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ENGINEERING MULTILAYER BIO-BASED COATINGS FOR PAPER PACKAGING: FROM FUNCTIONAL LAYER DESIGN TO INDUSTRIAL APPLICATION

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ABSTRACT

Multifunctional paper packaging requires coating systems that can simultaneously provide passive barrier performance and active functionality, although these functions may impose different requirements on coating composition and structure. This study investigated multilayer bio-based coatings based on starch, beeswax, and condensed quebracho tannin, with an emphasis on how coating architecture influences barrier performance and antioxidant accessibility. In the barrier-first architecture, application of a starch–beeswax layer reduced air permeance from 6.297 to 0.549 μm/(Pa·s) and increased grease resistance from Kit 0 to Kit 10. Addition of an outward-facing starch–beeswax–tannin active topcoat maintained these barrier properties, with a final air permeance of 0.514 μm/(Pa·s) and Kit 10. Antioxidant performance was strongly dependent on the organization of the tannin-containing coating. In the active-first architecture, covering starch–tannin layers with the barrier coating consistently reduced 24-h radical scavenging activity by approximately 15 percentage points across tannin concentrations of 10–70 wt%. At 50 wt% tannin, radical scavenging activity decreased from 91.48% for the exposed active layer to 76.72% after barrier coating, whereas the barrier-first architecture with an outward-facing starch–beeswax–tannin topcoat reached 95.26%. Because the architectures differed in both layer organization and active-topcoat composition, the comparison is interpreted at the architecture level rather than as an isolated layer-sequence effect. Overall, the results demonstrate that composition, layer position, and layer sequence should be considered together as engineering design variables when developing multifunctional paper coatings. This architecture-based approach provides a framework for integrating renewable barrier and active materials into fiber-based packaging while preserving the distinct functions required from each region of the coated structure.

Keywords: active paper packaging; bio-based coatings; multilayer coatings; tannins; barrier properties

1. INTRODUCTION

Fiber-based packaging is an attractive renewable structural platform because it combines low mass, stiffness, printability, convertibility, and an established recovery infrastructure. Its fibrous construction, however, is also the source of a central engineering limitation. Interfiber voids provide pathways for air and other transported species, while cellulose-rich surfaces readily interact with water and many liquids. Consequently, paper used for demanding packaging applications commonly requires a coating that closes surface pores, limits transport through the sheet, and improves resistance to water and grease (Rastogi and Samyn, 2015; Versino et al., 2023).

These passive functions place different demands on a coating. A continuous film-forming phase is needed to bridge fiber irregularities and reduce connected porosity, whereas resistance to liquid water often requires a hydrophobic component. Starch is attractive as a renewable, paper-compatible film former, but its hydrophilicity can limit moisture resistance. Incorporating a lipid such as beeswax can add hydrophobic character, yet the resulting formulation must still wet the substrate, form a coherent layer, and remain processable during coating and drying. The engineering problem is therefore not simply to add barrier ingredients, but to organize them so that the porous sheet is sealed efficiently with a practical coating mass.

Active packaging introduces an additional requirement. Rather than acting only as an inert boundary, an active package is designed to interact with the packaged product or its surrounding environment, for example by scavenging reactive species or providing antioxidant activity (Yildirim et al., 2018). Condensed tannins are renewable polyphenolic materials with radical-scavenging capacity, and a starch matrix provides a convenient route for applying them to paper. Their presence in a coating, however, is not sufficient by itself: the active component must remain accessible to the phase in which its function is required.

This creates a potential conflict within a multifunctional coating. A passive barrier is intentionally designed to restrict transport, whereas an antioxidant layer must permit sufficient contact or diffusion for the active component to respond. If the active layer is buried beneath a hydrophobic barrier, the same structure that improves resistance to penetration may also reduce measurable antioxidant accessibility. Multilayer construction offers a way to separate these competing requirements spatially. By assigning barrier and active functions to different layers, and by treating layer

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position and sequence as design variables, the coating architecture can be adjusted without requiring one formulation to perform every function simultaneously (Wang et al., 2022).

The objective of this study was to evaluate multilayer coating architecture as an engineering strategy for integrating passive barrier and active antioxidant functions into paper packaging. Two structures containing starch, beeswax, and condensed quebracho tannin were compared: an active-first architecture in which the tannin-containing layer was covered by a starch–beeswax barrier layer, and a barrier-first architecture in which the tannin-containing layer remained outward-facing. Sequential air-permeance and grease-resistance measurements were used to identify when the passive barrier was established, while paired 24-h radical-scavenging measurements were used to determine how covering or exposing the active layer changed antioxidant accessibility. The resulting structure–performance relationships were then translated into design rules for multifunctional paper coatings.

2. FUNCTIONAL LAYER DESIGN STRATEGY

The development of multifunctional paper packaging requires consideration not only of the materials incorporated into a coating formulation, but also of how the functions provided by those materials are spatially organized within the coated structure. Barrier and active functions may impose different, and potentially competing, requirements on a coating system. A barrier layer is intended to restrict the transport of substances through the paper structure, whereas an active layer must remain sufficiently accessible to interact with its surrounding environment. Combining these functions within a single formulation may therefore limit the ability to independently optimize each function.

In the present study, a multilayer approach was used to organize barrier and active functions across two coating layers. A starch–beeswax layer was used to establish passive barrier performance, with starch serving as the film-forming matrix and beeswax providing the hydrophobic component. Tannin was incorporated into the active coating to provide antioxidant functionality. In Design I, the tannin-containing active layer was a starch–tannin formulation, whereas in Design II the outward-facing active topcoat was a starch–beeswax–tannin formulation. This architecture allowed the position of the tannin-containing active region relative to the underlying barrier layer to be evaluated.

Two multilayer architectures were evaluated by changing the order of coating application and, in Design II, the composition of the outward-facing active topcoat (Figure 1). The comparison was designed to determine how coating architecture could influence the balance between passive barrier performance and active functionality. Accordingly, the results are interpreted at the architecture level rather than as an isolated test of layer sequence.

2.1 Active-First Architecture

In the first configuration (Design I), the starch–tannin active layer was applied directly to the paper substrate, followed by the starch–beeswax barrier layer as the outward-facing coating. Four tannin concentrations were initially evaluated in the active layer to investigate the effect of tannin loading within this architecture.

The active-first configuration provides a logical approach for anchoring the tannin-containing layer to the fibrous substrate while placing the hydrophobic coating at the external surface, where it can serve as the primary resistance to penetration by water, grease, and other substances. From a conventional barrier-coating perspective, positioning the starch–beeswax layer externally is therefore attractive because the hydrophobic component is located directly at the interface between the paper package and its surrounding environment.

However, the requirements of an active packaging system introduce an additional consideration. Unlike a passive barrier component, an antioxidant must remain accessible to the environment in which its activity is required. Positioning the tannin-containing layer beneath the barrier layer creates an additional transport pathway between the active compound and the external environment. Consequently, this architecture provided an opportunity to examine whether a coating arrangement optimized primarily around external barrier protection could simultaneously maintain effective active functionality.

2.2 Barrier-First Architecture

The second configuration (Design II) placed the passive barrier layer first. A starch–beeswax coating was applied directly to the paper substrate, followed by an outward-facing starch–beeswax–tannin active topcoat. Based on the evaluation of tannin loading in Design I, the active topcoat contained 50 wt% tannin relative to dry starch.

The engineering rationale for this configuration was to separate the direction and location of the two intended functions. The starch–beeswax layer remained positioned between the fibrous substrate and the external environment, where it could restrict transport through the porous paper structure. At the same time, positioning the tannin-containing layer at the outer surface reduced the physical separation between the antioxidant component and the environment with which it was intended to interact.

The comparison between the two architectures therefore addresses a broader design consideration for multifunctional paper coatings: the optimal position of a functional material depends on where its function must occur. Components intended primarily to restrict transport may be positioned to protect or seal the fibrous substrate, whereas components intended to interact with the package environment may benefit from greater surface accessibility. In the present study, Design II combined a barrier-first arrangement with a starch–beeswax–tannin active topcoat, so the architecture comparison reflects both layer placement and active-topcoat formulation.

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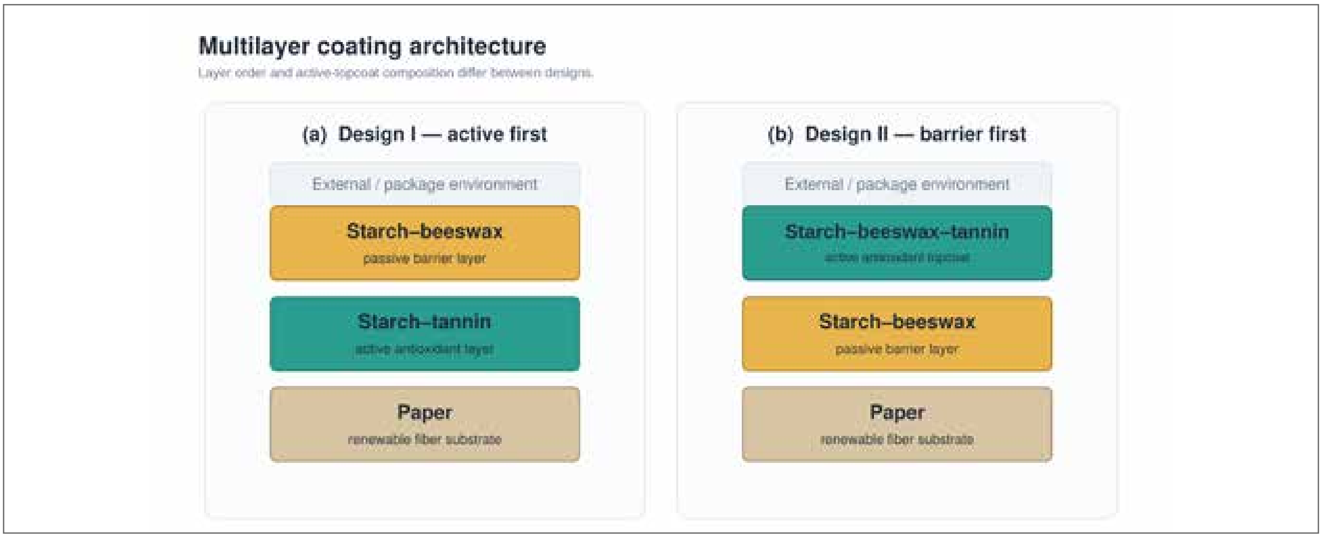

Figure 1. Multilayer coating architectures evaluated in this study: (a) Design I, paper → starch–tannin active layer → starch–beeswax barrier layer → external/package environment; and (b) Design II, paper → starch–beeswax barrier layer → starch–beeswax–tannin active topcoat → external/package environment. The Design II active topcoat retained beeswax and therefore differed compositionally from the Design I active layer

This approach provides a framework for evaluating multilayer coatings beyond the specific starch–beeswax–tannin system investigated here. By assigning individual functions to separate layers and considering their spatial position relative to the paper substrate and the intended package environment, coating architecture can be incorporated explicitly into the design of multifunctional fiber-based packaging.

3. MATERIALS AND METHODS

3.1 Materials

Unbleached kraftliner paper with a nominal grammage of 120 g/m², supplied by International Paper (USA) was used as the substrate. Modified corn starch (CATO-SIZE® 270A, Ingredion Inc. (USA) was used as the film-forming biopolymer. Condensed quebracho tannin was supplied by TANAC S.A. (Brazil). Beeswax (CAS 8012-89-3), Tween® 80 (CAS 9005-65-6), and Span® 20 (CAS 1338-39-2) were obtained from Sigma-Aldrich (USA). Deionized water was used to prepare all aqueous formulations, and methanol was used for the DPPH assay.

Two functional formulations were used: a tannin-containing starch coating intended to provide antioxidant activity and a starch–beeswax emulsion intended to provide passive resistance to transport and liquid penetration. Tannin loadings are reported relative to dry starch mass; beeswax loadings are likewise reported relative to starch unless otherwise noted.

Table 1. Composition, function, and verified dry coating additions for the two multilayer architectures.

Architecture	Layer	Functional coating	Main components	Tannin loading*	Verified dry coating addition	Primary function
Design I – Active-first	1	Active	Starch + quebracho tannin	10%	9.59 ± 0.83 g/m² (n=20)	Antioxidant
	1	Active	Starch + quebracho tannin	30%	7.64 ± 0.55 g/m² (n=20)	Antioxidant
	1	Active	Starch + quebracho tannin	50%	6.35 ± 0.43 g/m² (n=20)	Antioxidant
	1	Active	Starch + quebracho tannin	70%	6.43 ± 0.57 g/m² (n=20)	Antioxidant
	2	Barrier	Starch + beeswax + surfactants	–	3.09–3.39 g/m² (n=12–15)	Water/grease/air barrier
Design II – Barrier-first	1	Barrier	Starch + beeswax + surfactants	–	5.42 ± 0.28 g/m² (n=20)	Water/grease/air barrier
	2	Active topcoat	Starch + beeswax + quebracho tannin + surfactants	50%	3.56 ± 0.32 g/m² (n=10)	Antioxidant

*Tannin loading is relative to dry starch mass. Values are means ± workbook-recorded dispersion. Design I active-layer n = 20; Design I barrier-layer n = 12–15 depending on formulation; Design II barrier-layer n = 20 and active-topcoat addition n = 10.

3.2 Preparation of Coating Formulations

For Design I active coatings, a 20 wt% aqueous starch dispersion was heated to 80 °C under mechanical stirring and held for 20 min. The gelatinized starch was cooled to 25 °C, after which condensed tannin was added at 10, 30, 50, or 70 wt% relative to dry starch and mixed mechanically for 5 min. The recorded laboratory batch contained 84 mL deionized water and 21 g starch, with 2.1, 6.3, 10.5, or 14.7 g tannin, respectively.

For the Design I barrier coating, a 20 wt% starch dispersion was gelatinized at 80 °C for 20 min. Beeswax (at 10 wt% relative to dry starch) was melted separately at 100 °C. Tween 80 and Span 20 were added at a combined concentration of 1 wt% relative to the final starch–beeswax formulation. The molten wax/surfactant phase was combined with the hot starch phase at approximately 80 °C and stirred vigorously until a stable milky-white emulsion formed; the emulsion was then cooled to room temperature before coating.

For the Design II starch–beeswax formulation, a 30 wt% starch dispersion was gelatinized at 80 °C for 20 min under continuous stirring. The starch dispersion was cooled to approximately 50 °C before beeswax (15 wt% relative to starch) was added. Tween 80 and Span 20 were used at a 2:1 mass ratio, at a combined concentration of 1 wt% based on the combined starch and beeswax mass. The formulation was mixed with a laboratory stirrer at approximately 1000 rpm for 15 min and then cooled to room temperature.

The Design II active topcoat was a starch–beeswax–tannin formulation. After preparation of the starch–beeswax formulation described above, condensed tannin was added at 50 wt% relative to dry starch and mixed for 5 min.

3.3 Preparation of Multilayer-Coated Papers

Coatings were applied to the kraftliner using an automatic laboratory film applicator (K Control Coater, RK Print Coat Instruments, UK). Each functional layer was coated separately and dried in an oven at 105 °C for 1 min before the next layer was applied. After drying, flat weights were placed on the sheets to minimize curl.

For Design I, the starch–tannin active coating was applied directly to the paper, followed by the starch–beeswax barrier coating. The raw coating sheet records a red bar at 8 m/min for the 10 and 30% tannin active layers and a yellow bar at 5 m/min for the 50 and 70% tannin active layers. For Design II, both the starch–beeswax barrier layer and the starch–beeswax–tannin active topcoat were applied using the yellow bar at 5 m/min.

Verified dry coating additions are summarized in Table 1. In Design I, active-layer additions ranged from 6.35 to 9.59 g/m², and the subsequent barrier-layer addition ranged from 3.09 to 3.39 g/m². In Design II, the barrier layer added 5.42 ± 0.28 g/m² (n = 20) and the active topcoat added 3.56 ± 0.32 g/m² (n = 10).

After coating, all paper samples were conditioned for at least 24 h at 23 ± 1 °C and 50 ± 2% relative humidity before characterization.

3.4 Physical, Barrier, Mechanical, and Morphological Characterization

Grammage was determined according to TAPPI/ANSI T 410 om-23 and thickness according to TAPPI T 411 om-21; apparent density was calculated from grammage and thickness. Air permeance was measured by the Sheffield method according to TAPPI T 547 om-18, and surface roughness was measured according to TAPPI T 538 om-01. Air permeance is reported as a through-sheet air-flow property and is not interpreted as oxygen permeability.

Grease resistance was measured using the Kit test (TAPPI T 559 cm-22), and liquid-water absorptiveness was measured using the Cobb method (TAPPI T 441 om-20). Static water contact angle was measured with a 20-µL droplet of deionized water using a digital contact-angle instrument; five measurements were recorded per reported condition. Tensile properties were measured according to TAPPI T 494 in both machine and cross directions, with three replicate measurements per condition (n = 3).

Twenty coated sheets were prepared for each formulation, but individual tests used subsets as required by the method and available specimen area.

3.5 Antioxidant Activity

Antioxidant activity was evaluated using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical-scavenging assay. Paper specimens measuring 1 × 1 cm were exposed to 1 mL of 0.2 mM DPPH solution prepared in methanol. For coating-solution measurements, one drop of coating solution was used. Measurements were made in a standard quartz cuvette with a 1-cm optical path length. The DPPH solution was protected from light and stored under refrigeration until use. Absorbance was measured at 517 nm at 0, 10, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210, 240, and 1440 min. A DPPH-only control was monitored concurrently for autonomous decay.

Radical scavenging activity at time t was calculated as:

$$\mathbf{RSA_t\ (\%) = [1 - (A_t / A_0)] \times 100}$$

where A_0 is the initial absorbance and A_t is the absorbance at time t for the same sample series. The DPPH-only control was retained as a separate series; it was not subtracted from the stored RSA endpoints used in Figures 3 and 4.

For Design I, paper specimens containing 10, 30, 50, or 70 wt% tannin were evaluated before and after application of the starch–beeswax barrier layer. For Design II, the final barrier-first structure containing the 50% tannin topcoat was evaluated. Two absorbance measurements were recorded at each time point for the paper series, and the reported 24-h RSA endpoints were calculated from their mean absorbance.

3.6 Statistical Analysis

Results are reported descriptively as means with workbook-recorded standard deviations or dispersion values when replicate measurements were available. Cobb values (n = 2) are presented as preliminary descriptive measurements. RSA endpoints are reported from the mean of the two stored absorbance repeats, and no regression lines or correlation coefficients were fitted because the engineering comparison is paired by architecture and tannin concentration.

4. RESULTS AND DISCUSSION

The performance of the multilayer-coated papers was evaluated from the perspective of functional layer organization rather than coating composition alone. The two architectures provided a means of examining how passive barrier and active antioxidant functions could be distributed within a coated paper structure. The results demonstrate that the individual functions were not equally dependent on layer position. The starch–beeswax coating established most of the resistance to transport through the fibrous substrate, whereas the antioxidant response of the tannin-containing coating was strongly influenced by whether the active layer remained exposed or was covered by the barrier layer.

This distinction is important for multifunctional paper packaging because maximizing the performance of each individual coating component does not necessarily maximize the performance of the complete structure. Instead, the results indicate that coating architecture—including layer placement, sequence, and formulation—can be treated as a design variable for balancing barrier performance with accessibility of an active component.

4.1 Establishing the Passive Barrier Function

The barrier-first architecture (Design II) provides a useful basis for identifying the contribution of the individual coating steps because the paper was characterized sequentially as an uncoated substrate, after application of the starch–beeswax barrier layer, and after application of the starch–beeswax–tannin active topcoat. The largest change in transport-related properties occurred following application of the first layer the starch–beeswax barrier layer.

Air permeance decreased from 6.297 μm/(Pa·s) for the uncoated paper to 0.549 μm/(Pa·s) after application of the barrier layer, corresponding to a reduction of approximately 91%. Addition of the starch–beeswax–tannin active topcoat resulted in only a small further decrease, to 0.514 μm/(Pa·s). Thus, approximately 99% of the total reduction in air permeance obtained by the complete multilayer structure had already been achieved after application of the first functional layer.

A similar progression was observed for grease resistance. The uncoated kraftliner had a Kit rating of 0, whereas application of the starch–beeswax layer increased the rating to Kit 10. The subsequent tannin-containing active topcoat maintained the rating at Kit 10. These results indicate that the first starch–beeswax layer was sufficient to establish the measured grease-resistant function and, importantly, that deposition of the starch–beeswax–tannin topcoat did not eliminate the barrier already established beneath it.

Water absorptiveness followed the same general direction, although these results should be interpreted more cautiously because of the limited number of verified replicates. The available raw measurements gave a mean Cobb value of 293.5 ± 3.5 g/m² after application of the starch–beeswax layer and 276.5 ± 12.0 g/m² for the complete barrier-plus-active structure (n = 2). The final active layer therefore did not produce evidence of deterioration in liquid-water resistance. Rather, the measured values suggest that the underlying barrier remained functional after deposition of the tannin-containing topcoat.

Taken together, the air-permeance, grease-resistance, and water-absorption results show that the passive barrier function was established primarily during formation of the first starch–beeswax layer. This behavior is consistent with the intended role of the coating: the starch matrix can contribute to coverage and filling of the porous paper surface, while the dispersed beeswax introduces a hydrophobic component into the deposited layer. For the present study, however, the important engineering observation is not that every subsequently applied layer must independently provide barrier performance. Once the first functional layer established the principal resistance to transport through the substrate, the outward-facing layer could be further engineered to introduce accessible active functionality without eliminating the barrier performance established beneath it.

This provides the first design principle arising from the multilayer architecture:

Design Rule 1 — Establish the principal passive barrier before introducing accessible active functionality at the outer surface.

For multifunctional paper coatings, this approach allows subsequent layers to be optimized according to their intended function without requiring each coating layer to simultaneously provide the same combination of barrier properties. (see Figure 2).

4.2 Layer Architecture Controls Antioxidant Accessibility

The antioxidant results revealed a different dependence on coating architecture. Whereas passive barrier performance was largely established by the presence of the starch–beeswax layer, the radical-scavenging response of the tannin-containing coating depended strongly on whether that active layer remained exposed to the surrounding environment.

This effect was first observed in the active-first architecture (Design I). The starch–tannin coating was applied directly to the paper substrate at tannin concentrations of 10, 30, 50, and 70 wt% relative to starch, and its 24-h radical scavenging activity was measured before and after application of the starch–beeswax barrier topcoat.

With the active layer exposed, RSA values of 85.34, 82.11, 91.48, and 91.84% were obtained for the 10, 30, 50, and 70%

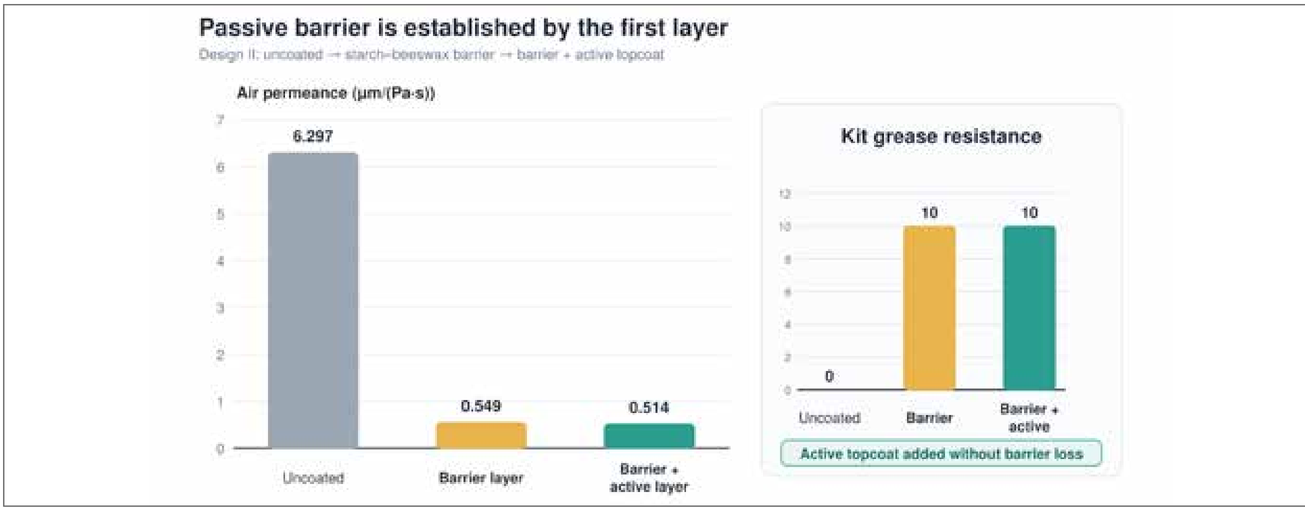

Figure 2. Development of passive barrier performance for Design II during the sequence uncoated → starch–beeswax barrier layer → barrier + tannin-containing active topcoat. Air permeance and Kit grease resistance are shown on separate quantitative scales. Most of the reduction in air permeance and all of the measured Kit resistance were established by the first barrier layer; air permeance is not oxygen permeability

tannin formulations, respectively. After the same active coatings were covered by the starch–beeswax layer, the corresponding RSA values decreased to 70.56, 67.00, 76.72, and 76.25%.

Importantly, the magnitude of this reduction was remarkably consistent across tannin concentrations. Covering the active layer decreased the 24-h RSA by 14.77, 15.11, 14.76, and 15.60 percentage points, respectively. The average reduction was therefore approximately 15.1 percentage points.

This result is more informative than simply observing that the multilayer-coated samples retained antioxidant activity. Increasing the amount of tannin did not eliminate the loss associated with covering the active layer. Even at 70% tannin, where the exposed coating produced an RSA of 91.84%, placement of the barrier coating over the active layer reduced the measured response to 76.25%. The behavior therefore suggests that the position of the antioxidant-containing layer within the multilayer structure influenced its measurable accessibility.

The present DPPH assay does not directly measure tannin migration or release, and the results should therefore not be interpreted as evidence of a controlled-release mechanism. Instead, they demonstrate an architecture-dependent antioxidant response: when the tannin-containing layer was separated from the surrounding test medium by the starch–beeswax coating, a smaller fraction of its radical-scavenging capacity was expressed during the assay period.

For active packaging design, this distinction is important. Increasing active-agent concentration alone may not compensate for unfavorable spatial positioning within a multilayer structure. The functional material must also be located where interaction with the intended environment can occur.

Design Rule 2 — Position active components according to where their interaction is required.

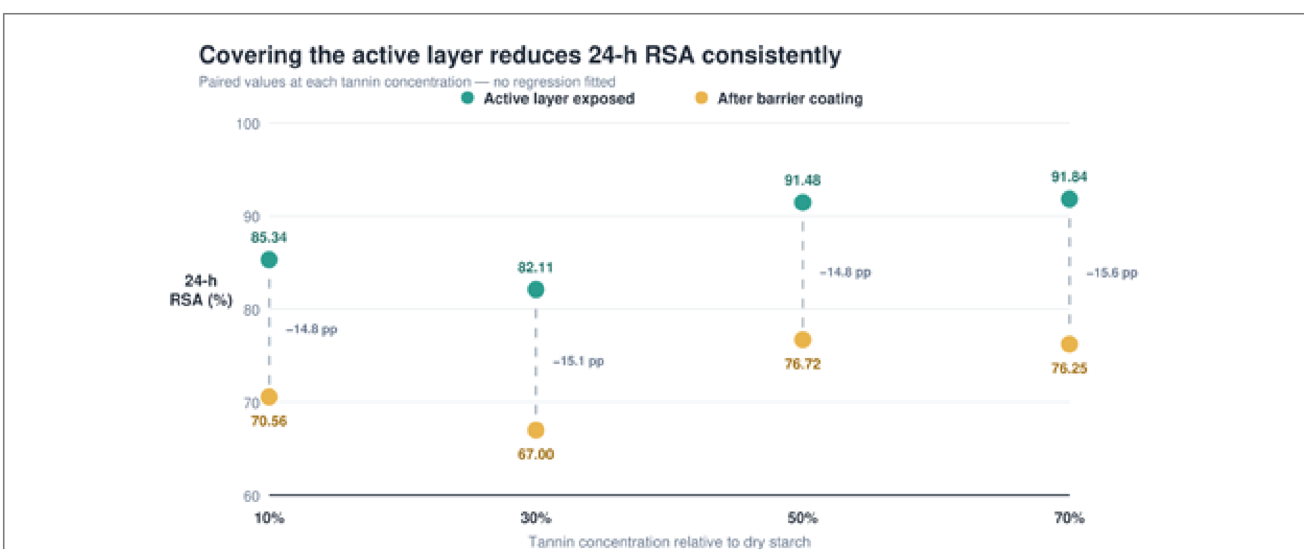

Figure 3. Twenty-four-hour radical scavenging activity (RSA) for Design I active layers containing 10, 30, 50, or 70 wt% tannin relative to starch, before and after application of the starch–beeswax barrier coating. Paired lines show the consistent decrease at each tannin concentration

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4.3 Barrier-First Architecture Mitigates the Barrier–Active Trade-Off

The comparison between the two coating architectures showed that the loss in antioxidant response observed in Design I was not observed in the barrier-first Design II structure. However, Design II differed not only in layer order but also in active-topcoat composition because the outward-facing topcoat contained starch, beeswax, and tannin. The comparison therefore reflects the combined effect of architecture and active-topcoat formulation rather than an isolated sequence effect.

This effect is most clearly illustrated by comparing the systems containing 50 wt% tannin relative to starch. In Design I, the starch–tannin layer produced a 24-h RSA of 91.48% when it remained exposed. After the starch–beeswax barrier layer was applied over the active coating, the measured RSA decreased to 76.72%. In Design II, a starch–beeswax barrier layer was applied directly to the paper substrate, followed by the outward-facing starch–beeswax–tannin topcoat containing 50 wt% tannin relative to dry starch. Under this barrier-first configuration, the final multilayer paper reached a 24-h RSA of 95.26%.

The increase from 76.72% in the covered active-first structure to 95.26% in the barrier-first structure represents a recovery of 18.54 percentage points in measurable antioxidant activity. Importantly, this improvement was achieved without sacrificing the passive barrier established by the underlying starch–beeswax layer. In the final Design II structure, air permeance remained low at 0.514 μm/(Pa·s), while grease resistance remained at Kit 10. The active topcoat therefore restored a high antioxidant response while preserving the principal barrier functions developed in the first coating layer.

These results show that the barrier–active trade-off observed in Design I was mitigated in a barrier-first architecture with an outward-facing tannin-containing topcoat. The barrier function was established adjacent to the porous paper substrate, where it could contribute to sealing the fibrous structure and restricting transport. At the same time, the tannin-containing topcoat was positioned at the external surface, where interaction with the surrounding medium was less restricted. Because the Design II topcoat also contained beeswax, the present data do not isolate spatial reorganization from formulation effects.

This result also illustrates why coating composition alone is insufficient to describe multifunctional performance. A system may contain both an effective barrier component and an effective antioxidant component, yet the full functionality of each may not be expressed if their spatial arrangement is unfavorable. In the present case, placing the tannin-containing formulation at the outer surface produced a coating structure in which the first starch–beeswax layer retained the principal measured barrier function while the outward-facing starch–beeswax–tannin topcoat provided greater antioxidant accessibility.

The 95.26% RSA obtained for the barrier-first structure was also close to the 96.30% RSA measured for the corresponding tannin-containing coating formulation in solution, suggesting that positioning the active layer at the surface allowed most of its antioxidant potential to remain measurable after coating. This comparison should be interpreted as evidence of preserved functional accessibility rather than direct proof of migration or release, since neither tannin transport nor migration kinetics were measured in the present study.

From an engineering perspective, the results show that multifunctionality can be improved by organizing coating functions across layers rather than requiring every layer to perform every role. A substrate-facing layer can establish the principal barrier, while an outward-facing tannin-containing topcoat can provide accessible antioxidant functionality.

Design Rule 3 — Organize competing functions spatially while considering layer composition, position, and sequence together.

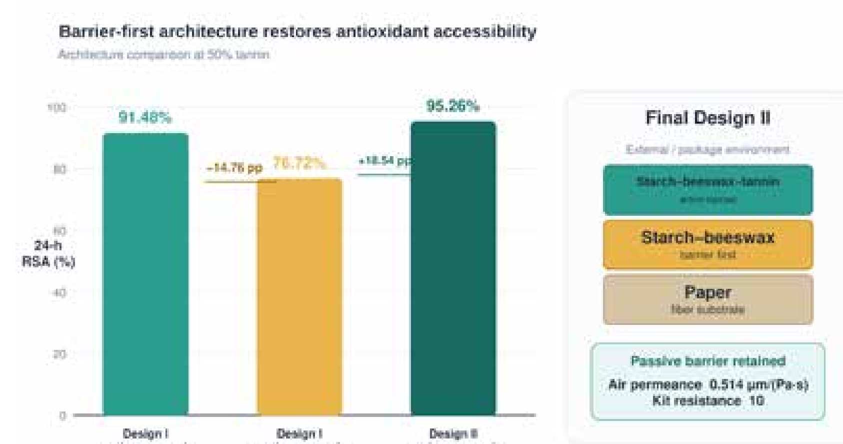

Figure 4. Architecture comparison at 50 wt% tannin. Covering the Design I starch–tannin active layer reduced 24-h RSA from 91.48 to 76.72%. The barrier-first Design II structure, containing an outward-facing starch–beeswax–tannin topcoat, reached 95.26% RSA while retaining low air permeance and Kit 10 grease resistance. Because the Design II active topcoat differed compositionally from the Design I active layer, this comparison should be interpreted as an architecture-level comparison rather than an isolated sequence effect

As a preliminary proof-of-concept, the potential relevance of the antioxidant coating to food packaging was also explored using raspberries stored in contact with uncoated and antioxidant-coated paper. Visual observations suggested differences in fruit deterioration during storage; however, this experiment was exploratory and was not designed as a quantitative shelf-life study. Only selected coating conditions were evaluated, and microbial growth, oxidation markers, and other quantitative indicators of food quality were not measured. The observations therefore do not demonstrate shelf-life extension, but they provide practical motivation for future studies evaluating whether the antioxidant functionality demonstrated by the DPPH assay can translate into measurable preservation effects in packaged foods.

4.4 Engineering Design Rules for Multifunctional Paper Coatings

The results demonstrate that the design of multifunctional paper coatings extends beyond the selection and concentration of functional ingredients. Layer position, sequence, and formulation together influence how individual functions are expressed within the complete coated structure. This is particularly relevant when combining functions with different physical requirements, such as restricting transport while maintaining accessibility of an active compound.

The present study suggests a modular approach in which the coating structure is designed according to where each function is required. A layer adjacent to the fibrous substrate can be used to control penetration and transport through the porous paper structure, while a surface-positioned layer can provide functionality that depends on interaction with the surrounding environment. In this way, individual layers can be optimized for different roles rather than requiring a single formulation to satisfy competing requirements.

Three broader principles emerge from this approach:

1. Separate functions when their material requirements compete. Passive barrier and active functions do not necessarily need to be provided by the same formulation or layer.
2. Position each functional component where its action is required. Components intended to restrict transport and those intended to interact with the package environment may have different optimal locations within the coated structure.
3. Treat architecture as a design variable. Composition, coating weight, layer position, and layer sequence should be considered together when tuning multifunctional performance.

These principles can be summarized by a simple design framework:

Composition + Layer Position + Layer Sequence → Functional Performance

The framework is not limited to the specific starch–beeswax–tannin system investigated here. It provides a basis for considering other combinations of renewable barrier and active materials in which individual functions can be assigned to different regions of a coated fiber-based structure.

4.5 From Laboratory Coating to Industrial Application

The multilayer structures evaluated in this study were produced by sequential laboratory bar coating with drying between individual layers. Translation to industrial production will therefore require consideration of how the proposed functional architecture can be reproduced at higher coating speeds and under different drying conditions. Rather than directly reproducing the laboratory process, industrial development should focus on maintaining the essential functional organization identified here: a substrate-facing layer that establishes the principal barrier and an outward-facing tannin-containing layer that provides accessible active functionality.

This architecture also creates opportunities to optimize the two coating steps according to their primary roles. The substrate-facing layer can be designed around sufficient coverage and resistance to transport through the fibrous substrate, whereas the outward-facing formulation can be optimized to balance active-compound accessibility with the other formulation requirements needed for coating performance. The present results, for example, showed little additional 24-h RSA when tannin concentration increased from 50 to 70% in the exposed active coating. Although this does not establish an industrial optimum, it illustrates the importance of defining the minimum material input required to achieve the targeted function, rather than maximizing functional-agent concentration.

Further development should therefore address coating rheology and solids content, drying requirements, interlayer adhesion, coating uniformity, and compatibility with converting operations. Equally important, the multilayer structure must ultimately be evaluated for repulpability and recyclability so that additional functionality does not compromise the end-of-life advantages expected from fiber-based packaging. Industrial translation of the concept thus requires moving from the functional architecture demonstrated here to a manufacturable and recyclable coating architecture.

The multilayer concept may also provide a platform for incorporating functional compounds obtained from renewable forest resources. The present study used commercial condensed quebracho tannin as the antioxidant component; in ongoing work, our group is investigating the extraction and recovery of antioxidant-rich fractions from sugar maple bark and their potential incorporation into paper-based coating formulations. In parallel, we are exploring alternative strategies in which tannin functionality is introduced directly into the pulp and fiber network rather than applied exclusively as a surface coating. Together, these research directions expand the design space from

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the source of the functional compound to its location within the paper structure. The architectural principles identified in the present study provide an important foundation for this work: obtaining a functional compound is only part of the challenge; where and how it is incorporated into the fiber-based material can determine how effectively that functionality is expressed.

5. CONCLUSIONS

This study demonstrates that coating architecture is an important design variable in multifunctional paper packaging. The results showed that barrier and antioxidant functions could be assigned to different layers and that their position within the coated structure influenced how effectively each function was expressed.

The starch–beeswax layer established the primary passive barrier, substantially reducing air permeance and increasing grease resistance. In contrast, the antioxidant response of the tannin-containing coating was strongly affected by its placement within the coated structure. Covering the Design I active layer with the barrier coating consistently reduced the measured 24-h radical scavenging activity, whereas the barrier-first Design II architecture, with an outward-facing starch–beeswax–tannin topcoat, resulted in 95.26% RSA while maintaining low air permeance (0.514 µm/(Pa·s) and Kit 10 grease resistance. Because the Design II active topcoat differed compositionally from the Design I active layer, this comparison supports an architecture-level design effect but does not isolate layer sequence as the sole cause. These findings demonstrate that multifunctionality can be improved through spatial organization of the coating components rather than simply by increasing functional-agent concentration.

More broadly, the results support a modular approach to functional paper design in which composition, layer position, and layer sequence are considered together. A substrate-facing layer can be engineered to control transport through the fibrous structure, while an outward-facing layer can be designed for interactions required at the package interface. This framework provides a basis for developing future fiber-based packaging systems incorporating renewable functional materials while maintaining the barrier performance required for practical applications.

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