in pure water the $^V\text{PVAc}$ coating readily dispersed releasing the bleaching agent. For comparison, PVA, a hydrophilic polymer, was used as outer wall material; not surprisingly, the resulting membranes provided low protection for the bleaching material, although the inner XG layers formed gels with water which slowed down diffusion phenomena in liquid detergent, thus increasing the stability. These results confirm that the advantage of XG/PVAc double coatings for capsules stem from the combined effect of the outer water-barrier layer and the inner water-sink layer.

In a different approach, silylation or acetalization of PVA films drastically modifies their surface properties, conferring a certain degree of hydrophobicity (decreased hydrophilicity) to such a highly hydrophilic polymer. A PVA material which effectively lies at the hydrophilic–hydrophobic borderline (contact angle = 84° for water on the acetalized $\text{C}_8\text{CHO-PVA}$) has been prepared by this method. Therefore, such a strategy may be used to increase the stability of PVA capsules in aqueous environments or water-containing formulations such as liquid detergents.

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