

Article

Impact of Surface Tension and Surface Energy on Spray Coating Paper with Polysaccharide-Based Biopolymers

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Abstract: The demand for sustainable packaging has increased the interest in biopolymer coatings as alternatives to plastic-based barriers on paper and board. Alginate and chitosan offer promising barrier properties by improving gas barrier and grease resistance. However, their high viscosity at low solid contents presents challenges for uniform coatings, especially in possible future large-scale applications but also in existing research. This study evaluates spray coating, a non-conventional application method in the paper industry, to apply biopolymer coatings, an approach underexplored in previous studies. The effects of substrate surface energy and biopolymer surface tension on air permeability, grease resistance, and water vapor transmission were evaluated. Contact angle measurements showed that surface energy strongly influences the wetting behavior of these biopolymers, with hydrophilic substrates and lower-surface-energy liquids promoting better droplet spreading. This improved wetting resulted in better barrier performance at low application weights, further enhanced by surfactant addition. At higher application weights, surface energy had less impact on barrier properties. SEM imaging revealed drying defects at increased coat weights, affecting film integrity. These findings demonstrate the potential of spray coating as a scalable method for biopolymer application while highlighting the need for optimized drying conditions to enhance film uniformity and barrier performance.

Keywords: barrier coating; spray coating; alginate; chitosan; surface tension; surface energy



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1. Introduction

Packaging materials play a crucial role in many fields like medical and pharmaceuticals packaging and industrial packaging, as well as in the food industry as they extend the shelf life both by mechanically protecting the packed goods and by ensuring a controlled atmosphere within the packaging [1]. The barrier requirements for food packaging vary significantly depending on the type of food being packaged. High-barrier applications include packaging for oils, nuts, and coffee, which require oxygen transmission rates (OTRs) below $10 \text{ cm}^3 \cdot \text{m}^{-2} \cdot \text{d}^{-1} \cdot \text{bar}^{-1}$ and water vapor transmission rates (WVTRs) below $10 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$. Other products, such as milk and dairy items, require similar WVTR levels but can tolerate much higher oxygen transmission rates, with values up to $1000 \text{ cm}^3 \cdot \text{m}^{-2} \cdot \text{d}^{-1} \cdot \text{bar}^{-1}$ being acceptable. In contrast, certain cheeses demand low oxygen transmission rates of around $10 \text{ cm}^3 \cdot \text{m}^{-2} \cdot \text{d}^{-1} \cdot \text{bar}^{-1}$, while their water vapor barrier requirements are more relaxed, allowing WVTR values below $1000 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ [2]. Conventional plastic-based packaging, while highly effective in providing these barrier properties, poses significant environmental challenges [3]. As a result, there is increasing interest in developing sustainable alternatives derived from renewable resources [4–7]. One such approach is the use of paper-based packaging materials coated with biodegradable biopolymers [8,9]. Paper provides structural

integrity and mechanical strength, while also being recyclable and biodegradable [3,10]. But, because of its low barrier properties compared to other packaging materials, the addition of barrier layers is necessary. Conventionally, these barrier layers are metal- or petroleum-based, but could be replaced with biopolymer coatings that, depending on the material and application demands, provide sufficient barrier properties for many packaging applications [9,11–14].

Biopolymers such as alginate and chitosan have gained attention as sustainable barrier coatings for paper substrates due to their biodegradability, film-forming ability, and non-toxicity. These biopolymers improve critical barrier properties such as air permeability, grease resistance, gas resistance, and, to a limited extent, water vapor resistance [14–21]. The above-mentioned barrier demands for different foods can theoretically be met with these materials since previous research has shown excellent barrier properties of around $1 \text{ cm}^3 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ for chitosan and alginate films regarding oxygen transmission rate [21]. While the water vapor transmission rate of these hydrophilic materials is not sufficient for most coating applications, it can be improved by crosslinking [22,23]; a combination with clay [24], curdlan [25], soy protein [26], and zein and essential oil [12]; or additional coatings with beeswax [27] or linseed oil [28]. In special applications, chitosan has even been shown to be able to produce superhydrophobic surfaces [29,30]. This leads to the possible application of these coatings even in extremely moist environments since superhydrophobic coatings have been shown to decrease water vapor transmission substantially [31]. Research has also shown the excellent grease barriers of these materials which are necessary for food packaging applications [32]. Various application methods for biopolymers have been discussed, such as rod coating [12,17,26,33], dip coating [34], slot-die coating [35,36], and spray coating [37,38]. Some of these coating methods have faced difficulties in achieving sufficiently high coat weights in one application step due to the high viscosity and low solid contents of alginate and chitosan solutions [39,40]. This would make large-scale industrial application difficult and shows the need for alternative application methods. Another advantage is the use of a non-contact method leading to a lower number of web breaks in the paper production process and potentially leading to a more uniform coating layer thickness compared to other conventional coating methods. Spray coating also offers the potential of applying coatings over a wider range of application weights for these materials as shown for micro-fibrillated cellulose (MFC) at even lower solid contents [41,42]. Previous studies have demonstrated that the spraying of MFC led to a homogeneous film on the paper substrate surface, reducing air permeability and improving mechanical properties [41,43]. The spray application of polysaccharides such as alginate, cationic guar gum, or chitosan on wet paper substrates has resulted in an increase in paper stiffness and strength, with the addition of alginate also reducing air permeability [37]. Spray coating has also been used to improve the extensibility of paper for further use in 3D packaging applications by the addition of gelatin and agar [44]. Coating trials using a film press in comparison to spray coating have been performed by this research group, leading to the conclusion that, for alginate and chitosan, the application weight is limited when a film press is used and that substrate hydrophobicity seems to have a major impact on the coating performance [38].

Important steps in spray coating include the atomization of the droplets, their impact and deposition on the substrate, and their spreading and film formation on the surface. Atomization is influenced by the coating material's properties, such as density, viscosity, and surface tension, along with the nozzle geometry and operating parameters. The main influencing factors affecting drop deposition are droplet density, velocity, size, and surface tension, as well as the surface characteristics of the substrate [45–47]. The subsequent spreading of the droplets and film formation are governed by the properties of the coating

material and substrate and their interaction. In the initial stages of film formation, spreading and surface wetting of the droplets play a crucial role, which can be quantified by the contact angle [47]. Young's equation (Equation (1)) describes this phenomenon by considering interfacial tensions at the three-phase boundary. Wetting is favored by low solid–liquid interfacial tension (γ_{sl}), high solid–vapor interfacial tension (γ_{sv}), and low liquid–vapor interfacial tension (γ_{lv}) [48,49].

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}}, \quad (1)$$

Another method of describing the spreading behavior of liquids on a substrate is the spreading coefficient stated in Equation (2), again described by the interfacial tensions of the individual materials and their interaction. This shows that for spreading to occur ($S > 0$), the solid surface energy (γ_{sv}) must be larger than the sum of the liquid surface tension (γ_{lv}) and solid–liquid interfacial tension (γ_{sl}). But, overall, the solid–liquid interfacial tension is described to be the greater determining value for wetting behavior than the individual surface tension of the liquid or surface energy of the solid [50].

$$S = \gamma_{sv} - \gamma_{lv} - \gamma_{sl} \quad (2)$$

Furthermore, the viscosity of the coating material affects droplet spreading, as high viscosity may hinder spreading before the solvent is evaporated during drying [47,51].

This study investigates the spray coating of alginate and chitosan on paper substrates, examining how substrate surface energy (modified by hydrophobization), biopolymer surface energy (modified by the addition of surfactant), and application weight influence the resulting barrier properties. By evaluating barrier properties such as air permeability, grease resistance, and water vapor transmission, and analyzing the coating morphology through SEM imaging, this work provides additional insights into the feasibility of spray application as a scalable and efficient method for biopolymer coatings in sustainable packaging. Even though the water vapor transmission rate of these polysaccharide-based materials has to be further improved for several food packaging applications, this study still increases our understanding of an alternative application method for highly viscous materials that can be used for specific packaging applications or as one layer in a multilayer packaging.

2. Materials and Methods

2.1. Paper Properties

The paper substrate used in this study was a testliner from 100% recycled fibers, industrially produced on a gapformer to reduce two-sidedness. To minimize variations in the paper's structural properties affecting the measured parameters, both the top and bottom sides of the paper were used, treated with enzymatically degraded starch on one side (hydrophilic side) and with the same starch and an added acrylic sizing agent on the other side (hydrophobic side). This approach ensured a consistent substrate for investigating the influence of surface energy on barrier film performance. A series of standardized paper tests were performed to characterize the substrate. The results, along with the number of samples and corresponding standard methods, are summarized in Table 1.

All measurements, except for grease resistance, were performed under standard conditions of 23 °C and 50% relative humidity in accordance with ISO 187:2022, which defines the standard atmosphere for the conditioning and testing of paper materials. The grease resistance test was conducted under ambient conditions in a ventilated hood. In addition to Cobb60 water absorption measurements, the surface hydrophobicity was further characterized using water contact angles and surface energy measurements. Water contact

angle measurements were performed using a Fibro Dat 1100 (Fibro System, Stockholm, Sweden) in accordance with TAPPI T 558, using 4 μL drops.

Table 1. Paper properties, standard test method, number of samples, values, and 95% confidence intervals.

Paper Property	Standard/Test Procedure	No. of Samples	Hydrophobic Side	Hydrophilic Side
Grammage	ISO 536:2019 “Paper and board—Determination of grammage”	10	$121.9 \text{ g}\cdot\text{m}^{-3} \pm 0.7$	
Roughness	ISO 8791-2:2013 “Paper and board—Determination of roughness/smoothness (air leak methods) Part 2: Bendtsen method”	10	$970 \text{ mL}\cdot\text{min}^{-1} \pm 77$	$1691 \text{ mL}\cdot\text{min}^{-1} \pm 72$
Air permeance	ISO 5636-3:2013 “Paper and board—Determination of air permeance (medium range)—Part 3: Bendtsen method”	10	$4.0 \mu\text{m}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1} \pm 0.1$	
Water vapor transmission rate	ISO 2528:2017 “Sheet materials—Determination of water vapour transmission rate (WVTR)—Gravimetric (dish) method”	3	$547.1 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1} \pm 31.2$	
Grease resistance (KIT)	T 559 cm-12 “Grease resistance test for paper and paperboard”	3	1.0 ± 0	1.8 ± 0.3
Cobb60	ISO 535:2023 “Paper and board—Determination of water absorptiveness—Cobb method”	10	$42.1 \text{ g}\cdot\text{m}^{-2} \pm 6.1$	$117.5 \text{ g}\cdot\text{m}^{-2} \pm 2.7$
Total surface energy	OWRK theory	12	$15.9 \text{ mN}\cdot\text{m}^{-1}$	$24.8 \text{ mN}\cdot\text{m}^{-1}$
Surface energy polar	OWRK theory	12	$0.1 \text{ mN}\cdot\text{m}^{-1}$	$11.0 \text{ mN}\cdot\text{m}^{-1}$
Surface energy dispersive	OWRK theory	12	$15.8 \text{ mN}\cdot\text{m}^{-1}$	$13.7 \text{ mN}\cdot\text{m}^{-1}$

The paper’s surface energy, including its polar and dispersive components, were calculated using the Owens–Wendt–Rabel–Kaelble (OWRK) method [52–54], as described in detail in prior research [55]. This method calculates surface energy components from contact angle measurements conducted with an OCA200 (DataPhysics Instruments, Baden-Württemberg, Germany). These measurements were carried out using 2 μL drops of three test liquids with varying polarity: deionized water, diiodomethane (ReagentPlus 99%, Sigma-Aldrich, St. Louis, MI, USA), and ethylene glycol (99%, Carl Roth, Karlsruhe, Germany). The surface tension values of the test liquids (total, polar, and dispersive components) required for the calculations were taken from the DataPhysics database. To minimize penetration effects while giving the drop sufficient time to stabilize on the substrate’s surface, contact angles were recorded immediately after drop placement. These times were optimized for each liquid, with measurements taken at 50 ms for water and diiodomethane and 20 ms for ethylene glycol. For each liquid, twelve drops were measured per paper sample, and the mean contact angle values were used to calculate the surface energy. The total as well as polar and dispersive components of the surface energy are presented in Table 1. The contact angles for the calculation and their confidence intervals are shown in Table S1

in the Supplementary Information as well as the mean value and confidence intervals of the resulting surface energies (Figures S1 and S2 in the Supplementary Information) at the outer borders of these confidence intervals.

2.2. Biopolymer Solutions

To prepare an aqueous alginate solution, sodium alginate powder (viscosity of 15–25 mPa·s at 1% in water at 25 °C, Sigma-Aldrich, St. Louis, MO, USA) was gradually added in small portions to deionized water preheated to 75 °C, to achieve a 5 wt% concentration. The solution was stirred continuously for 6 h at the same temperature.

For the 5 wt% chitosan solution, chitosan powder (88%–89% degree of deacetylation, BioLog Hefpe, Landsberg, Germany) was added to deionized water heated to 50 °C and stirred for 30 min. Subsequently, acetic acid ($\geq 99\%$, Carl Roth, Karlsruhe, Germany) was first diluted to 60% and added to achieve a final concentration of 4 wt% acetic acid. The mixture was stirred for an additional 2 h at 50 °C. Both biopolymer solutions were stored at 5 °C until further use.

For the addition of surfactant to the alginate and chitosan solutions, Tween 80 (Ph. Eur., Carl Roth, Karlsruhe, Germany) was first diluted to 10 wt%. Then, 0.2 wt% of the surfactant was added to the total water content in the respective biopolymer solutions. The amount of surfactant was selected based on pretrial experiments (Figures S3 and S4 in Supplementary Information), in which different surfactant concentrations were tested to identify the amount needed to reach a minimum in surface energy.

The surface tension of the solutions was measured using the pendant drop method with an OCA200 (DataPhysics Instruments, Baden-Württemberg, Germany). Drops were formed using a 1.83 mm cannula inside a glass cuvette with a lid, which was filled to approximately one-fifth of its volume with water to increase relative humidity and prevent the drop's surface from drying during measurement. The measurement temperature was maintained at 23 °C. For each material, five drops were formed and recorded. Due to marginal elongation of the drops over time, the surface tension value was recorded at 30 s after drop formation to ensure reproducible results. Table 2 shows the mean surface tension values and 95% confidence intervals.

Table 2. Surface tension of biopolymer solutions with and without surfactant.

Surfactant Added	Alginate	Chitosan
No	58.9 mN m ⁻¹ ± 0.2	62.7 mN m ⁻¹ ± 0.1
Yes	43.1 mN m ⁻¹ ± 0.2	42.5 mN m ⁻¹ ± 0.1

The viscosity of the biopolymer solutions (Figure 1) was measured using a Physica MCR 301 rotational rheometer (Anton Paar; Graz, Austria) equipped with a concentric cylinder geometry (CC28.7/Q1) with a gap width of 0.1 mm and a gap length of 15 mm. The shear rates were progressively increased from 1 s⁻¹ to 49,700 s⁻¹ and subsequently decreased to the same range. This shows that none of the materials show thixotropic behavior. The measurements were performed at 23 °C. To ensure reproducibility of the coating trials, these measurements were also performed over the duration of 14 days to rule out a change in viscosity as possible reasons for performance variations of the materials. These showed no significant change in viscosity for the coating trials over the course of two weeks (Figure S5 in the Supplementary Information).

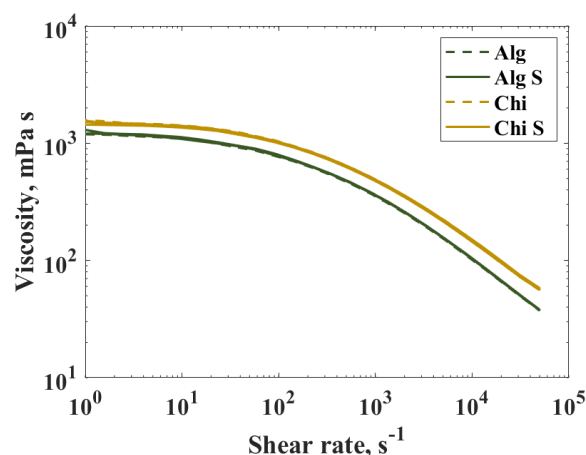


Figure 1. Viscosity of biopolymer solutions with and without surfactant.

2.3. Biopolymer Contact Angles

Contact angles of the biopolymers, with and without surfactant, were determined on both paper substrates using the sessile drop technique with an OCA200 instrument (DataPhysics Instruments, Baden-Württemberg, Germany). Prior to testing, the biopolymer solutions and paper substrates were conditioned at 23 °C and 50% relative humidity in accordance with ISO 187:2022. A 2 μ L liquid drop was dispensed onto the substrate using a 0.8 mm cannula, and the sample holder was repositioned to allow the drop to detach completely from the needle tip. The process was captured using a high-speed camera. Analysis of the drop behavior started after the drop detached from the needle tip and reached its maximum contact angle, using SCA202 software (V.5.0.32 build 5032, DataPhysics). For each liquid–paper combination, 12 drops were measured, and the mean contact angle along with the 95% confidence intervals are reported.

2.4. Coating

The spray coating trials were conducted using a custom-built spray coating unit, described in detail in [38]. As illustrated in the schematic in Figure 2, the setup enables roll-to-roll spray application onto paper substrates. The system consists of two spray nozzles, followed by a drying section equipped with six infrared dryers (3 kW each) and four hot air guns (2 kW each), positioned between the unwind and upwind sections.

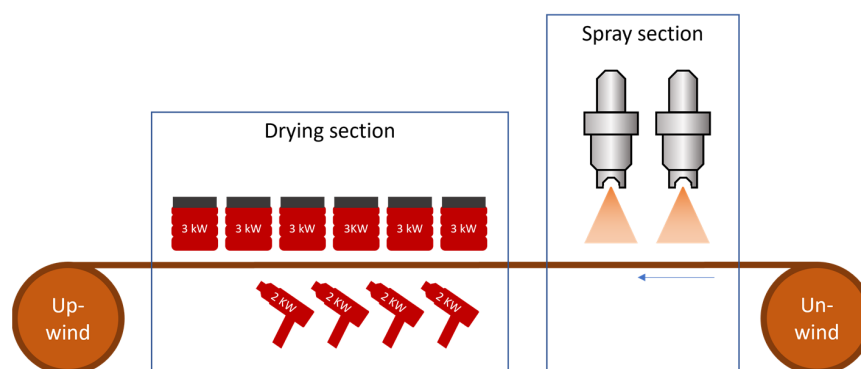


Figure 2. A schema of the purpose-built spray coating unit consisting of an unwind, spray section, drying section, and upwind. The blue arrow symbolizes the machine direction.

2.5. Coated Paper Characterization

The coated samples were analyzed using the same standard procedures as for the raw paper. The application weight was determined by comparing the grammage of the coated samples to that of the raw paper. Barrier properties, including air permeability, grease

resistance (KIT value), and water vapor transmission rate, were measured according to the standard methods described in Section 2.1. All tests were performed at three different positions across the cross-direction of the coating paper. Each sample was tested 30 times for grammage, application weight, and air permeability, and 9 times for grease resistance and water vapor transmission rate. In all graphs, the mean values along with 95% confidence intervals are presented.

2.6. Use of AI in This Article

ChatGPT 4.0 (OpenAI, USA), Perplexity.AI (USA), and Scite.ai (USA) were used in the preparation of this manuscript to search for scientific data and improve language style and readability. The authors reviewed and edited those sections and take full responsibility for the content of the publication.

3. Results and Discussion

3.1. Contact Angle

The measured contact angles of both biopolymers on the paper surfaces are presented in Figures 3 and 4. The results show that applying the drops on the hydrophobic side of the paper leads to the expected higher contact angles compared to the more hydrophilic side. On the more hydrophobic substrate, all contact angles exceed 90° , a commonly used threshold for describing limited wetting behavior and penetration into porous media [56]. In contrast, on the hydrophilic substrate, both biopolymers exhibit contact angles below 90° . The addition of surfactant, which reduces the surface tension of the biopolymers, in line with expectations, further decreases the contact angle. However, the effect of surfactant addition on contact angle is less pronounced than the influence of the paper's hydrophobicity. The effect of surface tension is more significant on the hydrophobic substrate compared to the hydrophilic one. Notably, the contact angles of chitosan continuously decrease over time, indicating that the drops spread further on the paper surface during the measurement period. This behavior is most likely caused by the higher viscosity of the chitosan and therefore slower wetting dynamics. The spreading behavior could contribute to enhanced surface coverage, which may improve barrier layer uniformity during the coating trials depending on the coating speed. It is important to note that the volumes of the investigated drops (Figures S6 and S7 in the Supplementary Information) do not significantly decrease over time, confirming that the observed decrease in contact angles is due to wetting rather than penetration into the substrate. Reduced penetration is expected to have a positive influence on barrier performance, as it ensures that the barrier material remains on the surface, forming an even and uniform layer.

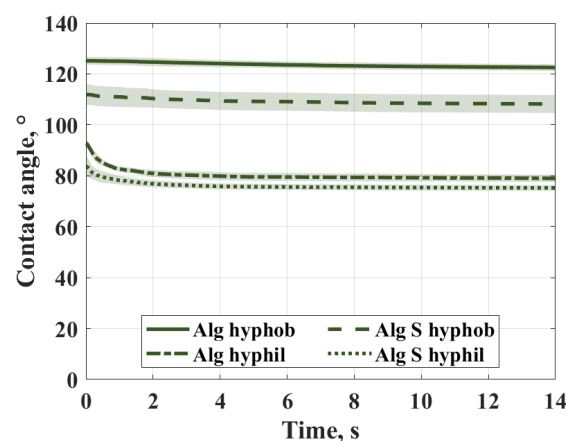


Figure 3. Contact angles of alginate with and without surfactant (S) on the hydrophobic and hydrophilic paper substrate; shaded areas show the 95% confidence interval.

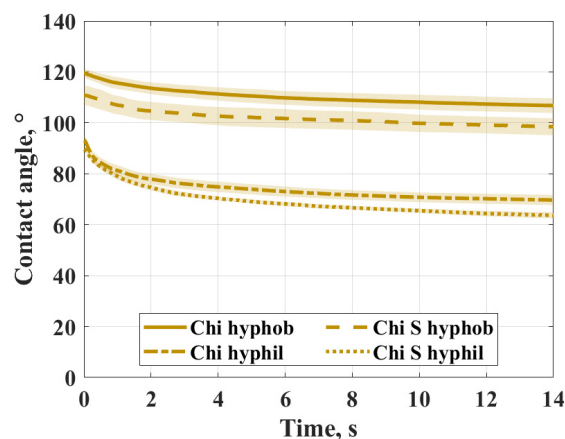


Figure 4. Contact angles of chitosan with and without surfactant (S) on the hydrophobic and hydrophilic paper substrate; shaded areas show the 95% confidence interval.

3.2. Air Permeance

Air permeance measurements, depicted in Figures 5 and 6, indicate a significant decrease from the $4 \mu\text{m}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ recorded for the uncoated raw paper for both applied biopolymers. Overall, chitosan application exhibits lower air permeance compared to alginate. This is most likely attributed to the lower contact angles measured for this material and therefore better surface coverage. In contrast, other gas transmission values (i.e., oxygen transmission) in the literature are lower for alginate than for chitosan films [21,57]; therefore, we ascribe the superior air permeance to the surface coverage and not to the material's inherent properties. At higher application weights of around $8 \text{ g}\cdot\text{m}^{-2}$, the samples become impermeable to air, regardless of the biopolymer used or the paper surface energy. At lower application weights of approximately $4 \text{ g}\cdot\text{m}^{-2}$, improved barrier properties are observed on the more hydrophilic substrate, where chitosan coatings already resulted in an air permeance of $0 \mu\text{m}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$. The addition of surfactant further reduces air permeance rates for both biopolymers, with the effect being more pronounced upon application to the more hydrophobic substrate.

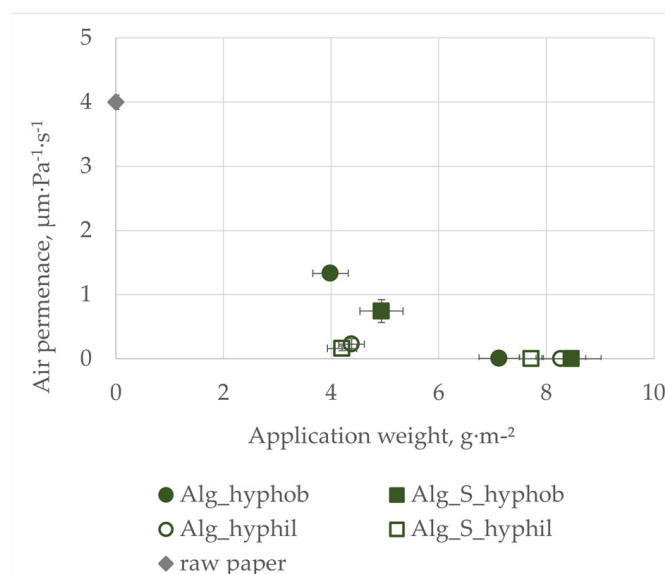


Figure 5. The air permeance of alginate with and without surfactant (S) on the hydrophobic and hydrophilic paper substrate.

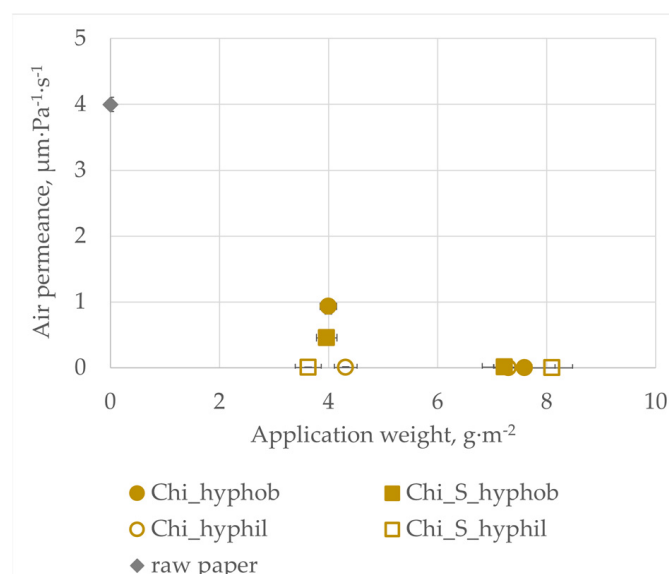


Figure 6. The air permeance of chitosan with and without surfactant (S) on the hydrophobic and hydrophilic paper substrate.

3.3. Grease Resistance (KIT)

The grease resistance results (see Figure 7) show only a slight improvement for alginate at lower application weights around $4 \text{ g} \cdot \text{m}^{-2}$. However, they still demonstrate the advantage of application on a more hydrophilic substrate. Chitosan coatings (see Figure 8) at lower application weights around $4 \text{ g} \cdot \text{m}^{-2}$ give better grease resistance compared to alginate, especially when applied to the hydrophilic substrate where a performance comparable to higher application weights of around $8 \text{ g} \cdot \text{m}^{-2}$ on the hydrophobic substrate is achieved. At coat weights of approximately $8 \text{ g} \cdot \text{m}^{-2}$, the addition of surfactant does not increase the grease resistance of either material, and also, at lower application weights, no significant improvements can be seen. For grease resistance, the hydrophobicity of the paper substrate has a greater influence on the barrier performance than the surface energy of the biopolymers.

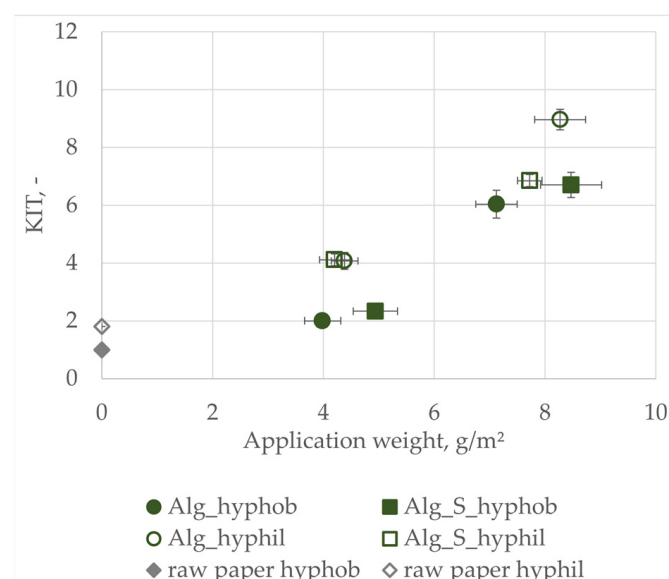


Figure 7. The grease resistance (KIT value) of alginate with and without surfactant (S) on the hydrophobic and hydrophilic paper substrate.

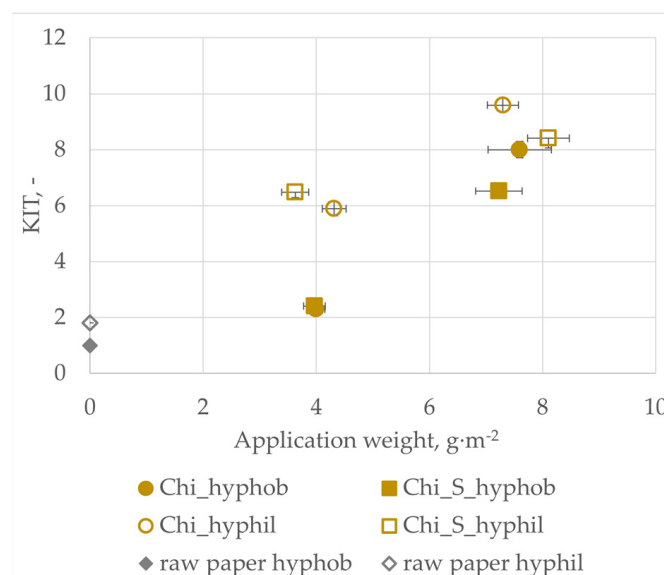


Figure 8. The grease resistance (KIT value) of chitosan with and without surfactant (S) on the hydrophobic and hydrophilic paper substrate.

3.4. Water Vapor Transmission Rate

In terms of water vapor transmission rates, alginate (Figure 9) is outperformed by chitosan (Figure 10) across the entire range of application weights. At lower application weights, the benefits of applying biopolymers to a hydrophilic substrate are still evident, but are less pronounced as in the air permeance and grease resistance tests described above. The addition of surfactant does not show a clear effect with regard to barrier properties in this measurement. Higher application weights generally result in lower water vapor transmission rates; however, these results are no longer influenced by the addition of surfactant or the hydrophobicity of the paper surface. For both coating materials, similar performance is achieved by applying biopolymers with surfactant to a hydrophilic substrate at lower application weights and by using coatings with higher application weights. The hydrophilic nature of biopolymers does not make them ideal candidates for water vapor barrier applications. The water vapor transmission rates observed in this study align with previous research on the same materials [15]. The intrinsic properties of the biopolymers may limit further improvements in WVTR, suggesting that surface energy and surface tension optimization play a secondary role in influencing this barrier performance. These results are insufficient for many food packaging applications described in the introduction, but goods like cheese that demand high oxygen but only moderate water vapor barriers could be a possible target for these materials. However, studies have demonstrated that WVTRs can be reduced by combining alginate or chitosan with other materials [12,25,27,58,59] or through post-treatment modifications [26,28]. But, since the water vapor transmission of polysaccharide films increases with relative humidity, this aspect requires special consideration regarding potential applications, particularly when accounting for fluctuating environmental conditions throughout a package's lifetime [24,60,61].

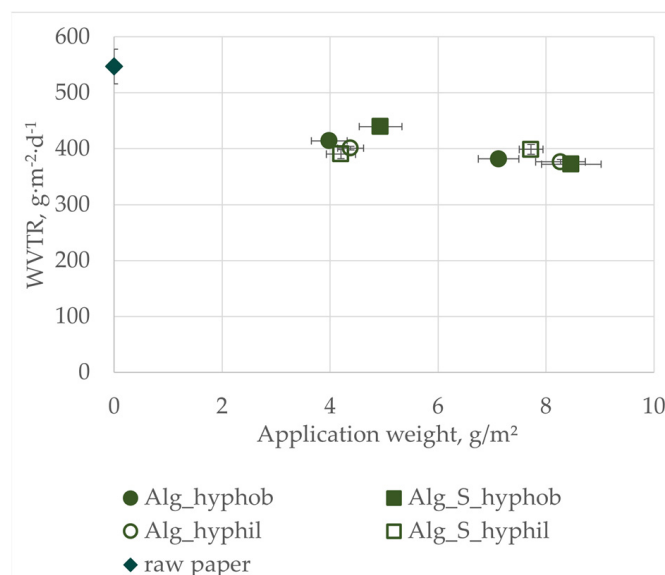


Figure 9. Water vapor transmission rates of alginate with and without surfactant (S) on hydrophobic and hydrophilic paper substrate.

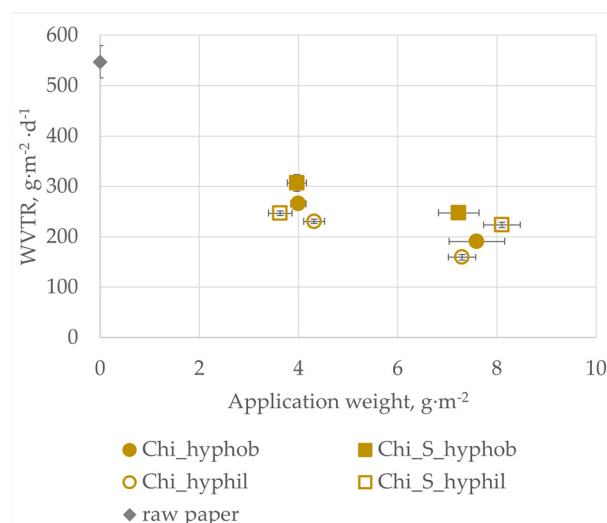


Figure 10. Water vapor transmission rates of chitosan with and without surfactant (S) on hydrophobic and hydrophilic paper substrate.

3.5. SEM Images

SEM images revealed that, while the coatings form a reasonably uniform film on the paper surface, they exhibit too many defects to fully realize their potential as barrier layers.

The SEM images of alginate coatings without added surfactant in Figures 11–14 show the distribution of the layers on the paper surface. Figures 11 and 12 depict lower application weights of approximately $4 \text{ g}\cdot\text{m}^{-2}$. On the hydrophobic substrate (Figure 11), the alginate appears to have spread unevenly, leaving areas where the surface remains uncovered, resulting in poorer barrier properties. In contrast, the alginate coating on the hydrophilic substrate (Figure 12) shows fewer defects and a better overall surface coverage, resulting in better barrier properties. At higher application weights, the SEM images (Figures 13 and 14) reveal that the increased application amount leads to improved surface coverage, but numerous holes in the barrier layer compromise the barrier performance. Upon closer inspection, round alginate bubbles, which appear to have burst or collapsed, are visible. This is likely caused by the intensive drying conditions and the high share of IR

drying of the pilot coater, attributed to the limited length of the drying section of 1.4 m with a total IR drying capacity of 18 kW and an air-drying capacity of 8 kW, where the samples remained for a duration of around 10–20 s depending on the application weight. The increased number of pinholes on the hydrophilic substrate at higher application weights is presumably caused by enhanced wetting leading to a more uniform surface coverage, which in turn can exacerbate drying defects, as, due to the drying conditions, trapped water vapor cannot escape efficiently. Successful efforts have been made to mitigate these effects, such as removing the samples from the coater after spraying and drying them in an external air dryer. However, at present, this approach is unsuitable for the envisaged continuous roll-to-roll application, limits sample size, and is therefore not further pursued. A more desirable drying method would be air impingement drying, which is also applicable to large-scale production. Unfortunately, the current design of the pilot spray coater is not able to accommodate this method, thus making it a key focus for a future rebuild of the pilot coater.

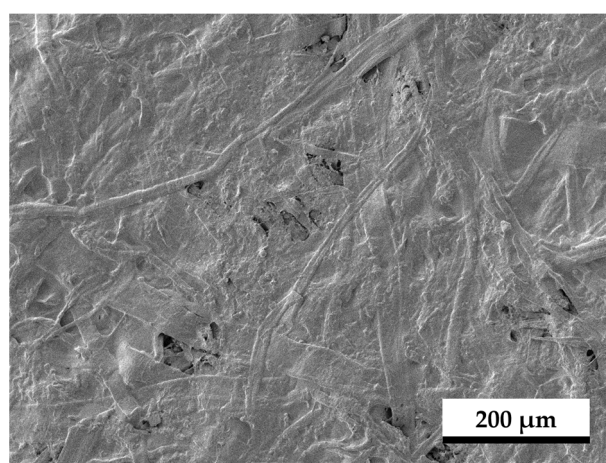


Figure 11. SEM image of alginate coated on hydrophobic substrate (350× mag), with application weight of $4.0 \text{ g} \cdot \text{m}^{-2}$.

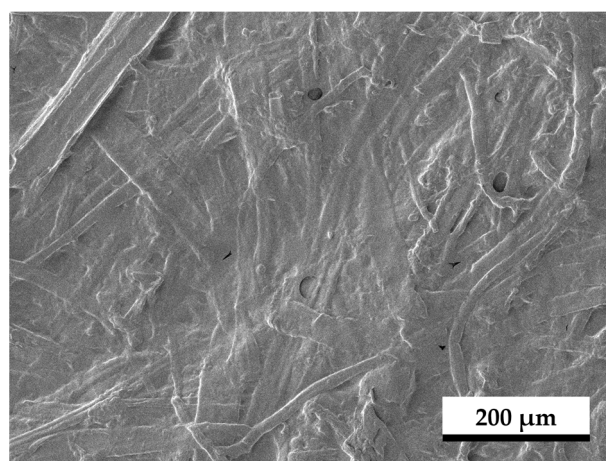


Figure 12. SEM image of alginate coated on hydrophilic substrate (350× mag), with application weight of $4.4 \text{ g} \cdot \text{m}^{-2}$.

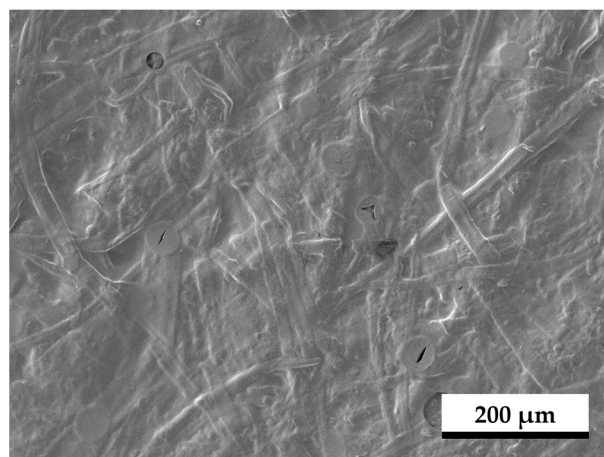


Figure 13. SEM image of alginate-coated hydrophobic paper (350× mag), with application weight of $7.1 \text{ g} \cdot \text{m}^{-2}$.

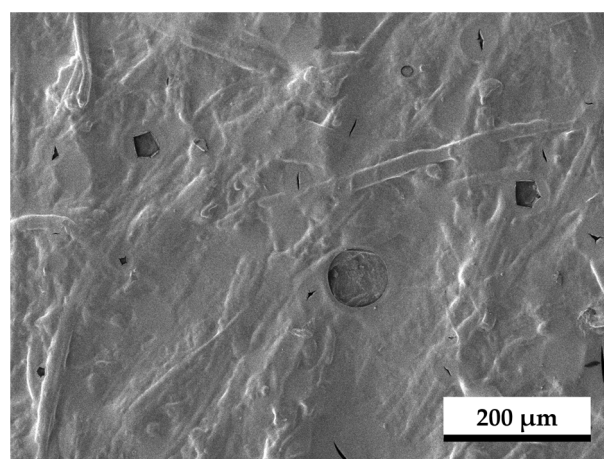


Figure 14. SEM image of alginate-coated hydrophilic paper (350× mag), with application weight of $7.7 \text{ g} \cdot \text{m}^{-2}$.

Figures 15–18 show chitosan coatings at higher application weights. Defects similar, but more pronounced, to those observed in alginate coatings are prominent especially in the samples with surfactant (Figures 17 and 18). All chitosan-coated samples exhibit good spreading of the biopolymer over the surface, but they also display a kind of “bubble” formation in the coating layer. The formation of these “bubbles” is, again, likely a result of the rapid drying process in the pilot coater, where film formation on the coating surface, especially for materials with superior film forming properties, such as chitosan, traps water vapor in these “bubbles”, preventing it from escaping.

At lower application weights, the addition of surfactant appears beneficial for barrier properties. However, at higher application weights, the surfactant seems to disturb the integrity of the film surface. Although this disruption surprisingly does not significantly worsen the measured barrier properties, it also fails to provide the same advantages observed when coating materials of lower surface tension are applied to a more hydrophilic substrate at lower application weights for both materials.

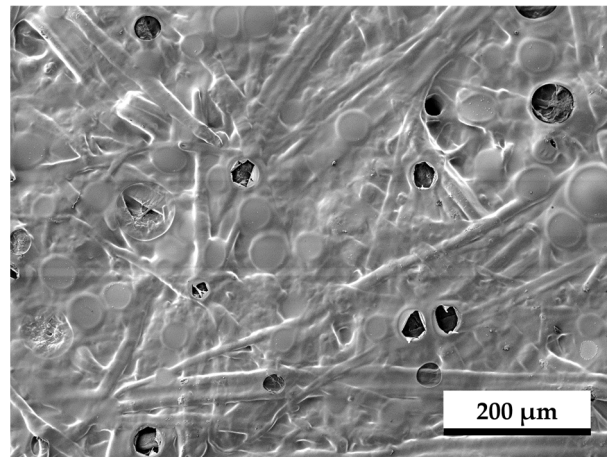


Figure 15. SEM image of chitosan-coated hydrophobic paper (350× mag), with application weight of $7.6 \text{ g} \cdot \text{m}^{-2}$.

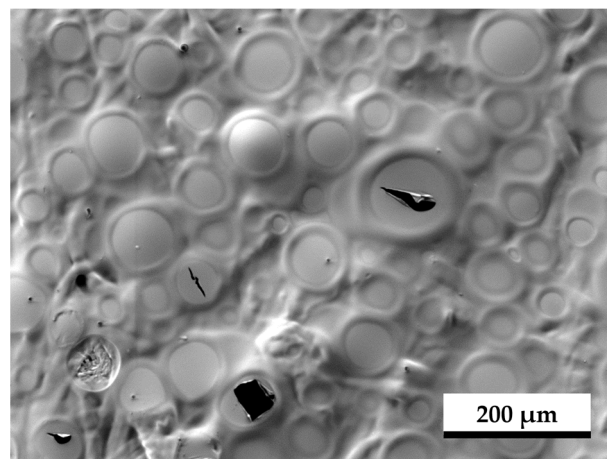


Figure 16. SEM image of chitosan-coated hydrophilic paper (350× mag), with application weight of $7.3 \text{ g} \cdot \text{m}^{-2}$.

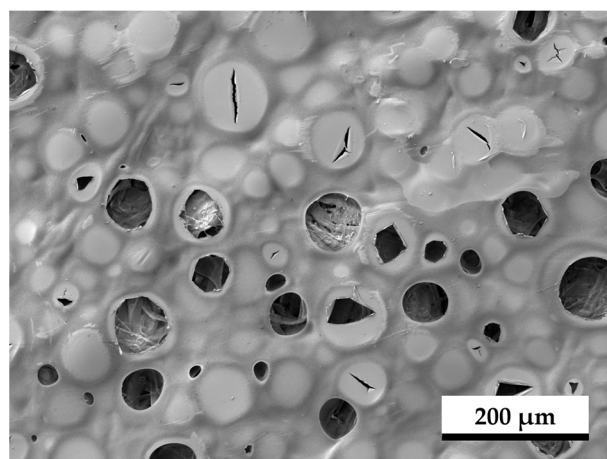


Figure 17. SEM image of chitosan with surfactant-coated hydrophobic paper (350× mag), with application weight of $7.2 \text{ g} \cdot \text{m}^{-2}$.

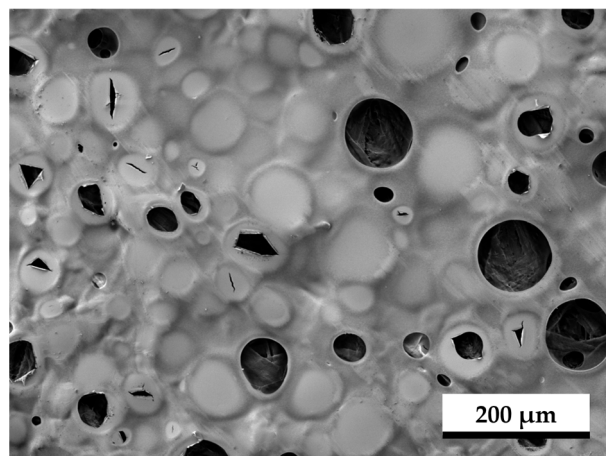


Figure 18. SEM image of chitosan with surfactant-coated hydrophilic paper ($350\times$ mag), with application weight of $8.1\text{ g}\cdot\text{m}^{-2}$.

4. Conclusions

This study highlights the potential and challenges of using alginate and chitosan as barrier coatings for paper substrates applied via spray coating. The results demonstrate that both materials exhibit promising barrier properties, but their performance is strongly influenced by application weight, substrate properties, the addition of surfactants, and the drying process.

Using a purpose-built spray coating unit, two different biopolymers of varying surface tension, with and without added surfactant, were applied to paper surfaces of different surface energy. The resulting coatings were evaluated for their barrier properties relevant to food packaging applications, including air permeability, grease resistance, and water vapor transmission rates. Prior to coating and barrier testing, contact angles of the coating materials were measured on both surfaces. These measurements showed that the addition of surfactants significantly improved the wetting of the biopolymers, regardless of paper properties. However, the hydrophobicity of the paper substrate had a stronger influence on wetting behavior than the surface tension of the biopolymers.

For air permeance, both alginate and chitosan coatings achieved complete impermeability at higher application weights ($8\text{ g}\cdot\text{m}^{-2}$), irrespective of substrate properties or surfactant addition. At lower application weights ($4\text{ g}\cdot\text{m}^{-2}$), the combination of hydrophilic substrates and biopolymers with surfactants provided significant improvements in barrier performance. Similar trends were observed for grease resistance. In both measurements, chitosan slightly outperformed alginate. The water vapor transmission rate also showed that chitosan exhibited superior performance compared to alginate. Across all barrier tests, the advantages of low-surface-tension coating materials applied to hydrophilic surfaces were most evident at lower application weights. At higher application weights, these trends were less pronounced, likely due to severe drying defects in the barrier film.

SEM imaging revealed that while the biopolymer coatings formed reasonably uniform films, defects such as “bubbles” and other surface irregularities were common, particularly at higher application weights. These defects were likely caused by the rapid drying process in the pilot coater. Addressing these drying-related challenges is expected to further enhance the barrier performance of these biopolymer coatings.

In summary, this study demonstrates that the spray application of alginate and chitosan can hold promise as sustainable barrier coatings for paper substrates, particularly when optimized for substrate hydrophobicity and coating material surface energy. Future research should focus on mitigating drying-induced defects and exploring alternative drying methods to improve the uniformity and performance of these barrier films.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/coatings15030335/s1>, Table S1: Contact angles of the three different test liquids for surface energy calculations. Mean values from 12 drops and 95% confidence intervals. Figure S1: Surface energy of the hydrophobic substrate. All combinations of mean values and extreme values of the measured contact angles of the three test liquids from Table S1 were used. The mean value and the confidence intervals (KI) of all these calculated values are shown. Figure S2: Surface energy of the hydrophilic substrate. All combinations of mean values and extreme values of the measured contact angles of the three test liquids from Table S1 were used. The mean value and the confidence intervals (KI) of all these calculated values are shown. Figure S3: Surface tension over time of alginate with 0%, 0.05%, 0.1%, 0.2% and 0.3% surfactant added. Figure S4: Surface tension over time of chitosan with 0%, 0.05%, 0.1%, 0.2% and 0.3% surfactant added. Figure S5: Viscosity of alginate, alginate with surfactant and chitosan after 1, 2, 5 and 14 days. Figure S6: Volumes of alginate drops with and without surfactant on the hydrophobic and hydrophilic paper substrate. Figure S7: Volumes of chitosan drops with and without surfactant on the hydrophobic and hydrophilic paper substrate.

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Abbreviations

The following abbreviations are used in this manuscript:

Alg	Alginate
Chi	Chitosan
hyphob	Hydrophobic
hyphil	Hydrophilic
S	Surfactant

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