Phenolic Compound-Incorporated Sodium Caseinate Barrier Coatings for Paper Packaging

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Sodium caseinate (SC)-based barrier coatings containing tannic acid (TA) and ferulic acid (FA) were applied to paper substrates as biodegradable alternatives to synthetic polymer coatings. The objective was to evaluate the effects of phenolic compound type, phenolic compound loading, and coating weight on the structural, thermal, barrier, and mechanical properties of SC-coated papers and to establish suitable coating conditions for biodegradable paper-based packaging applications. FT-IR analysis indicated that TA and FA interacted with SC mainly through hydrogen bonding and other noncovalent intermolecular interactions, with no detectable evidence of ester bond formation under the investigated conditions. The addition of TA or FA shifted the thermal decomposition of the SC coating to a higher temperature range and improved air, grease, and water-related barrier properties. Barrier performance depended strongly on phenolic compound loading and coating integrity, with excessive TA loading causing surface cracking and reduced air resistance. All coated papers showed the maximum measurable oil resistance, and moderate increases in tensile strength were observed. These results suggest that TA- and FA-containing SC coatings are promising biodegradable barrier coatings for paper-based packaging, particularly for dry or grease-containing food applications requiring improved air and oil resistance.

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INTRODUCTION

The increasing demand for convenience foods and ready-to-eat meals has accelerated the use of single-use packaging, prompting a growing interest in sustainable alternatives to petroleum-based materials (Rochman *et al.* 2013). Among the various candidates, paper-based packaging has attracted considerable attention owing to its renewability and recyclability (Khwaldia *et al.* 2010; Rastogi and Samyn 2015). However, the use of paper as a functional packaging material remains challenging because its cellulose-based structure is inherently hydrophilic and porous, resulting in poor barrier properties against moisture and gases (Khwaldia *et al.* 2010).

To overcome these limitations, paper packaging is commonly combined with high-barrier synthetic polymers (Andersson 2008). Although this approach effectively improves barrier performance, it compromises biodegradability and recyclability, as the polymer layers are difficult to separate from the paper substrate after use (Lee *et al.* 2021; Lee *et al.* 2022). Consequently, the development of biodegradable barrier coatings capable of

replacing conventional synthetic polymers has become an important focus of current research (Jahangiri *et al.* 2024).

Protein-based biopolymers are considered promising candidates for this purpose owing to their excellent air and oil barrier properties (Chen *et al.* 2019). Sodium caseinate (SC), a milk-derived protein, exhibits favorable film-forming ability, good thermal stability, and low air permeability (Lin *et al.* 2020; Schou *et al.* 2005). However, its strong affinity for water limits its moisture barrier performance, thereby restricting its broad application in packaging systems (Chen *et al.* 2019). Crosslinking has therefore been widely explored as an effective strategy to improve both the barrier and mechanical properties of SC-based films (Cao *et al.* 2007).

Crosslinking can be achieved through physical interactions, such as hydrogen bonding, electrostatic interactions, hydrophobic interactions, and π–π stacking; chemical reactions, such as Schiff base formation, Michael addition, esterification, and amide bond formation; or enzymatic reactions, such as transglutaminase-mediated coupling (Azeredo and Waldron 2016; Garavand *et al.* 2017). Although synthetic aldehyde-based crosslinkers, such as glutaraldehyde, exhibit high crosslinking efficiency, their potential toxicity has raised concerns regarding their use in food-related packaging materials (Marquié 2001; Silva *et al.* 2004). Therefore, natural crosslinkers have received increasing attention. Among them, phenolic compounds are particularly attractive because they are abundant, cost-effective, and capable of interacting with proteins through multiple noncovalent interactions and, under suitable oxidative or activating conditions, may also participate in covalent reactions (Lin *et al.* 2020; Shahidi and Dissanayaka 2023; Chen *et al.* 2022). Tannic acid (TA) and ferulic acid (FA) are representative phenolic compounds that can act as natural crosslinkers and have been reported to enhance mechanical strength, thermal stability, and barrier properties in various protein- and polysaccharide-based film systems (Gupta *et al.* 2023).

Tannic acid, a plant-derived polyphenol containing multiple phenolic hydroxyl groups, can form extensive hydrogen-bonding networks with hydroxyl and amino groups in biopolymers, leading to physically crosslinked structures (Zhang *et al.* 2023). Ferulic acid, a hydroxycinnamic acid derivative, has been reported to interact with biopolymers through hydrogen bonding and, under appropriate reaction conditions, may also participate in esterification or radical-mediated reactions; these interactions have been associated with improved mechanical properties and barrier performance in protein-based films (Gupta *et al.* 2025).

Despite these advances, direct comparisons of TA and FA as natural phenolic compounds for modifying SC-based barrier–coated paper remain underexplored. Moreover, systematic investigations into how phenolic compound type, loading level, and processing conditions influence the barrier and physical properties of SC-based packaging materials are still lacking.

The objective of this study was to evaluate TA and FA as natural phenolic compounds for SC-based paper barrier coatings and to examine the effects of phenolic compound type, phenolic compound loading, and coating weight on the structural, thermal, barrier, and mechanical properties of the coated papers. In particular, this study aimed to establish suitable coating conditions for improving air, grease, and moisture-related barrier performance while maintaining or enhancing mechanical properties for biodegradable paper-based packaging applications.

EXPERIMENTAL

Materials

Sodium caseinate, composed of α_{s1}-casein, α_{s2}-casein, β-casein, and κ-casein, was purchased from Sigma-Aldrich and supplied as a white powder with a nitrogen content of 13.5% to 16.0% and a sodium content of ≤3%. For characterization, an aqueous sodium caseinate solution was prepared in H_2O at a solid content of 10 wt.%. The solution exhibited a viscosity of 37 to 39 cP, as measured using a DV-E™ Viscometer (AMETEK Brookfield, USA) equipped with spindle No. 62, and a pH of 6.4 to 6.5. TA (M_w = 1,701.20 g/mol, 99.5%, Sigma-Aldrich) and FA (M_w = 194.18 g/mol, 98%, Daejung, South Korea) served as phenolic compounds for modifying the SC coating formulation.

A wood-free paper intended for food packaging, supplied by Moorim P & P Co., Ltd. (Ulsan, Korea), was employed as the base paper. The OptiTopo surface deviation (OSD) roughness was measured using an OSD instrument (L&W, Sweden). The base paper had a basis weight of 61.4 ± 0.4 g/m^2, a thickness of 64.0 ± 0.5 μm, a density of 0.85 ± 0.004 g/cm^3, and an OSD roughness of 1.01 ± 0.02 μm.

Coating

SC (5 g) was dispersed in distilled water and stirred at 80 °C for 1 h using a magnetic stirrer to prepare the coating solution. Unless otherwise specified, the total solid content of the coating solution was adjusted to 10 wt.%. TA and FA, used as phenolic additives, were separately dissolved in distilled water at room temperature and subsequently added to the SC solution. The phenolic compounds were incorporated at levels of 2.5, 5, 7.5, and 10 wt.% relative to the dry weight of SC. For all coating formulations, the amount of distilled water was adjusted to obtain the target total solid content, including SC and the added phenolic compounds. To investigate the effect of coating weight on the properties of the coated paper, the total solid content of the coating solutions was adjusted to 10, 12.5, and 15%.

The coating solutions were then applied to the base paper under controlled laboratory conditions. Prior to coating, the base paper was conditioned at 23 °C and 50% relative humidity for at least 24 h. Coating was performed using a laboratory bar coater (Auto Bar Coater, Gist Co., Korea) at a coating speed of 40 mm/s and a coating pressure of 0.1 kPa, following previously reported procedures (Lee *et al.* 2024; Lim *et al.* 2024). After coating, the samples were dried in a hot-air oven at 40 °C for 30 min. The dried coated papers were subsequently pressed using an automatic press at 80 °C and 80 kg/cm^2 for 5 min to mitigate shrinkage induced by moisture removal during drying.

The surface morphology of the coated papers was observed using field-emission scanning electron microscopy (FESEM, JSM-7601F, JEOL, Japan).

Fourier transform infrared (FT-IR) spectroscopy was employed to investigate possible intermolecular interactions between SC and the phenolic compounds, TA and FA. Spectra were recorded using an FT-IR spectrometer equipped with a microscope (Thermo Scientific, USA). The coated paper samples were analyzed in transmittance mode over a wavenumber range of 4000 to 500 cm^{-1}.

The thermal stability of the SC-coated papers containing TA or FA was investigated *via* thermogravimetric analysis (TGA) using a thermal analyzer (SDT Q600). Measurements were performed under a nitrogen atmosphere by heating the samples from room temperature to 600 °C at a constant heating rate of 10 °C/min.

Barrier Properties

The barrier properties of papers coated with SC only and SC containing TA or FA were evaluated in terms of air permeability, water absorption, water vapor transmission rate (WVTR), and oil resistance. Air permeability was measured using an air permeance tester (L&W, Sweden) in accordance with ISO 5636-3 (2013). Water absorption was determined following ISO 535 (2023), with the Cobb value measured after 60 s of water contact at room temperature. The WVTR was determined using the calcium chloride method specified in KS T 1305 (2016), with tests conducted at 40 °C and 90% relative humidity for a duration exceeding 24 h. Oil resistance was assessed using the Kit test in accordance with TAPPI T 559 (2022).

Mechanical Properties

The mechanical performance of papers coated with SC only and SC containing TA or FA was evaluated by measuring tensile strength and strain using a tensile testing instrument (L&W, Sweden), in accordance with ISO 1924-3.

RESULTS AND DISCUSSION

Morphological, Structural, and Thermal Characterization

Surface morphology analysis via SEM

First, SC-based coatings with different solution compositions were prepared, and the resulting coated papers were analyzed *via* SEM to evaluate the influence of TA or FA type and loading on surface coverage.

Under the SC-only coating condition, a partial filling of pores relative to the base paper was observed; however, individual fiber morphologies were still discernible, indicating that the surface coverage was not fully uniform. After the addition of TA or FA, the fiber outlines became scarcely visible compared to the SC-only condition, and a more homogeneous and continuous coating layer was formed. This observation suggests that the phenolic compounds contributed to the formation of a denser coating structure, possibly through intermolecular interactions with SC (Feng *et al.* 2025).

By contrast, surface cracks were observed in the coating layer under the 10 wt.% TA condition. This behavior is likely owing to excessive interactions between TA and SC, which increased internal stress within the coating matrix and induced film cracking during drying. A similar result was reported by Yuan *et al.* (2021), who attributed crack formation in TA-containing gelatin films to excessive interaction density within the film matrix.

For the FA-crosslinked samples, surface morphologies comparable to those of the TA-crosslinked coatings were observed, showing smoother surfaces than the SC-only–coated paper. Notably, no surface cracks were detected even under the 10 wt.% FA condition, indicating that FA incorporation provided a more stable coating structure without inducing excessive internal stress. This finding is in line with previous observations by Yerramathi *et al.* (2021), who attributed such stability to FA-induced molecular tailing in polymers, which facilitates the formation of a highly homogeneous polymer network.

When the effect of coating weight on the surface morphology of paper was investigated, there were no pronounced differences in surface coverage with increasing coating weight, and the fibers were not completely covered by the coating layer.

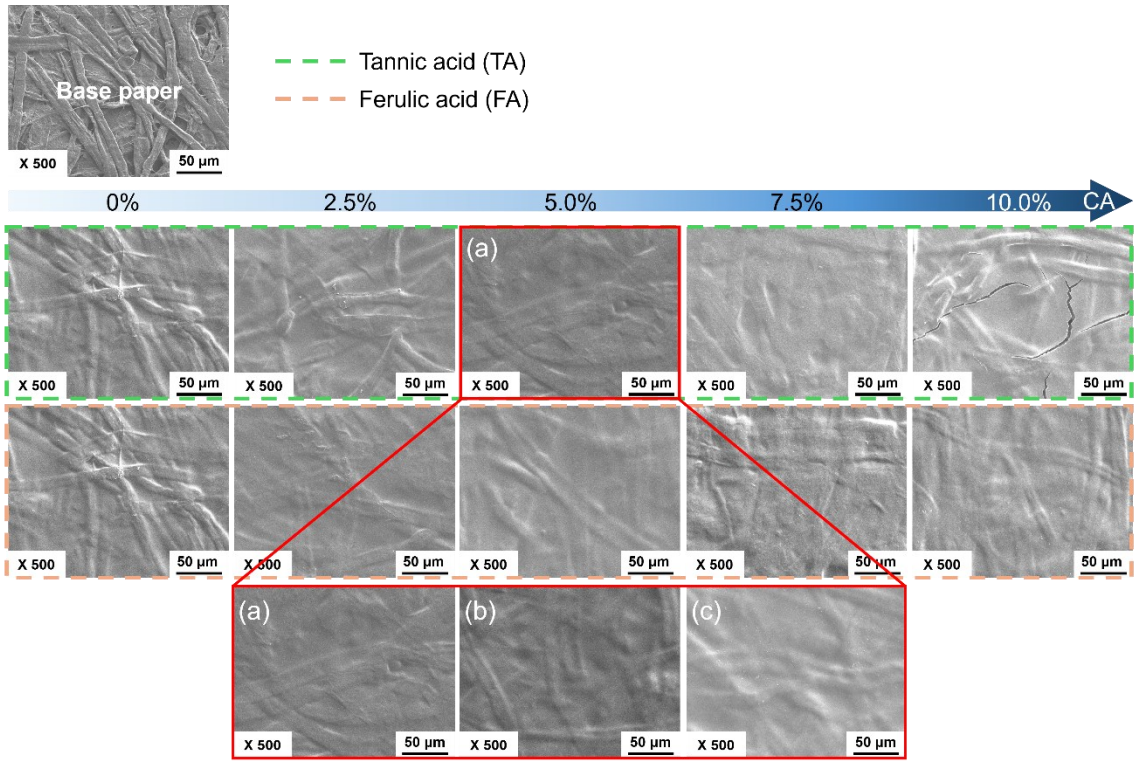

Fig. 1. FE-SEM images (×500) showing the surface coverage of paper coated with SC only and SC containing TA or FA at various loadings. Unless otherwise noted, all samples were prepared with a coating weight of 5 g/m^2. Images (a–c) show the effect of coating weight (5, 7.5, and 10 g/m^2) at a fixed TA content of 5 wt.%.

FT-IR analysis

FT-IR analysis was conducted to investigate the chemical structure and to assess possible intermolecular interactions between SC and the phenolic compounds. The FT-IR spectra of the SC-coated base paper containing TA and FA are shown in Fig. 2. The characteristic absorption bands of SC include a broad band at 3278 cm^{-1}. This was assigned to O–H and N–H stretching vibrations. A band at 2978 cm^{-1} was attributed to –CH_2 stretching. A band at 1630 cm^{-1} was associated with C=O stretching (amide I). A band at 1529 cm^{-1} was attributable to N–H bending (amide II); and a band at 1239 cm^{-1} corresponding to C–N and N–H stretching (amide III) was consistent with the results of a previous report (Li *et al.* 2016). An additional band at 1411 cm^{-1} was attributed to O–H bending vibrations, while the absorbance band at ~1042 cm^{-1} was assigned to C–O and C–N stretching vibrations (Guo *et al.* 2021).

It is well documented that crosslinking can be achieved through physical, chemical, or enzymatic approaches, which involve noncovalent interactions, covalent bond formation, and enzyme-mediated coupling, respectively (Azeredo and Waldron 2016; Garavand *et al.* 2017). In the TA-containing SC coatings, the observed FT-IR spectral changes appeared to be mainly associated with noncovalent intermolecular interactions rather than clear evidence of covalent bond formation. With increasing TA loading (Fig. 2a), a slight decrease in the intensity of the broad O–H/N–H stretching band at 3278 cm^{-1} was observed without a noticeable change in band width, suggesting the involvement of O–H and N–H groups in intermolecular interactions between SC and TA (Menezes *et al.* 2019). The amide I band also shifted slightly from approximately 1633 to 1631 cm^{-1}, indicating a change in

the hydrogen-bonding environment around the carbonyl groups of SC. It has been reported that stronger hydrogen bonding involving C=O groups can reduce the electron density of the carbonyl group and affect the amide I absorbance band (Turbiani *et al.* 2011). In addition, the intensities of the amide I, amide II, and amide III bands decreased with increasing TA content, which further supports the presence of intermolecular interactions affecting the C=O, N–H, C–N, and N–H vibrations of SC (Jackson and Mantsch 1995; Guo *et al.* 2021). The C–O/C–N stretching band also shifted from approximately 1053 to 1042 cm^{-1} as the TA loading increased, suggesting interactions between the phenolic hydroxyl groups of TA and the polar functional groups of SC (Yen *et al.* 2008). Importantly, no distinct absorbance band was observed near 1730 cm^{-1} under any of the tested conditions, indicating that ester bond formation between SC and TA was not detectable by FT-IR.

A similar interpretation can be applied to the FA-containing SC coatings (Fig. 2b). With increasing FA loading, the amide I band shifted from approximately 1633 to 1625 cm^{-1}, suggesting a change in the hydrogen-bonding environment around the carbonyl groups of SC. However, unlike the TA-containing samples, no pronounced changes in the intensities of the O–H/N–H, amide II, amide III, or C–O/C–N bands were observed over the examined spectral range. In addition, no distinct absorption band was detected near 1730 cm^{-1}, indicating that ester bond formation between SC and FA was not detectable by FT-IR. This result is in line with the limited reactivity of carboxylic acids toward ester formation in the absence of catalysts or activating agents (Bender 1960). Furthermore, no new absorbance band or clear spectral feature attributable to newly formed amide bonds was observed in either the TA- or FA-containing SC coatings. Although newly formed amide bonds may overlap with the intrinsic amide I and amide II bands of SC, the absence of new bands or pronounced spectral changes indicates that amide bond formation was not detectable by FT-IR under the present coating conditions. Therefore, the FT-IR results suggest that FA also interacted with SC mainly through physical crosslinking based on hydrogen bonding and other noncovalent intermolecular interactions, rather than through detectable covalent ester or amide bond formation.

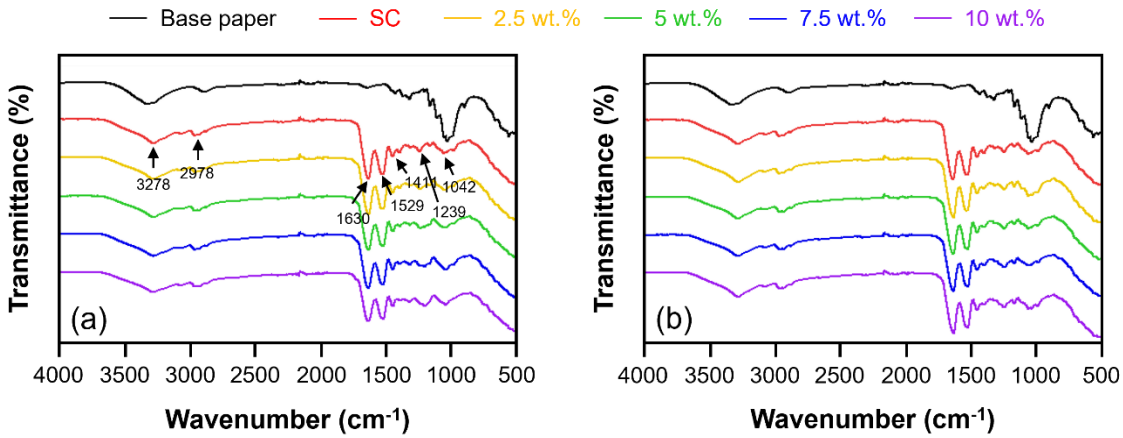

Fig. 2. FT-IR spectra of SC-coated paper containing TA (a) and FA (b) at different phenolic compound loadings. The numerical values in the legend indicate the TA or FA content (wt.%) relative to SC.

Thermal stability analysis via TGA

The TGA and derivative thermogravimetry (DTG) curves of the SC-coated base paper containing TA and FA are shown in Fig. 3, and the onset decomposition temperatures

and temperatures at maximum weight loss are summarized in Table 1. All samples exhibited a major thermal decomposition stage in the temperature range of 250 to 350 °C. The SC-only–coated paper showed an onset of thermal decomposition at 293 °C, which was ~10 °C higher than that of the uncoated base paper. By contrast, all TA-containing samples exhibited decomposition onset temperatures at ~310°C, corresponding to an increase of ~20 °C relative to the SC-only–coated paper. This result indicates that thermal decomposition of the SC coating started at a higher temperature after the addition of TA. However, no pronounced differences were observed among the TA-containing samples, indicating that the TA content did not significantly affect the onset temperature of thermal decomposition.

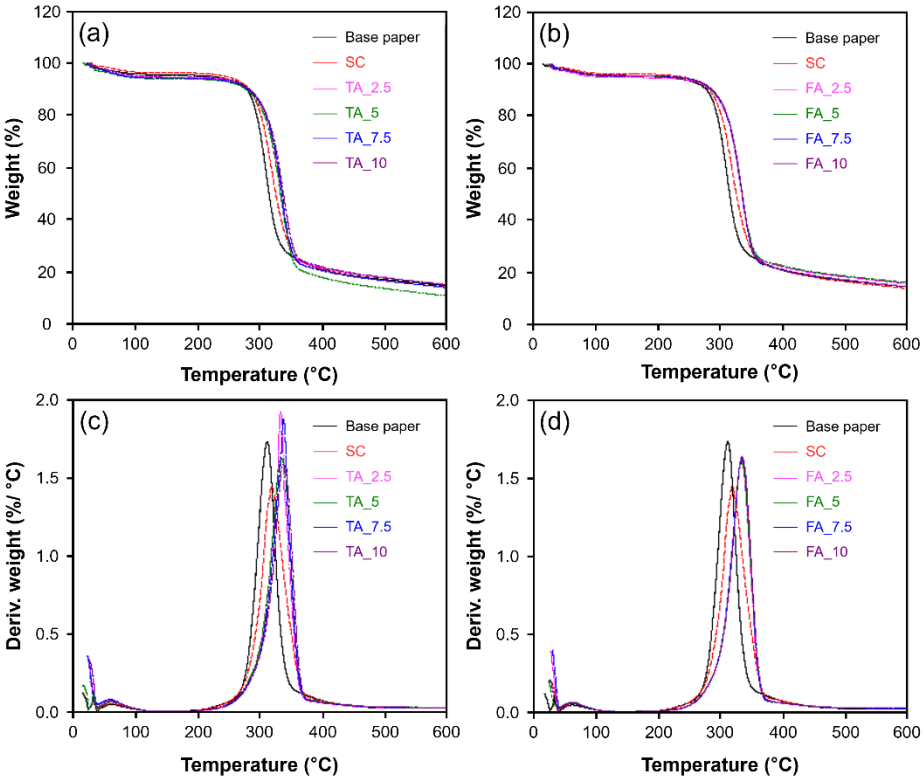

Fig. 3. TGA (a, b) and DTG (c, d) curves of SC-coated base paper containing TA (a, c) and FA (b, d) at different TA or FA loadings (TA_2.5 to TA_10 and FA_2.5 to FA_10). The numerical values indicate the TA or FA loading (wt.%) relative to SC.

Similarly, the FA-containing samples showed decomposition onset temperatures at ~310 °C, which was comparable to those of the TA-containing samples, with no clear dependence on FA content. The temperature at maximum weight loss for the SC-only–coated paper was ~20 °C. This was higher than that of the uncoated base paper, whereas all TA- and FA-containing samples exhibited higher maximum weight loss temperatures than the SC-only–coated paper. This behavior suggests that the addition of TA or FA shifted the thermal decomposition of the SC coating to a higher temperature range, possibly due to intermolecular interactions within the coating matrix (Feng *et al.* 2025). Overall weight loss did not differ markedly among the samples, with all conditions exhibiting weight losses in the range of 84% to 88%.

Table 1. Onset Temperature (T_{onset}) and Derivative Peak Temperature (DT_p) for Base Paper, SC-coated Paper, and SC-coated Papers Containing TA or FA

Sample*	T_{onset} (°C)	DT_p (°C)
Base paper	288.5	330.3
SC	293.7	343.8
TA_2.5	311.9	346.9
TA_5	307.7	351.9
TA_7.5	313.3	350.0
TA_10	309.9	352.2
FA_2.5	307.2	350.5
FA_5	307.2	351.1
FA_7.5	307.2	351.8
FA_10	307.6	351.7

* The numerical values indicate the TA or FA loading (wt.%) relative to SC.

Barrier Properties

Air permeability

The air barrier performance of food packaging materials plays a critical role in retarding food deterioration and oxidative degradation by limiting the permeation of oxygen and other gases. In particular, high air barrier properties are required for fresh-food packaging, where shelf-life extension is closely associated with controlled air transmission (Cui *et al.* 2015). The Gurley air permeability test evaluates the air resistance of a paper specimen by measuring the time required for 100 cm^3 of air to pass through it. A higher Gurley seconds value indicates greater resistance to air flow and, consequently, improved air barrier performance (Sam *et al.* 2025).

Under the SC-only coating condition, the air resistance was increased by more than ~320-fold compared to the base paper, indicating a substantial enhancement in air barrier performance (Fig. 4a). When TA was added, the 5 wt% TA condition exhibited an additional increase of ~10% relative to the SC-only–coated paper, resulting in the highest air resistance among the tested samples. By contrast, a pronounced decrease in air resistance was observed at the 10 wt.% TA condition. This reduction can be attributed to air leakage through surface cracks, as evidenced by the FE-SEM observations (Fig. 1), suggesting that excessive TA loading adversely affected coating integrity. A similar result was reported by Zhu *et al.* (2019), who attributed this behavior to air leakage through surface cracks.

For the FA system, the 2.5 wt% FA sample showed superior air resistance compared to the SC-only–coated paper, whereas further increases in FA content resulted in comparable values without significant additional increase (Fig. 4a). Overall, both TA- and FA-containing SC coatings were effective in enhancing air resistance, although their optimal performance depended on the phenolic compound type and loading level.

The effect of coating weight on air permeability was also investigated under the 5 wt% TA condition. No pronounced differences were observed with increasing coating weight (Fig. 4a), suggesting that, within the investigated range, coating weight had a limited influence on air permeability.

WVTR

The changes in WVTR of SC-coated papers containing TA and FA are shown in Fig. 4b. WVTR measurements were conducted at 40 °C and 90% relative humidity. The water vapor barrier performance of packaging materials plays a critical role in limiting

moisture permeation through the packaging wall, thereby helping to maintain the quality of packaged foods during storage and distribution (Siracusa 2012).

Compared to the uncoated base paper, the SC-only–coated paper exhibited an approximately 26% reduction in WVTR. A similar WVTR value was observed for the 2.5 wt% TA condition, indicating a limited additional effect at low TA loading. By contrast, the 5 wt% TA sample showed a further decrease in WVTR of approximately 20% relative to the 2.5 wt% TA sample, whereas increasing the TA content beyond this level resulted in a reduced effect on water vapor barrier performance. A comparable trend was observed for the FA-containing samples. These results suggest that the incorporation of phenolic compounds reduced the mobility of water vapor through the SC film matrix by forming intermolecular interactions within the coating layer (Pereda *et al.* 2010).

A slight increase in WVTR was observed with increasing coating weight, which may be attributed to enhanced water vapor adsorption associated with the high density of hydroxyl groups present in the coating components (Shafee and Naguib 2003). In addition, the water vapor barrier performance of SC-based coatings may be limited by the hydrophilic nature of the SC matrix and by local defects or small cracks in the coating layer. Previous studies have reported that additional hydrophobic sealing layers, such as wax-based or beeswax-containing coatings, can further reduce water vapor transmission in paper-based packaging materials by covering surface defects and providing a more continuous barrier layer (Zhang *et al.* 2014; Jahangiri *et al.* 2025). Therefore, the incorporation of an additional sealing layer may be considered in future work to reduce the influence of small cracks or defects and further control air and water vapor permeation.

Cobb size degree

The $Cobb_{60}$ value represents the mass of water absorbed during a 60 s exposure. The $Cobb_{60}$ values are presented in Fig. 4c. A lower Cobb value indicates greater resistance to water penetration. Under the SC-only coating condition, the Cobb value was comparable to that of the base paper. However, when the TA or FA loading exceeded 5 wt.%, a pronounced decrease in Cobb value was observed, corresponding to an ~55% increase in water resistance relative to the SC-only–coated paper. At higher TA or FA loadings, a slight increase in Cobb value occurred, which may be related to the high density of hydroxyl groups introduced by excess TA or FA, partially offsetting the barrier effect, as also shown in Fig. 4b. A more pronounced increase in Cobb value was observed when the coating weight was adjusted to 7.5 g/m^2 (Fig. 4c). This is consistent with previous reports on SC-based coatings, where increased coating weight led to reduced water resistance owing to the inherent hydrophilicity and swelling behavior of SC (Khwaldia 2010).

Kit test

The oil resistance of the coated papers is presented as the Kit rating in Fig. 4d. A higher Kit number, approaching 12, indicates greater oil resistance, whereas a Kit rating of 0 indicates no measurable oil resistance. The Kit solutions consist of low-density, nonpolar organic compounds, including castor oil, toluene, and *n*-heptane, with densities below 1 g/cm^3 (Kjellgren 2005). Therefore, resistance to Kit solution penetration cannot be explained only by the hydrophilic nature of the coating surface. Rather, grease resistance is closely related to the formation of a dense, continuous, and defect-limited barrier layer that can block the penetration pathways of nonpolar liquid components. In this context, SC is advantageous because it is hydrophilic and has excellent film-forming ability, allowing it to fill surface pores and form a cohesive coating layer on the paper surface (Khwaldia *et*

al. 2004). Similar mechanisms have been discussed for greaseproof paper systems, in which resistance to oils and greases is attributed to highly dense and nearly impermeable layers, together with the reduction of pores or defects that can act as penetration pathways (Hubbe and Pruszynski 2020).

The uncoated base paper exhibited a Kit rating of 0, indicating the absence of measurable oil resistance. By contrast, all coated samples showed the maximum measurable Kit rating of 12, regardless of TA or FA type or loading. This result suggests that the SC-based coating layer sufficiently covered the paper surface and blocked the penetration of the Kit solutions. The high Kit rating is therefore attributed not only to the hydrophilic character of SC, but also to the dense and continuous coating structure formed by SC and the reduced accessibility of pores and defects in the paper substrate.

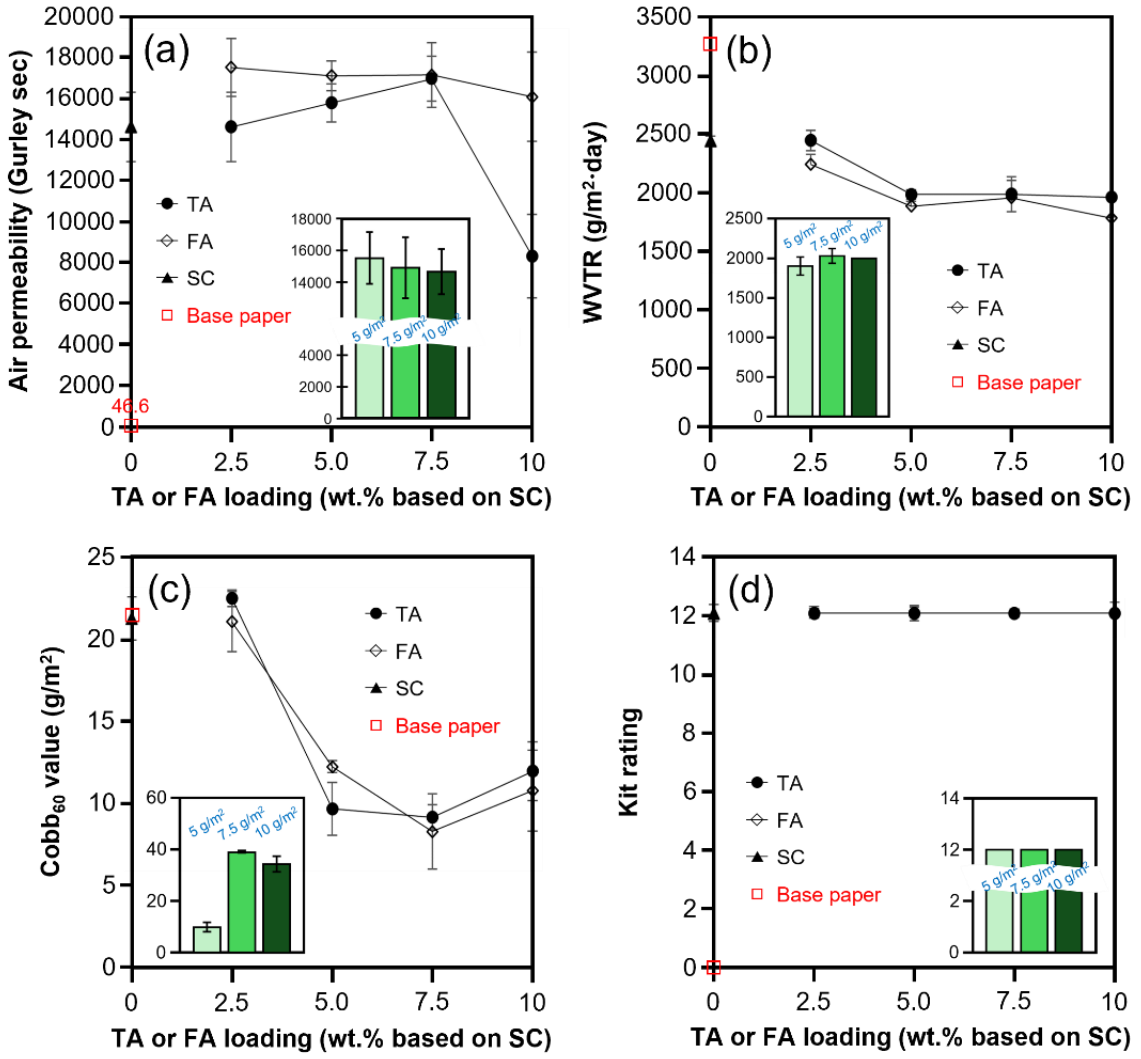

Fig. 4. Barrier properties of papers coated with SC only or SC containing TA or FA under different coating conditions: (a) air permeability, (b) water vapor permeability, (c) Cobb value, and (d) oil resistance (Kit value). Unless otherwise noted, all samples were prepared at a coating weight of 5 g/m^2. The inset figures show the barrier performance of papers coated under TA 5 wt.% conditions with different coating weights (5, 7.5, and 10 g/m^2). The uncoated base paper is included for comparison.

Mechanical Properties

The tensile strength and elongation at break of SC-coated papers containing TA and FA are shown in Fig. 5. Under the 5 wt.% TA condition, the tensile strength increased by approximately 10% compared to the SC-only–coated paper, and a similar trend was observed for the FA-containing samples. This increase suggests the formation of a more compact and interconnected protein matrix, likely resulting from intermolecular interactions within the SC coating layer (Pereda *et al.* 2010). Comparable behavior has been reported for gelatin films containing TA and FA, where phenolic compound-induced matrix densification resulted in increased tensile strength and reduced elongation at break (Cao *et al.* 2007).

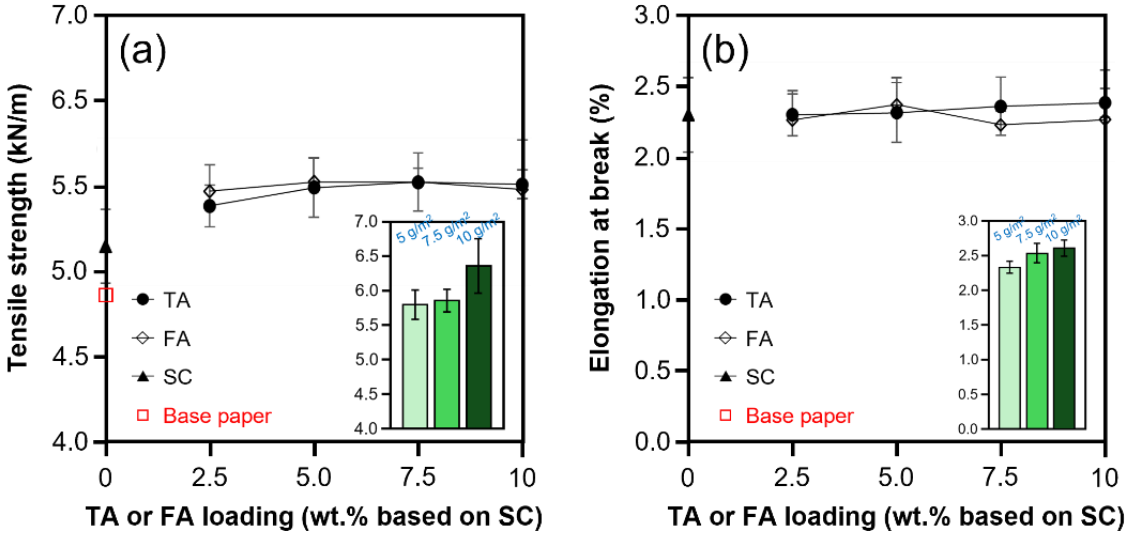

Fig. 5. Mechanical properties of paper coated with SC only or SC containing TA or FA under different coating conditions: (a) tensile strength and (b) elongation at break. Unless otherwise noted, all samples were prepared at a coating weight of 5 g/m^2. The inset figures show the mechanical properties of papers coated under 5 wt.% TA conditions with different coating weights (5, 7.5, and 10 g/m^2). The uncoated base paper is included for comparison.

Consistent with this structural interpretation, elongation at break decreased for the SC-only–coated paper relative to the base paper, whereas only minor variations were observed with increasing TA or FA loading in the SC coatings. This suggests that the addition of phenolic compounds mainly increased the stiffness of the SC matrix rather than its extensibility. Similar trends have been reported for biopolymer films containing polyphenolic compounds, in which matrix densification resulted in increased tensile strength and reduced elongation at break (Rivero *et al.* 2010). At elevated TA loadings, however, a slight reduction in tensile strength was observed, which may be associated with partial phase separation induced by excessive TA addition, as previously reported for tannin-modified gelatin systems (Peña *et al.* 2010).

Regarding the effect of coating weight on mechanical properties, tensile strength remained comparable between coating weights of 5 and 7.5 g/m^2, whereas a pronounced increase was observed at 10 g/m^2. By contrast, the elongation at break increased gradually with increasing coating weight. Although not included in this study, wet tensile strength testing would provide useful additional evidence for evaluating the stability of the SC-based coating network in the presence of water. In addition, surface friction was not

measured in the present study, although it is an important property for further processing and converting of coated papers, including feeding, stacking, and handling. Therefore, future work should evaluate the static and dynamic coefficients of friction, as well as blocking behavior, under practical converting and storage conditions.

CONCLUSIONS

1. Sodium caseinate (SC)-based paper coatings containing tannic acid (TA) or ferulic acid (FA) exhibited higher thermal decomposition temperatures and improved barrier properties compared with the SC-only coating. Fourier transform infrared (FT-IR) analysis indicated that the interactions between SC and the phenolic compounds were governed mainly by hydrogen bonding and other noncovalent intermolecular interactions rather than detectable ester bond formation.
2. Barrier performance depended on the phenolic compound type and loading level. The 5 wt% TA condition showed the highest air resistance, whereas excessive TA loading caused surface cracking and reduced barrier performance. FA-containing coatings exhibited more stable air-barrier performance without visible cracking.
3. All coated papers showed the maximum measurable oil resistance, and moderate increases in tensile strength were observed after the addition of TA or FA. These results indicate that TA- and FA-containing SC coatings have potential as biodegradable barrier coatings for paper-based food packaging, particularly for dry or grease-containing foods requiring air and oil resistance.
4. Further improvements are still needed for moisture-related barrier performance, wet mechanical stability, and practical converting properties. Future studies should examine multilayer or hydrophobic sealing strategies, dry and wet tensile properties, static and dynamic surface friction, and blocking behavior under practical storage and converting conditions.

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