

Aging and degradation of oil and grease barrier papers coated with bio-based starch–wax emulsion

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ABSTRACT: The long-term performance and stability of bio-based barrier coatings are critical for sustainable packaging. In this study, the aging and degradation of a biobased starch–wax emulsion coating were examined on two different base papers. Coated samples were stored for 8 months at 23°C and 50% relative humidity (RH) in their original reels to minimize external exposure and isolate internal aging effects. Multiple aging intervals were analyzed using advanced methods to assess both chemical composition and physical structure.

The water vapor transmission rate (WVTR) of both coated papers increased during the first 15 days, but after eight months, the WVTR dropped below the initial values. Fourier transform infrared (FTIR) results supported these trends by showing a marked rise in the polarity index (PI), occurring predominantly within the first 15 days. The overall observations, including increases in the PI, carbonyl index (CI), and absolute absorbance in the hydroxyl region, confirm that both hydrolysis and oxidation occurred during aging.

The gradual increase in the aliphatic C–H stretching peaks indicated that wax components moved toward the surface over time. The non-uniform surface enrichment of oleophilic wax following migration contributed to the decline in Kit rating upon aging by facilitating oil and grease wetting and penetration. At the same time, increased wax concentration at the surface helped improve the water vapor barrier performance during long-term aging. Scanning electron microscopy (SEM) imaging revealed distinct surface cracks over time on the starch-wax emulsion coated papers. The FTIR analysis supported these observations through an increase in the conformational disorder index (CDI) with aging. Physical changes were further reflected in the barrier performance, as the heptane vapor transmission rate (HVTR) increased significantly for both coated papers over the 8-month period.

Application: This paper describes the natural aging and degradation of a sustainable oil and grease barrier coating: starch-wax emulsion on two different base papers. We studied the main chemical and physical changes in this common oil and grease barrier coating at intervals of 0, 15, 90, 180, and 240 days.

The increasing consumer demand for sustainable packaging materials has encouraged a growing interest in eco-friendly barrier coatings that can ultimately replace unsustainable alternatives [1]. Paper-based packaging materials are inherently renewable and biodegradable, but they require surface treatment to provide sufficient resistance against the penetration of oil and grease, particularly in food service and packaging applications [1]. Among the several bio-based coating formulations, starch–wax emulsion systems are recognized as viable candidates due to their renewable nature. Starch exhibits good film-forming behavior and has been widely used in paper coating, including surface sizing and functional coating applications [2]. If formulated with natural waxes, the hydrophobic properties of the starch-based systems can be improved, and the systems will remain biodegradable [3]. The addition of waxes to the starch matrix exhibits a synergistic effect, improving both the water and oil barrier properties due to the formation of a more uniform and continuous coating layer [3].

Still, there are key questions about how the bio-based barrier coatings perform over time, particularly under commercial conditions. Understanding how these coatings age is crucial to estimating their lifetime and optimizing their formulations. As barrier coatings age, they can undergo various chemical and physical transformations, many of which are prompted by factors such as temperature, humidity, oxygen, and physical stress [4]. For those that are starch-based, there are additional obstacles to overcome such as degradation by enzymes [5]. These changes ultimately lead to a deterioration of both the barrier properties and the structural integrity of the coating.

The properties of substrates are also crucial for the performance and aging of barrier coatings. Base papers differ in their surface properties, porosity, and chemistry, which may affect coating penetration and holdout [6]. The interaction between the coating and the substrate becomes particularly important during aging, as changes in the paper structure can directly affect the integrity of the coating.

Fourier transform infrared (FTIR) analysis and scan-

ning electron microscopy (SEM) imaging, in combination with barrier property measurement, provide a comprehensive understanding of how chemical and physical changes translate into functional properties. A comprehensive aging investigation demands integrated chemical and physical analyses to link performance changes to molecular-level transformations, cost-effectiveness, and potential in delivering barrier functionality.

This paper addresses the unknown aspects of how starch–wax emulsion barrier coatings age and degrade over time on different paper substrates. By employing a blend of natural aging and detailed investigation, we may finally be able to understand the key mechanisms that govern the aging of these sustainable coatings. This research helps us gain a better understanding of bio-based barrier coatings and provides useful guidance for producing sustainable packaging with improved durability and stability.

LITERATURE REVIEW

Starch-based barrier coatings

Among renewable polymers, starch is one of the most favorable candidates for developing sustainable barrier coatings due to its natural abundance, biodegradability, and good film-forming ability [7]. The molecular structure of starch, comprising amylose and amylopectin, offers opportunities for chemical modifications and functional enhancements [8]. The linear configuration of amylose and the highly branched structure of amylopectin play key roles in determining the film's mechanical strength, barrier performance, and flexibility [9]. The application of starch in paper coating has evolved over the last few decades from a pure surface size to more complex functional coatings. Today, starch-based coatings are typically formulated with additives and modifiers that enhance water resistance, oil barrier performance, and mechanical strength [8].

Wax integration and synergistic effects

The incorporation of natural waxes into starch coatings is a significant advancement in the field of bio-based barrier technology. Waxes are inherently hydrophobic and can enhance the barrier performance of starch while maintaining the environmental friendliness of the coating system.

The selection of an appropriate type of wax is a key factor influencing the final coating performance. Carnauba wax, a wax derived from the leaves of the Brazilian palm tree, has been extensively studied for paper coating due to its excellent barrier properties and compatibility with starch systems [10]. Santos et al. demonstrated that modifying cationic starch with carnauba wax increased its hydrophobicity and reduced its surface wettability [11]. Another suitable material for barrier coating applications is microcrystalline wax. Liu et al. investigated microcrystalline wax emulsions as fluorine-free coatings for paper-based food packaging [3]. They found that microcrystal-

line wax with a lower surface tension than edible oils could penetrate the pores of paper and form a physical shield against liquid penetration. The results indicated that applying 6 g/m² of microcrystalline wax to starch-pretreated paper significantly improved the barrier properties, achieving a Kit rating of 10/12, reducing the Cobb₆₀ value to 12.5 g/m², and decreasing water vapor permeability by 81.9%.

The mechanism of wax–starch interactions involves both physical and chemical contributions. Physically, wax particles become embedded within the starch matrix, creating a longer and more tortuous diffusion path for penetrant molecules [12]. Chemically, hydrogen bonding between the hydroxyl groups of starch and the polar components of waxes can improve interfacial compatibility and strengthen the overall coating structure [11].

Barrier properties and performance evaluation

A thorough understanding of the mass-transfer mechanisms and the factors influencing permeant migration is essential for evaluating the performance of barrier-coated papers [13]. For oil and grease barriers, the primary concern is preventing lipophilic substances from penetrating the coating and reaching the substrate. This requires not only immediate resistance to liquid contact but also long-term resistance to vapor transmission. Marianelli et al. reviewed recent developments in oil and grease resistance testing and emphasized the need for reliable, quantitative methods for evaluating waterborne barrier coatings [1]. Their work highlighted the importance of using multiple complementary test methods to obtain a comprehensive understanding of barrier behavior and to ensure that laboratory evaluations accurately predict real-world performance.

Aging mechanisms and degradation pathways

Polymer-based barrier coatings can undergo aging and degradation through multiple mechanisms, which may occur simultaneously or sequentially depending on environmental conditions and material composition. In starch-based systems, the primary degradation pathways proceed through hydrolytic, oxidative, thermal, and biological processes.

Hydrolytic degradation occurs when water cleaves the bonds in polymer chains, reducing their molecular weight [14]. This is particularly relevant in the case of starch-based coatings, given the hydrophilic nature of starch.

Oxidative degradation occurs when oxygen or oxygen-containing species react with polymer chains, leading to chain scission and, in some cases, the formation of cross-links [15]. In a starch-wax system, both starch and wax can be affected, resulting in changes in barrier performance and structural deformations.

Thermal aging is important in cases where coated papers are subjected to high temperatures in processing or

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storage. When coated papers are heated, they may decompose or develop colored compounds [16].

Biodegradation (via enzymes and microorganisms) may be a problem for starch-based coatings. Being biodegradable is beneficial for the environment, but it can lead to a reduction in the lifespan of these coatings [17]. Controlling the rate of biological degradation is important to ensure the coatings function as intended [18].

Analytical techniques for coating characterization

A comprehensive understanding of the aging behavior of barrier coatings requires the combined use of functional, chemical, and structural characterization techniques. Barrier property measurements such as heptane vapor transmission rate (HVTR), water vapor transmission rate (WVTR), and Kit test provide direct insight into changes in functional performance of oil and grease barrier coatings during aging. However, linking these changes to the underlying chemical and physical processes is essential for a full understanding of the degradation mechanisms.

Fourier transform infrared (FTIR) spectroscopy has proven particularly valuable for monitoring chemical transformations in polymer-based systems [19]. When spectra were baseline-corrected and normalized, FTIR data could be interpreted semi-quantitatively using a modified Beer–Lambert relationship appropriate for attenuated total reflectance (ATR) measurements, where absorbance depends on molar absorptivity, concentration, and the ATR penetration depth. In addition, the use of multiple indices reduced penetration-depth effects and allowed for a more reliable interpretation of spectral variations. An FTIR analysis enables the detection of key chemical and structural degradation pathways; however, for reliable interpretation, intensity changes across the entire wavenumber range must be evaluated collectively, as different spectral shifts may reflect distinct yet interconnected degradation processes.

Substrate effects and coating-paper interactions

The effects of barrier coatings on paper substrates manifest important roles in both short-term performance and long-term stability. Paper grades also differ in terms of surface characteristics, porosity, chemical structure, moisture content, coating adhesion, and penetration [20–22].

It is crucial to consider how the coating penetrates into the paper, as this strongly influences the resulting barrier performance. Excessive penetration can reduce the effective coating thickness and compromise its protective function. Insufficient penetration, on the other hand, can lead to poor adhesion and eventual coating delamination. Achieving the right balance between penetration and surface coverage is therefore essential [6]. This is particularly important for starch–wax coatings because of their relatively high viscosity and strong interactions with cellulose substrates.

MATERIALS AND METHODS

Materials

Base paper substrates

Two base papers were selected to assess the influence of substrate properties on coating performance and aging behavior:

- One-side smooth base paper (40 g/m²): has a one-side smooth surface due to calendering, low surface energy (38.9 mN/m, Owens-Wendt-Rabel-Kaelble method [23]), and minimal porosity.
- Pigment-coated base paper (78 g/m²): contains a pigment layer, resulting in higher surface energy (46.3 mN/m) and increased surface roughness.

The surface characteristics of both papers are summarized in **Table I**, and **Fig. 1** shows SEM images of both papers.

The Parker Print Surface (PPS) smoothness values were 2.67 μm for the one-side smooth base paper and 3.71 μm for the pigment-coated base paper. Bekk smoothness values were 1236 s and 144 s, respectively. The pigment-coated paper also exhibited much higher ash content (TAPPI Standard Test Method T 211 om-22 “Ash in wood, pulp, paper and paperboard: combustion at 525°C”) at 37.59% vs. 2.84% for the one-side smooth paper. Water contact angle measurements (**Fig. 2**) further reflect the difference in surface energy, with 102° for the calendered one-side smooth paper and 45° for the pigment-coated paper.

These differences in surface energy, roughness, and chemical composition provide a basis for comparing the interaction of the starch–wax coating with the two substrates and evaluating its performance during aging.

Starch–wax emulsion coating formulation

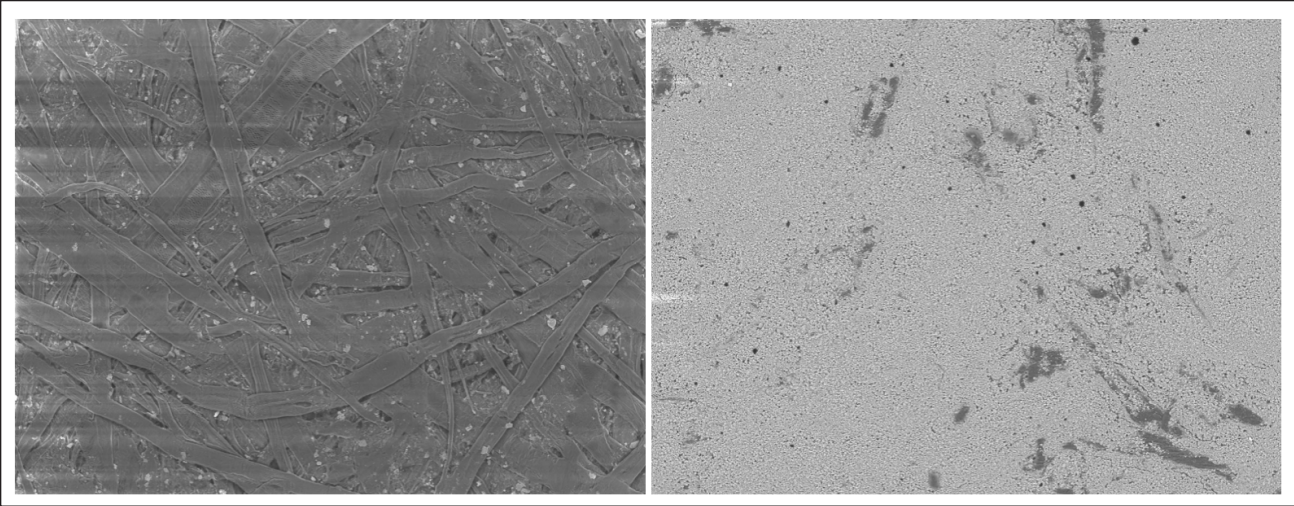
A starch–wax barrier coating emulsion was employed to provide resistance to oil, grease, and water vapor, primarily due to its wax content. The emulsion contained 43.3% total solids, had a pH of 7.3, and a Brookfield viscosity of 397 mPa·s at 100 rpm (Spindle 3, 24°C). The coating was prepared following established starch–wax emulsion protocols [11], ensuring stability and rheological properties suitable for uniform application. Briefly, starch was dispersed in water, and a hydrophobic phase was emulsified under high-shear mixing. Specific details of the starch, wax, and proprietary stabilizers are not disclosed to protect intellectual property; these omissions do not affect the reproducibility of the observed property changes during aging, as hydrolytic phenomena are inherent to all starch types due to the presence of hydroxyl groups.

Coating application

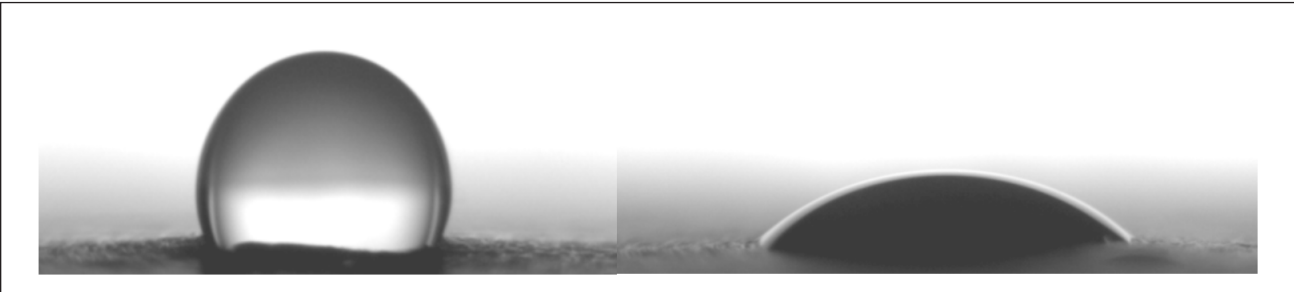
The coating was applied using a roll-to-roll pilot coater at the Omya Technology Center in Egerkingen, Switzerland, followed by two air-drying steps at 165°C with an air-blow speed of 5 m/s. Rod coating was employed at a line speed

Property	Unit	One-Side Smooth Base Paper	Pigment-Coated Base Paper
Grammage	g/m ²	40 ± 3	78 ± 2
Thickness	µm	42 ± 2	78 ± 2
Parker Print Surface smoothness (PPS, 1 MPa, top side)	µm	2.67 ± 0.10	3.71 ± 0.20
Bekk smoothness	s	1236 ± 30	144 ± 10
Surface energy	mN/m	38.9 ± 1.9	46.3 ± 1.4
Ash content	%	2.84 ± 0.6	37.59 ± 0.5
Moisture content	%	5.96 ± 0.20	4.25 ± 0.20

1. Physical and surface characterization of the base papers. Comparison between one-side smooth base paper and pigment-coated base paper.



1. Scanning electron microscope (SEM) images of base papers at 200× magnification. Left: one-side smooth base paper; right: pigment-coated base paper. Scale bars = 500 µm.



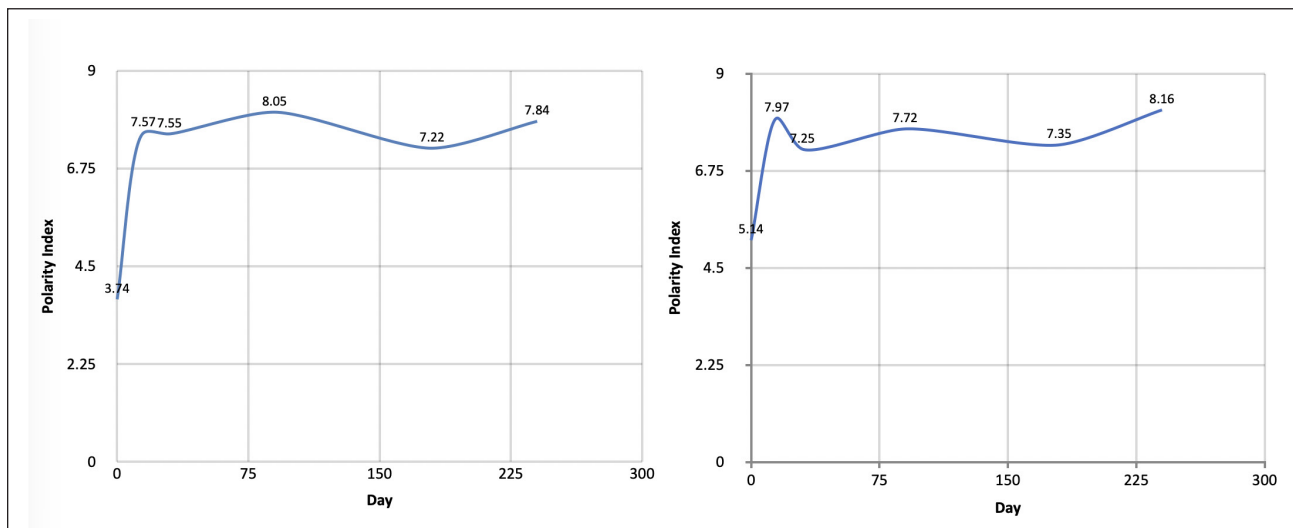
2. Water contact angle of base papers. Left: one-side smooth base paper (102°); right: pigment-coated base paper (45°).

of 20 m/min. A target dry coat weight of 8 g/m² was set for all samples. Coating weights were verified gravimetrically, and the coated papers were carefully inspected for defects or uneven areas that could influence barrier performance.

Aging protocol

A natural internal aging system with practical testing intervals was used to study the stability of the starch-wax emul-

sion coated papers. Specimens were taken from the deep interior of the coated reels, from the innermost layers where exposure to ambient air is minimal and the movement of oxygen and water vapor is strongly restricted. Under these conditions, oxygen levels are expected to be much lower than in the surrounding air, roughly 2–5 vol% due to diffusion limitations, while laboratory air at 23°C and 50% relative humidity (RH) contains about 21 vol% O₂ with moisture



3. Polarity index from normalized spectra (O–H and C=O regions divided by stable skeletal stretching reference band) for starch-wax emulsion coatings on one-side smooth (left) and pigment-coated (right) base papers

freely available. The coated reels, from which samples were collected, were stored in a conditioned room maintained at 23 °C (± 1°C) and 50 % (± 2%) RH. Aging effects were evaluated after 15 days, 1 month, 3 months, 6 months, and 8 months. These time intervals were selected to capture both short-term and long-term changes in coating performance.

RESULTS AND DISCUSSION

The chemical and physical properties of starch–wax emulsion barrier coatings applied to two different base paper substrates changed significantly over the aging period. The findings indicate that the performance of bio-based barrier systems depends strongly on the interaction between the coating formulation, substrate properties, and aging time.

Chemical changes

The ATR-FTIR spectroscopy was employed to monitor chemical changes in the coatings during aging, following standard analytical protocols for polymeric materials. Measurements were conducted on a Shimadzu IRAffinity-1 instrument (Shimadzu; Kyoto) using a diamond ATR crystal. The ATR is a surface-sensitive technique in which an IR beam undergoes total internal reflection within the crystal, producing an evanescent wave that penetrates the sample surface. For paper substrates, the effective penetration depth is approximately 0.5–5 μm, depending on the wavenumber.

The spectra were collected with 40 scans per sample at a resolution of 4 cm⁻¹ over the spectral range of 400–4000 cm⁻¹, using the Happ–Genzel apodization function. Baseline correction was performed by estimating the local baseline via a moving window of fixed width (200 points). Within each window, the 5th percentile of the absorbance values was taken as the local baseline estimate, producing a bottom envelope of the spectrum. This baseline curve was then subtracted from the original spectrum to correct

for background drift. Finally, the spectra were normalized using Min–Max normalization to scale the baseline-corrected spectra to a range of 0 to 1, allowing direct comparison of peak intensities between samples.

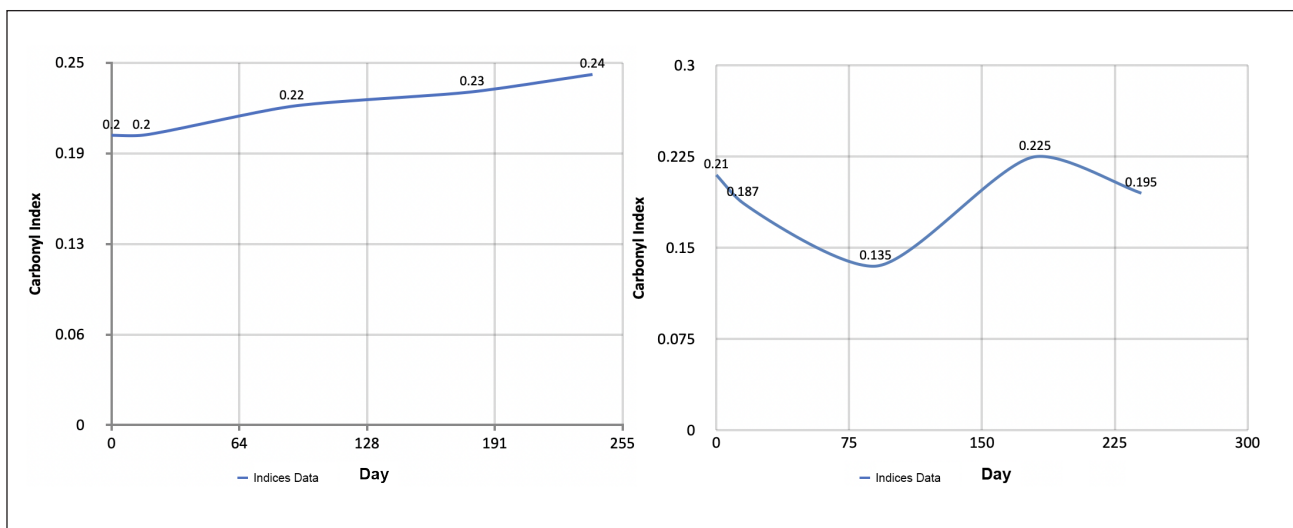
Polarity index and carbonyl index

The polarity index (PI) and carbonyl index (CI) were evaluated to investigate chemical changes in the system and to determine which degradation mechanisms were initiated and how they progressed over time. Both the polarity and carbonyl indices were calculated by normalizing the absorbance of their respective regions to a stable reference band (1300–1320 cm⁻¹, corresponding to high-frequency skeletal stretching) that remained constant across all aging intervals.

The PI was used to quantify the increase in polar functional groups during aging. The PI served as an early and sensitive indicator of hydrolysis and oxidation, reflecting the chemical evolution of the system. As shown in **Fig. 3**, the increase in PI was associated with the formation of new O–H groups (3700–3000 cm⁻¹) and various carbonyl groups (1810–1650 cm⁻¹), indicating the development of new polar compounds at the coating surface. The PI was calculated by normalizing these absorbance regions to a strong, stable reference band at 1300–1320 cm⁻¹, which corresponds to in-plane skeletal C–O/C–C motions of the glucose ring and local internal vibrations of each glucose unit, and which remains stable under different degradation mechanisms, using the formula:

$$PI = \frac{A_{O-H} + A_{C=O}}{A_{ref}} \quad (1)$$

where A_{O-H} , $A_{C=O}$, and A_{ref} are the absorbances of the hydroxyl region, the carbonyl region, and the reference band, respectively.



4. Normalized carbonyl region (1810–1650 cm^{-1}), sensitive to oxidation-derived functional groups, divided by a stable skeletal stretching reference band for starch-wax emulsion coatings on one-side smooth (left) and pigment-coated (right) base papers.

The PI increased by 109% for the starch-wax emulsion coated one-side smooth base paper and by 59% for the starch-wax emulsion coated pigment-coated base paper over the 8-month period, with the most significant change occurring during the first 15 days. This pronounced rise in polar functionalities, particularly within the first 15 days, indicates clear chemical modifications within the coating layer that can subsequently trigger physical alterations in the system, as the loss or formation of functional groups influences both the structural integrity and the barrier performance of the coating. Additional measurements indicated a reduction in moisture content over time. After 8 months of aging, the starch-wax emulsion coated one-side smooth base paper showed a decrease of 9.16% (from an initial 6.22%), while the starch-wax emulsion coated pigment-coated base paper exhibited a 6.0% reduction from an initial moisture content of 4.9%. This decrease suggests moisture loss associated with its consumption during hydrolytic processes.

The CI was used to monitor the formation of oxidation products and to determine the onset and progression of oxidative degradation. This index targets the carbonyl region (1810–1650 cm^{-1}), which is highly sensitive to oxidation-derived functional groups and can also capture secondary carbonyls formed after hydrolysis. The CI was calculated by normalizing the absorbance of the carbonyl region ($A_{\text{C=O}}$) to the same strong, stable reference band at 1300–1320 cm^{-1} , using the formula:

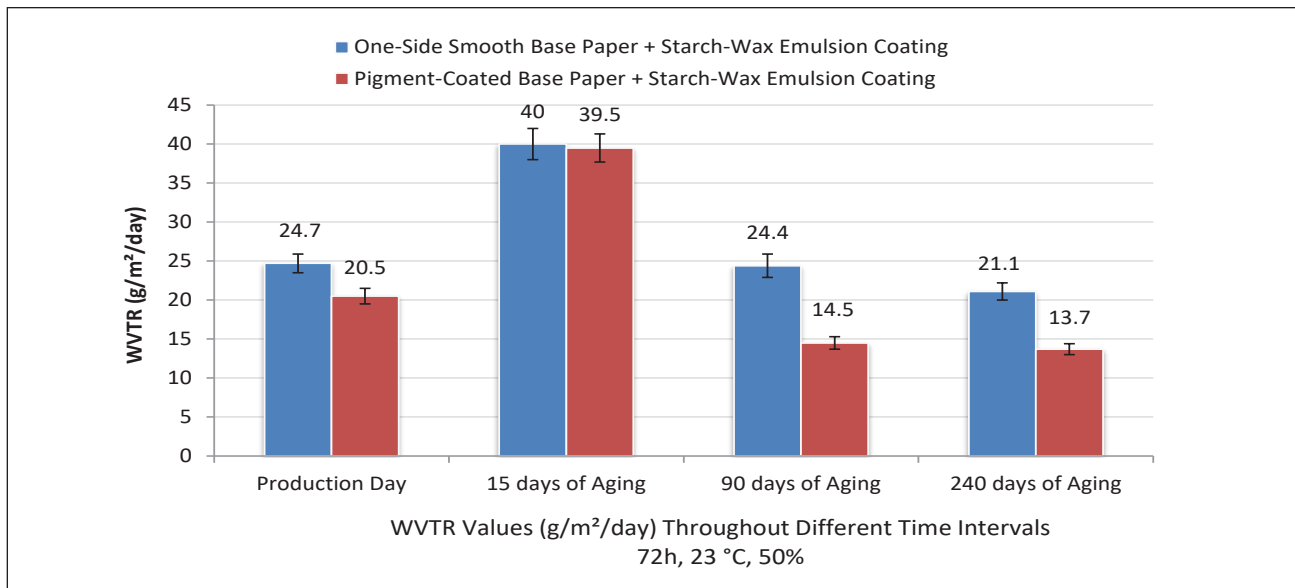
$$\text{CI} = \frac{A_{\text{C=O}}}{A_{\text{ref}}} \quad (2)$$

As illustrated in **Fig. 4**, C=O formation was not detectable during the first 15 days, despite earlier evidence that the PI increased sharply over this period, indicating that

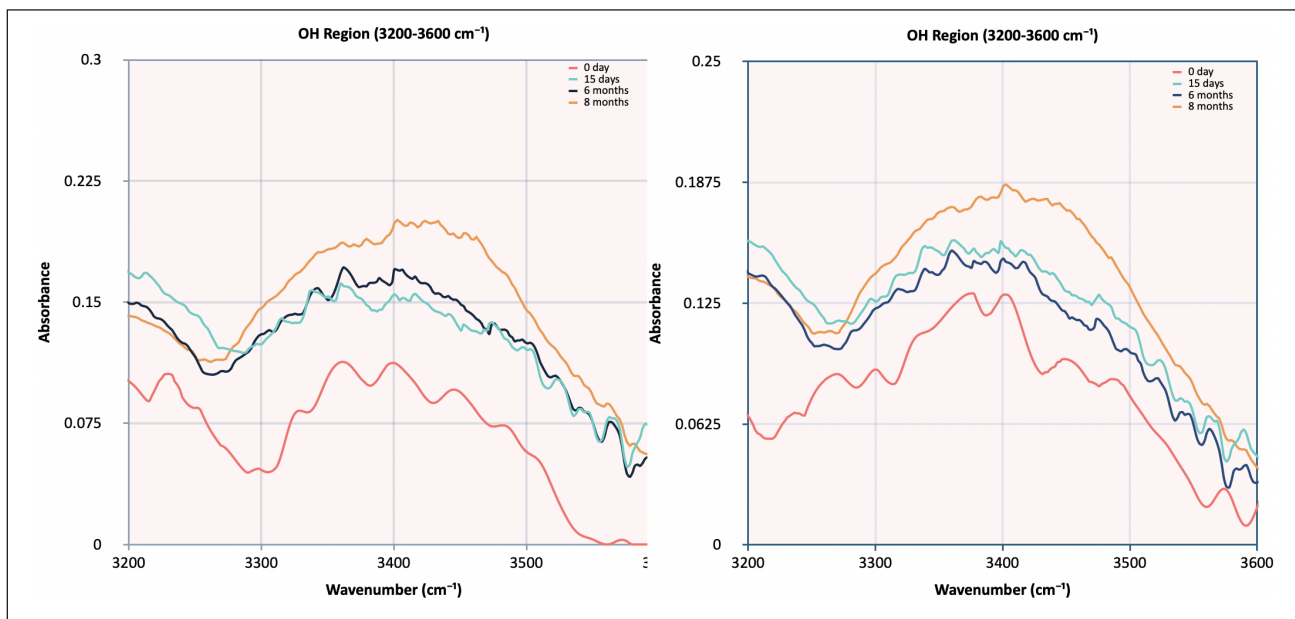
oxidation did not dominate the early aging stage. Instead, the substantial rise in CI at later aging periods demonstrates that oxidation occurred after hydrolysis, which acted as the initial degradation mechanism in the coating system. In addition, the starch-wax emulsion coated pigment-coated base paper exhibited a lower CI at intermediate aging times compared to the production day (0 day), which can be attributed to its higher porosity relative to the starch-wax emulsion coated one-side smooth base paper. The increased porosity provides capillary pathways that facilitate wax migration into the paper structure and toward the surface. As a result, the surface region probed by FTIR becomes relatively depleted in carbonyl-containing functionalities, leading to a decrease in the apparent carbonyl index. While wax migration occurs in both systems, as discussed in a later section on the absolute absorbance of the aliphatic C–H region (2800–3000 cm^{-1}), the effect of surface wax enrichment is more pronounced in the starch-wax emulsion coated pigment-coated substrate due to the higher porosity of its substrate. This interpretation is supported by WVTR results (**Fig. 5**), where the starch-wax emulsion coated pigment-coated sample shows a significant reduction in permeability over time, even surpassing its initial barrier performance. Such behavior is consistent with progressive pore filling and redistribution of hydrophobic wax components within the porous network and at the surface.

An important consideration is that the wax component does not undergo hydrolysis, as it lacks hydrolyzable functional groups. Therefore, changes observed within the first 15 days, identified based on the results as hydrolytic degradation, are attributed to the starch component rather than the wax.

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5. Water vapor transmission rate (WVTR) of starch-wax emulsion coatings applied to smooth and pigment-coated base papers at different aging intervals.



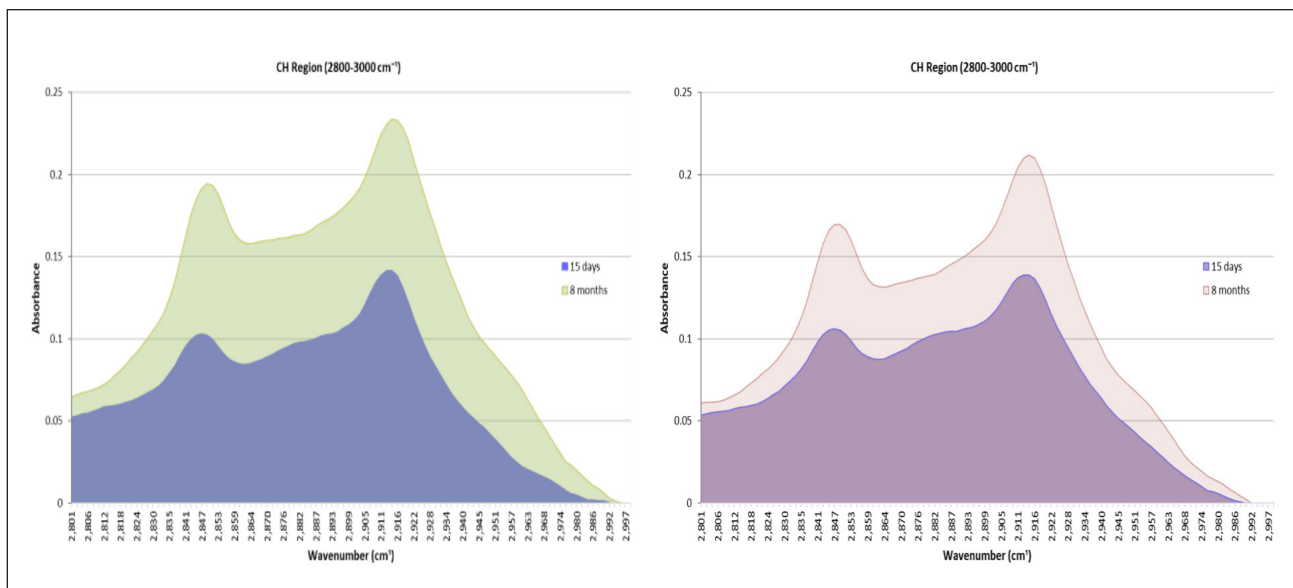
6. Normalized absolute O-H absorbance (3200–3600 cm⁻¹) for starch-wax emulsion coatings on one-side smooth (left) and pigment-coated (right) papers.

Absolute absorbance of the hydroxyl group region (3200–3600 cm⁻¹)

The O–H stretching vibrations were monitored to assess changes in hydroxyl functionalities. According to **Fig. 6**, absolute absorbance in the hydroxyl region increased significantly over time, with a sharp rise within the first 15 days, confirming gradual hydrolysis from the early aging intervals. The FTIR spectra showed clear time-dependent changes for both starch-wax emulsion coated paper substrates, consistent with the early increase in WVTR values observed after 15 days (Fig. 5).

Absolute absorbance of the aliphatic C–H region (2800–3000 cm⁻¹)

The aliphatic C–H stretching absorbance increased over time, as shown in **Fig. 7** by comparing spectra of starch-wax emulsion coated papers aged for 15 days and 8 months. The stronger peaks indicate a higher concentration of aliphatic chains at the surface, confirming significant wax migration during aging. This is further supported by physical observations such as blocking in the coated reels. The substantial improvement in WVTR over time is attributed to this wax migration, which results in



7. Absolute aliphatic C–H absorbance (2800–3000 cm^{-1}) for starch-wax emulsion coatings on one-side smooth (left) and pigment-coated (right) papers.

a high concentration of aliphatic compounds on the surface, increasing resistance to water vapor penetration and thereby improving the WVTR values.

Barrier property changes related to chemical transformations in the system

WVTR change

The WVTR measurements were performed according to TAPPI T 448 om-17 “Water vapor transmission rate of paper and paperboard at 23°C and 50% RH.” As shown in Fig. 5, WVTR values increased during the first 15 days, resulting from initial hydrolysis in the system. This trend was consistent for both coated papers. At longer aging intervals (3 and 8 months), WVTR values decreased due to significant wax migration, as supported by the increased C–H absorbance, which effectively rebalanced the system and improved the barrier performance.

Variations in initial WVTR and other barrier properties, along with differences in degradation intensity during aging, between starch–wax emulsion coated one-side smooth and pigment-coated base papers are attributed to differences in base paper porosity and coating–substrate interactions. The pigment-coated base paper allows deeper penetration of the coating into its porous structure, whereas the calendered one-side smooth base paper limits penetration, resulting in a more surface-confined coating layer.

Kit test (grease resistance evaluation)

Grease resistance was evaluated using the Kit test, which measures the ability of paper to resist penetration by a series of standardized test liquids of increasing aggressiveness (castor oil–toluene–heptane mixtures at varying ra-

tios). The highest-numbered solution that does not produce visible staining defines the Kit value. Measurements were conducted following TAPPI Standard Test Method T 559 cm-22 “Grease resistance test for paper and paperboard.”

As shown in **Fig. 8**, Kit values decreased after 8 months of natural aging compared to the production day, indicating a reduction in grease resistance. This decline is attributed to the migration and redistribution of wax components within the coating. Increased surface concentration of aliphatic C–H groups, observed in FTIR analysis, reflects wax migration toward the surface. The resulting surface lipophilicity, combined with localized heterogeneity, facilitates penetration by the test liquids, leading to lower Kit values over time.

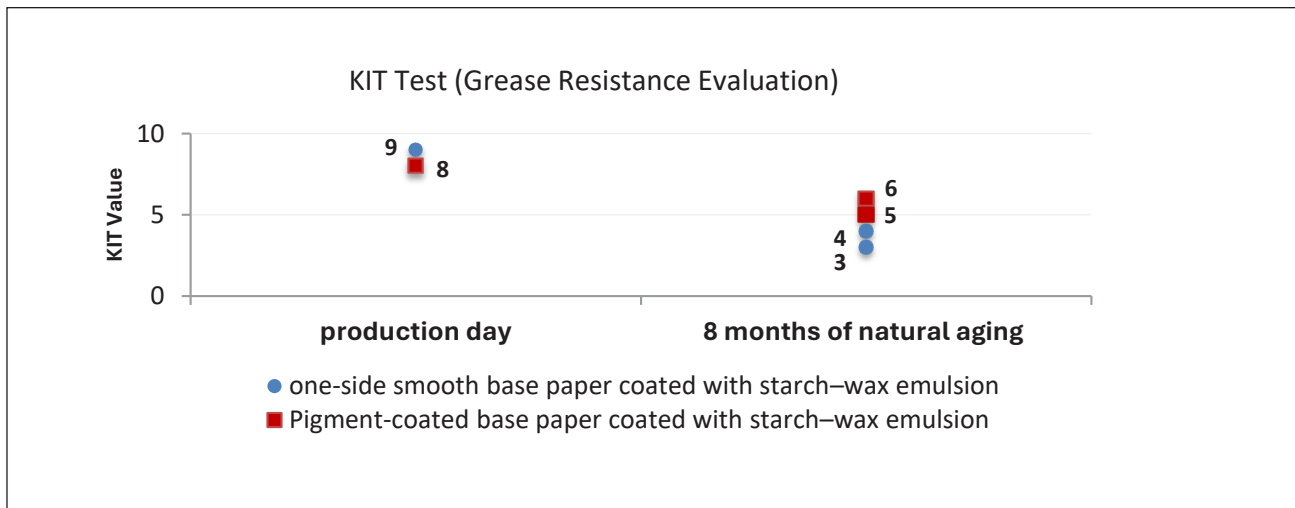
Physical changes

Structural changes are another key observation in the aging and degradation of bio-based starch–wax emulsion barrier coatings. Physical and structural modifications were evaluated using the conformational disorder index (CDI) and SEM imaging. These structural changes in the coating over time directly influenced barrier performance, as reflected in the loss of HVTR properties.

Conformational disorder index

To evaluate physical changes in the system, the CDI was calculated for one-sided smooth base paper coated with the starch–wax formulation, comparing fresh samples with those aged for 8 months.

The FTIR studies of starch derivatives by Bruijnes et al. have demonstrated that the fingerprint region between 1200 and 900 cm^{-1} is highly sensitive to the tertiary structure and conformational order of glucose polymers. In this



8. Grease resistance evaluation (Kit) test of starch-wax emulsion coatings on one-side smooth and pigment-coated base papers, comparing values on the production day and after 8 months of natural aging.

region, band sharpening, band broadening, frequency shifts, and intensity variations correlate directly with molecular order, with increased band broadening and intensity redistribution associated with reduced crystallinity and higher conformational freedom of starch chains [24].

Based on these observations, a CDI was defined in this study as the ratio of the integrated absorbance of the conformationally sensitive fingerprint region to a stable internal reference band:

$$CDI = \frac{A_{900-1200}}{A_{ref}} \quad (3)$$

where $A_{900-1200}$ represents the integrated absorbance of skeletal C–O–C, C–C, and glucopyranose ring vibration modes, and A_{ref} corresponds to a strong band in the 1300–1320 cm^{-1} region, selected for its minimal sensitivity to conformational changes. The 65.3% increase in CDI after 8 months indicates enhanced conformational disorder, reflecting enhanced molecular mobility of starch chains and, increased structural heterogeneity arising from physical rearrangements during aging, which are also reflected by crack formation observed in the SEM images (Fig. 9).

SEM analysis

The SEM image was taken using secondary electrons (SE2) at an accelerating voltage of 15 kV, a working distance of 8.5 mm, and a magnification of $\times 100$ (scale bar: 200 μm).

The surface features of the freshly prepared starch-wax emulsion coated one-side smooth base paper exhibited a relatively smooth and continuous surface, as shown in Fig. 9. As the coating aged, SEM observation revealed that after 8 months, the coating's surface started to break down, and microcracks were formed on its surface.

Barrier property changes related to physical transformations in the system

HVTR change

Measurement of HVTR was conducted using a modified version of the WVTR method, adapted for organic vapor transmission. The HVTR provides important insight into the barrier effectiveness of starch-wax emulsion coatings against organic vapors and how this performance changes with aging.

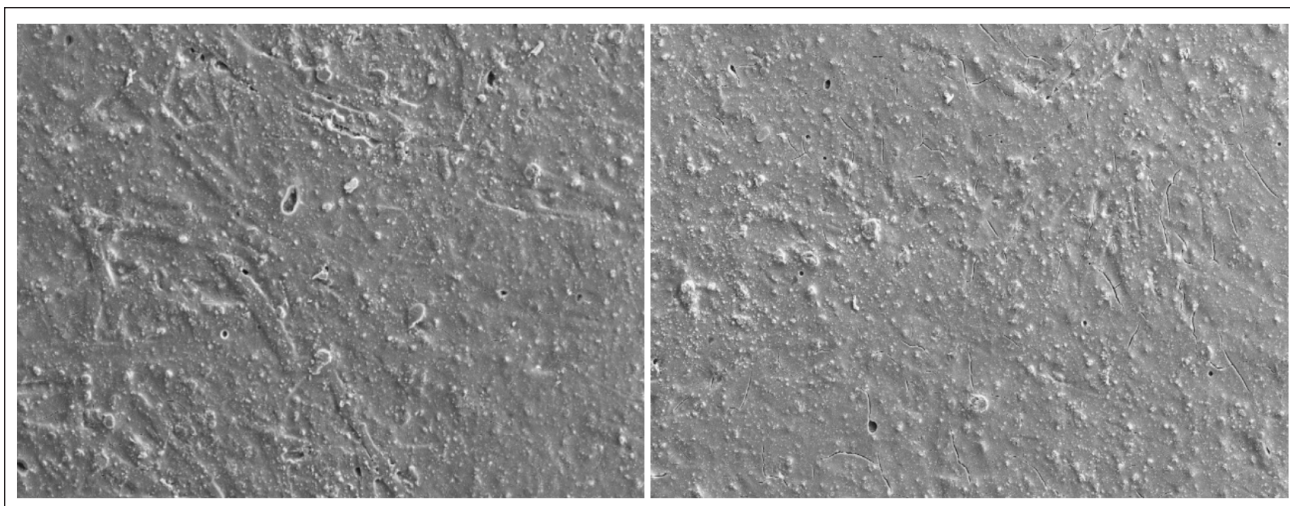
Heptane vapor transmission is strongly influenced by the coating's microstructure because heptane has low surface tension and high volatility, making it highly sensitive to physical defects. As the coating develops micro-cracks and increased porosity, molecular pathways for heptane permeation become more accessible.

As shown in Fig. 10, low HVTR values were observed initially, until approximately the first two weeks, which is also attributed to hydrolysis introducing polar compounds that temporarily hinder the penetration of non-polar heptane. However, the HVTR values increased significantly over the following 8 months.

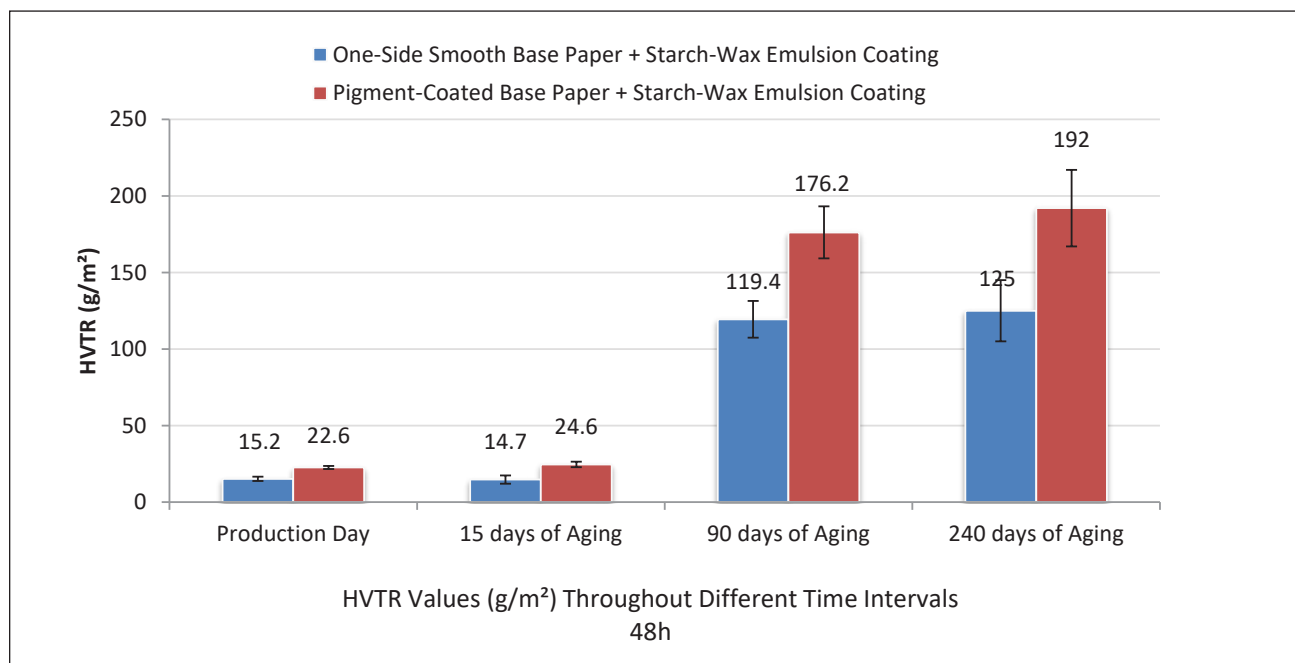
CONCLUSION

We studied the aging of starch-wax emulsion barrier coatings on two distinct base papers and observed clear chemical, physical, and barrier-property changes over time.

The FTIR analysis revealed the key chemical transformations in the system. A continuous increase in the hydroxyl region indicated pronounced hydrolytic activity beginning within the first 15 days, exclusively associated with the starch compounds rather than the wax, due to the abundant presence of hydrolyzable groups. Oxidative degradation, on the other hand, became evident later and progressed over the 8-month period, as indicated by the gradual formation of carbonyl groups throughout the system. In parallel, wax migration was confirmed by the



9. Scanning electron microscope (SEM) images of starch-wax emulsion coatings on one-side smooth base paper at 100 $\times$ magnification. Left: non-aged sample; right: sample after aging, showing microcrack formation.



10. Heptane vapor transmission rate (HVTR) of starch-wax emulsion coatings applied to one-side smooth and pigment-coated base papers at different aging intervals.

steady increase in aliphatic C–H absorbance and by physical blocking observed in the coated reels. These chemical changes caused notable structural modifications. The CDI increased by 65.3% after 8 months for the starch-wax emulsion coated one-sided smooth base paper, indicating great physical rearrangement. The SEM imaging supported this, showing the development of surface cracks resulting from these structural changes.

Barrier properties responded accordingly. The WVTR increased significantly during the first 15 days for both starch-wax emulsion coated papers due to early hydrolysis and the higher concentration of hydroxyl groups. After 8

months, extensive wax migration compensated for these effects and lowered WVTR again. In contrast, HVTR increased steadily throughout aging, as the coating's microstructure became increasingly permeable, except during the first 15 days where polar hydroxyl groups temporarily hindered non-polar heptane penetration. Kit values also decreased, confirming reduced oil and grease resistance and demonstrating the sensitivity of barrier performance to both chemical and physical degradation.

When comparing the substrates, the two base papers exhibited distinct barrier performance and degradation behavior during aging when coated with the starch-wax

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emulsion, reflecting differences in surface energy, porosity, and coating–substrate interactions. This behavior arises from the deeper penetration of the coating into the porous pigment-coated base paper, whereas the calendered one-side smooth base paper restricts penetration, resulting in a more surface-localized coating. These differing interactions determine coating distribution and, consequently, influence barrier performance during aging, emphasizing the importance of substrate structure in long-term stability.

Taken together, the combined FTIR absorbance data and derived indices confirmed three dominant degradation mechanisms in starch–wax emulsion barrier coatings:

- Hydrolytic degradation, introducing hydroxyl groups and promoting chain cleavage (dominant in the first 15 days).
- Oxidative degradation, evidenced by carbonyl formation occurring only during the later stages of aging.
- Pronounced wax migration, strongly influencing surface chemistry, structure, and barrier behavior.

LITERATURE CITED

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This topic was chosen because bio-based barrier papers are increasingly developed, and understanding their degradation is crucial to design biodegradable packaging with reliable barrier performance and adequate shelf life. This research goes beyond previous studies by linking aging and degradation of oil- and grease-resistant coatings directly to changes in barrier performance.

The most difficult aspect was identifying degradation pathways that cause physical changes and alter barrier performance. This was addressed using FTIR analysis alongside barrier measurements.

Through this study, we learned that degradation is an inevitable phenomenon in bio-based barrier coatings — aligning with their biodegradability — but it can negatively affect shelf life, so it must be carefully managed to balance both goals. The most interesting finding was that degradation begins at very early stages, highlighting the need to monitor and manage changes from the start.

Mills can use these findings to develop bio-based barrier coatings that are both durable and functional while maintaining biodegradability. The next step is to study degradation of barrier-coated papers under harsh conditions, such as high humidity or elevated temperatures.

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