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Enhancing mechanical durability and moisture stability in low-energy Citric acid-crosslinked Carboxymethyl cellulose films for cherry tomato preservation

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Research Article

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Enhancing mechanical durability and moisture stability in low-energy Citric acid-crosslinked Carboxymethyl cellulose films for cherry tomato preservation

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Abstract

Carboxymethyl cellulose (CMC) is a highly promising biopolymer for sustainable packaging; however, its application is restricted by inherent brittleness and moisture sensitivity. Although citric acid (CA) crosslinking strengthens the polymer matrix, conventional high-temperature curing often induces thermal degradation, thereby reducing mechanical strength. To solve these limitations, this study developed a low-energy crosslinking strategy. Instead of conventional high-heat curing, the optimal formulation (2.25 wt% CMC, 20 wt% CA) was established through a two-phase mechanism: a brief kinetic activation at 80 °C (3 min) to initiate esterification, followed by a thermodynamically driven drying phase at 40 °C that shifts the esterification equilibrium forward. This optimised matrix exhibited exceptional durability, demonstrating a 1.3-fold increase in tensile strength and a 4.7-fold increase in elongation at break compared to pristine CMC films. Structural and thermal evaluations (ATR-FTIR, TGA) verified the formation of a stable covalent ester network. The mechanical durability of this network effectively provides superior moisture stability and a reduced water vapour transmission rate. In practical trials, the crosslinked films maintained the sensory quality of cherry tomatoes over 21 days. These findings present a highly efficient, low-energy strategy for fabricating biodegradable films for fruit preservation.

Keywords: Carboxymethyl cellulose; Citric acid; Crosslinking; Biodegradable films; Fruit preservation

Introduction

Effective packaging is essential to meet the rising global demand for highly perishable fresh produce, such as cherry tomatoes, to ensure quality preservation and reduce storage-related waste. Currently, synthetic petroleum-based plastics like polyethylene and polypropylene are the materials of choice due to their availability on a large scale, affordability, suitable mechanical strength, and excellent moisture barrier properties [1]. However, their resistance to biodegradation causes them to persist in the environment, where their gradual physical fragmentation generates hazardous microplastics. This has created a pressing need to develop sustainable, eco-friendly alternatives to conventional packaging that ensure food safety.

In this context, biopolymers derived from renewable resources have emerged as viable substitutes [2]. Among these, Carboxymethyl cellulose (CMC) - an anionic, water-soluble derivative of Cellulose - has garnered attention due to its abundance, non-toxicity, and excellent film-forming capacity [3]. The potential of pristine CMC matrices to extend shelf life and maintain the postharvest quality of fresh produce has been widely validated in recent research. For

instance, Ali et al. (2022) demonstrated that applying a 1.5 wt% CMC coating to harvested bananas stored at 20 °C for 15 days inhibited weight loss to 6% and delayed the onset of decay to 9%, thereby preserving peel colour [4]. Similarly, another study by Ali et al. (2022) found that a 1% pristine CMC coating successfully reduced weight loss (from 11.41% to 4.95%) and preserved their visual appearance and nutritional value over a 20-day storage period at 20 °C [5]. Furthermore, applying a 1% CMC coating to 'Banarsi' aonla fruits also reduced weight loss and disease incidence by 2.98-fold during a 10-day ambient storage period at 20 °C [6].

Despite these promising applications, the utility of pristine CMC films is constrained by their brittleness and high hydrophilicity. During preservation, the continuous transpiration of fresh produce generates a moisture-rich environment. Prolonged exposure to this moisture disrupts the intermolecular hydrogen bonds within the CMC matrix, leading to excessive swelling and loss of structural integrity. Consequently, reinforcing the polymer network through crosslinking strategies has become a critical research imperative.

While physical crosslinking methods - such as gamma irradiation [7], ultraviolet irradiation [8], and electron beam processing [9] - are simple, comparative studies by Perez-Puyana et al. (2024) indicate they are less effective than chemical crosslinking methods at reducing water absorption and solubility [10]. Unlike physical methods, which lack permanent network junctions and struggle to prevent water absorption in humid conditions, chemical crosslinking agents form robust covalent bonds. This creates a stable network, yielding materials with higher resistance to deformation [11].

Conventionally, high moisture stability in polysaccharide-based films has been achieved using highly reactive chemical cross-linkers, such as glutaraldehyde (GLA) [12], and epichlorohydrin [13], or by employing post-treatment methods, such as exposure to hydrochloric acid vapour [14]. However, the cytotoxicity and environmental persistence of these agents render them incompatible with food-contact applications and prevent them from meeting modern standards for safety and sustainability [15].

In order to overcome these limitations, citric acid (CA) has emerged as a green, non-toxic, and food-grade crosslinking agent [16]. Under thermal activation, CA induces chemical crosslinking between polymer chains via esterification. This thermally driven process provides the essential kinetic energy to facilitate the reaction between the carboxyl groups of CA and the hydroxyl groups on the CMC backbone, generating covalent ester linkages that enhance the mechanical durability of the polymer matrices [16-18]. For example, Wen et al. (2021) [19] reported that as the CA content reached 5 wt%, the tensile strength of Carboxymethyl chitosan/polyvinyl alcohol films increased from 21.03 MPa to 29.65 MPa. Similarly, Awadhiya et al. (2016) also demonstrated that 10 wt% CA crosslinking enhanced the tensile strength of agarose bioplastic films from 25.1 MPa to 52.7 MPa [20].

Despite these promising applications, the utility of CA-crosslinked CMC films is hindered by severe kinetic and thermodynamic limitations. Kinetically, the esterification reaction between CA and the CMC chains requires a high activation energy (47.8 kcal/mol), necessitating substantial thermal input [18]. Thermodynamically, the subsequent esterification releases water as a byproduct, necessitating a "dry state" to continuously drive the chemical equilibrium forward [16]. To overcome this kinetic barrier, most conventional protocols demand high-energy curing conditions, such as 140 °C for 30 min [21], or 110 °C for 10 min [22]. While effective at overcoming the kinetic activation barrier for ester crosslinking, these conventional high-temperature treatments operate near the thermal decomposition thresholds of both CA and the CMC backbone. Consequently, such high-energy input frequently induces thermal degradation, leading to an undesirable brownish discolouration that compromises the transparency essential for consumer acceptance [23]. Furthermore, excessive thermal exposure often triggers over-crosslinking, which restricts polymer chain mobility and renders the resulting films brittle [22].

To bridge these gaps, this study proposes a two-phase, low-energy crosslinking strategy to enhance the mechanical durability and moisture stability of pristine CMC films. By synergistically combining a brief kinetic thermal activation with a thermodynamically driven drying phase, this approach effectively establishes a covalent ester network while entirely circumventing the thermal degradation and embrittlement associated with conventional high-energy protocols.

To systematically achieve this, key processing parameters - namely CMC and CA concentrations, reaction temperature, and curing time - were statistically optimised based on the films' mechanical durability through tensile

strength (TS) and elongation at break (EAB). Subsequently, the chemical, morphological, and thermal properties of the optimal crosslinked network were validated using Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy, Field Emission Scanning Electron Microscopy (FE-SEM), and Thermogravimetric Analysis (TGA). Finally, the films' moisture stability was evaluated using moisture content, water vapour transmission rate, and water immersion tests. Furthermore, their practical efficacy as a protective coating was validated by monitoring the quality of fresh cherry tomatoes over a 21-day ambient storage period.

Experimental

Materials

Carboxymethyl cellulose (CMC, viscosity 300-800 mPa.s) was purchased from Shanghai Zhanyun Chemical Co., Ltd., China. Citric acid monohydrate (CA, $M_W \approx 210.14$ g/mol), acting as the crosslinking agent, was also supplied by Shanghai Zhanyun Chemical Co., Ltd, China. Sorbitol (≥ 98%, BioFroxx, Germany) was utilised as a plasticiser. Deionised water was used as the solvent for all solutions.

Fresh cherry tomatoes (*Solanum lycopersicum* var. *cerasiforme*), selected for uniform size and the absence of physical or fungal defects, were procured from Nguyen Lam Thanh Strawberry Garden (Da Lat, Vietnam) for the *in vivo* preservation trials.

Fabrication and statistical optimisation of the crosslinked CMC/CA films

The crosslinked CMC/CA films were fabricated via a solution-casting method integrating a two-phase crosslinking strategy (**Fig. 1**). Initially, CMC (1.5 - 2.5 wt%) and a sorbitol plasticiser (50 wt% relative to CMC) were dissolved in deionised water, followed by the addition of CA (0 - 40 wt% relative to CMC) to form a homogeneous reaction mixture.

To identify the optimal low-energy crosslinking conditions, the mixtures underwent a brief thermal activation phase at controlled reaction temperatures (25 – 145 °C) and curing times (1 – 10 min). This step drives the initial dehydration and esterification reactions, following the mechanism widely proposed in the literature (**Scheme 1**) [18,22]. The mixtures were subsequently degassed to remove entrapped air, cast into Petri dishes, and then dried at 40 °C for 24 h. This continuous evaporation of water shifts the esterification equilibrium forward according to Le Chatelier's principle, thereby establishing covalent crosslinks between the CA and CMC hydroxyl groups [16,24]. Prior to characterisations, the resulting films were peeled off and conditioned under vacuum for at least 48 h.

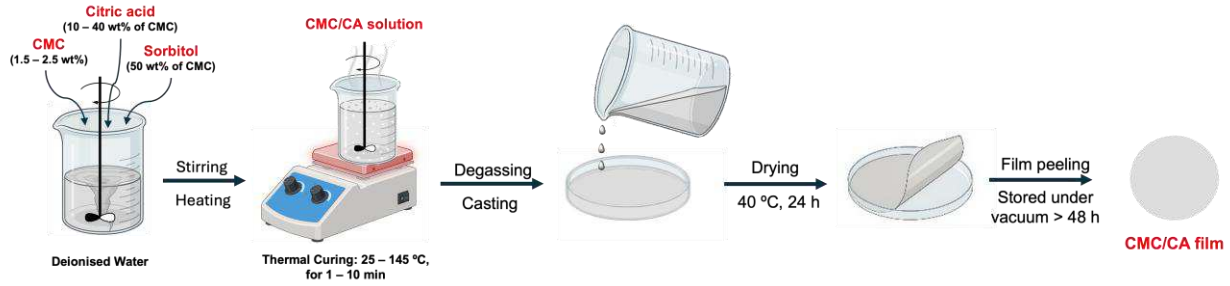
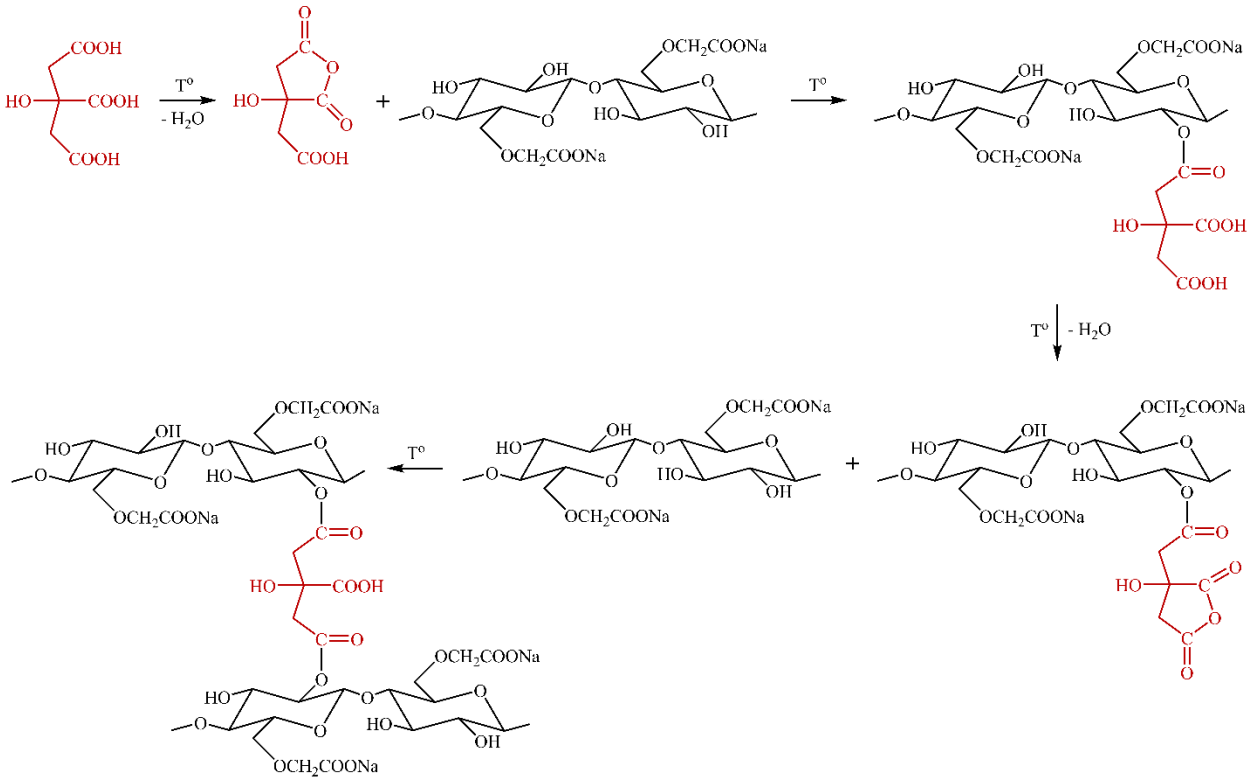


Fig. 1 Schematic representation of the two-phase low-energy crosslinking workflow for CMC/CA films



Scheme 1. Schematic representation of the esterification mechanism between CMC and CA, as proposed in previous studies [18,22].

The mechanical durability of the films, including Tensile Strength (TS, MPa) and Elongation at Break (EAB, %), was evaluated using a Z2.5 universal testing machine (Zwick, Germany). Uniform rectangular strips of the samples were tested under controlled conditions (24 ± 1 °C and 50 ± 1% relative humidity). The TS and EAB values were measured to assess the impact of key processing parameters - namely CMC concentration, CA concentration, reaction temperature, and curing time - on the structural integrity of the crosslinked networks.

All quantitative experiments were performed in at least triplicate ($n \geq 3$), and the data were expressed as mean ± standard deviation. Statistical significance among the varied processing groups was determined using a one-way Analysis of Variance (ANOVA) followed by Tukey's Honestly Significant Difference (HSD) post-hoc test, with a p-value < 0.05 considered statistically significant for parameter optimisation.

Morphological, chemical, and thermal characterisation

To preserve the internal porous architecture without structural collapse, the samples were freeze-dried prior to imaging. The structural features and surface morphologies of both the pristine CMC and the crosslinked CMC/CA films were then evaluated using a Field Emission Scanning Electron Microscope (FE-SEM; Hitachi S-4800, Japan).

To verify the formation of covalent ester linkages, the chemical structure of the films was analysed using an ATR-FTIR spectrometer (FTIR Affinity-1S, Shimadzu, Japan). The spectra were recorded over the wavenumber range of 400 - 4000 cm^{-1}, averaging 32 scans at a resolution of 4 cm^{-1}.

The thermal stability of the films was evaluated using a thermogravimetric analyser (Labsys TGA 1600, Setaram, France). 5 mg of each sample was placed in an alumina crucible and heated from room temperature to 900 °C at a constant heating rate of 10 °C/min under an airflow of 2.5 L/h. Both thermogravimetric (TGA) and derivative thermogravimetric (dTG) curves were recorded to systematically determine the characteristic mass-loss stages, the onset and peak degradation temperatures (T_{max})

Moisture stability assessments and practical application in cherry tomato preservation

Moisture content of the films

The moisture content (MC) of the films was determined by quantifying their moisture absorption capacity. The film samples were dried in an oven until a constant weight was achieved (W_{dry}). Subsequently, the dried films were placed in a controlled-humidity chamber for 24 h to reach their fully hydrated state and re-weighed (W_{wet}). The MC was then calculated as the percentage of mass gained relative to the initial dry weight by the following equation:

$$MC(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

Water vapour transmission rate of the films

Water vapour transmission rates (WVTR) reflect the film's ability to allow water vapour to move from the sample to the environment. To quantify its impact on WVTR, measurements were performed according to the methods described by J.L. Wiles et al. [25].

The film samples were securely sealed over the opening of cylindrical glass vials containing anhydrous silica gel. These test assemblies were subsequently placed in a controlled-humidity chamber. The continuous mass gain of the vials, resulting from water vapour permeation through the films, was measured periodically until the readings stabilized state was reached. The WVTR was determined through the following equation:

$$WVTR(g/m^2/day) = \frac{G}{A \cdot t} \quad (2)$$

where, G represents the steady-state mass gain of the vial (g), A represents the exposed permeation area of the film (m^2), and t represents the testing time (day). For optimal accuracy, the ratio G/t was directly extracted from the linear slope of the mass gain versus time plot.

Water immersion stability of the films

To evaluate the crosslinking efficiency and the films' resistance to aqueous disintegration, a dry film sample (0.2 g) of each formulation was immersed in 10 mL of deionised water at room temperature. The structural integrity, swelling behaviour, and partial dissolution of the polymer matrices were visually recorded after a 15-minute interval to assess their dimensional stability. All experiments were performed in triplicate (n = 3), and the images shown represent the most representative results.

Cherry tomato preservation assay

To validate the practical efficacy of the optimised low-energy crosslinked CMC/CA films, an *in vivo* shelf-life trial was conducted using the aforementioned cherry tomatoes. Prior to the assay, the fruits were surface-disinfected using a dilute sodium hypochlorite solution, thoroughly rinsed with distilled water, and air-dried. The prepared samples were randomly divided into three groups: unwrapped (control), wrapped in pristine CMC films, and wrapped in the optimised CMC/CA films. All test groups were stored under identical ambient conditions (27-28 °C, 70-80% RH) for 21 days. The preservation performance was evaluated through daily visual monitoring for shrinkage, loss of turgidity, and fungal decay.

Results and Discussion

Optimisation of CMC and CA concentrations

The mechanical properties of polymer films play a pivotal role in determining their viability for practical packaging applications.[26] Achieving an optimal balance between tensile strength (TS) and elongation at break (EAB) serves as a reliable indicator of a good polymeric network [27]. To establish a material matrix prior to investigating the kinetic curing conditions, the base formulation was systematically optimised by varying the concentrations of CMC and CA.

Effect of CMC concentration on pristine CMC films

Initially, the effect of CMC concentration (1.50 to 2.50 wt%) on the mechanical properties of pristine CMC films was evaluated, with the other processing parameters kept constant (a fixed Sorbitol plasticiser content of 50 wt% and no CA added). As shown in **Fig. 2**, the mechanical properties of the pristine CMC films were significantly influenced by

the CMC concentration (ANOVA, $p < 0.05$). Increasing the CMC content from 1.50 to 2.25 wt% improved both TS (from 31.01 to 35.94 MPa) and EAB (from 7.38% to 8.78%). This enhancement stems from the increased availability of reactive hydroxyl and carboxymethyl groups, which facilitated intermolecular hydrogen bonding and generated a denser polymeric network [27]. However, further increasing the CMC concentration to 2.50 wt% led to declines in both TS and EAB. This decline occurs because excessive polymer crowding and electrostatic repulsion between adjacent carboxymethyl groups hinder the formation of an intermolecular network, rendering this polymer matrix more brittle [28]. Therefore, a CMC concentration of 2.25 wt% was identified as the optimal condition for subsequent parameter optimisations, offering a well-balanced combination of mechanical strength and flexibility.

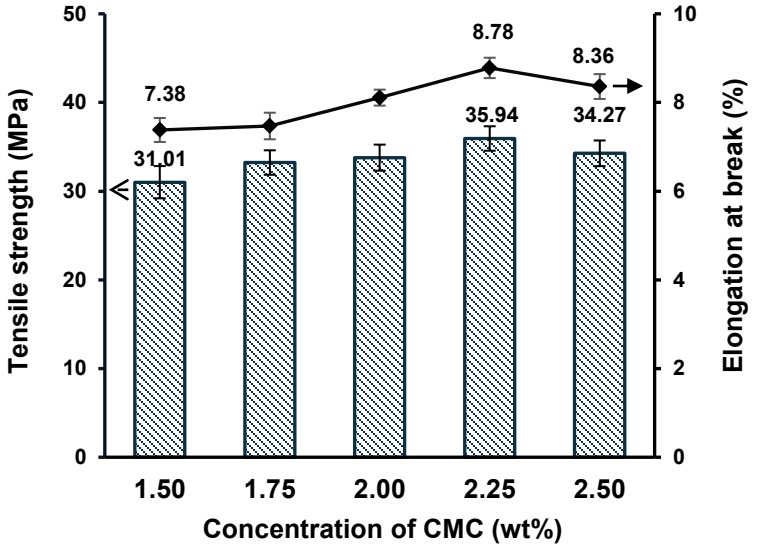


Fig. 2 Mechanical durability of the pristine films as a function of CMC concentration

Effect of CA concentration on crosslinked CMC/CA films

Pure CMC films generally exhibit poor self-crosslinking due to the scarcity of highly reactive hydroxyl groups and strong electrostatic repulsion between carboxylate groups, which favour intramolecular linkages over intermolecular networking [29-31]. Introducing CA as a crosslinking agent is a crucial strategy to overcome this limitation and reinforce the internal polymer network.

To evaluate the effect of CA concentration, films with a fixed CMC concentration of 2.25 wt% were crosslinked under high-energy conditions (145 °C for 5 min) [32]. This approach established a baseline to determine the maximum crosslinking density and the absolute CA saturation threshold prior to conducting kinetic optimisations.

As illustrated in **Fig. 3**, the films' mechanical integrity also varied significantly with CA concentration (ANOVA, $p < 0.05$). Increasing CA from 0 to 20 wt% improved both TS and EAB. Conversely, increasing the CA concentration beyond 20 wt% (to 40 wt%) led to a decline in both TS and EAB. This deterioration is attributed to over-crosslinking, which restricts polymer chain mobility and makes the matrix brittle. Similar over-crosslinking threshold behaviours have been reported in other CA-modified biopolymer films. For instance, Wilpiszewska et al. (2019) reported a drastic 4-fold plummet in the TS of starch films when CA concentrations reached excessive levels (60%) [33]. Similarly, Sabzevari et al. (2025) documented a reduction in the flexibility of CMC/chitosan films, with the EAB decreasing from 45% to 36% as the CA content increased from 12% to 24% [27]. These findings align with the deterioration trends observed by Yousefi et al. (2024) at high CA crosslinker contents [34]. Consequently, a CA concentration of 20 wt% was identified as the optimal crosslinker content.

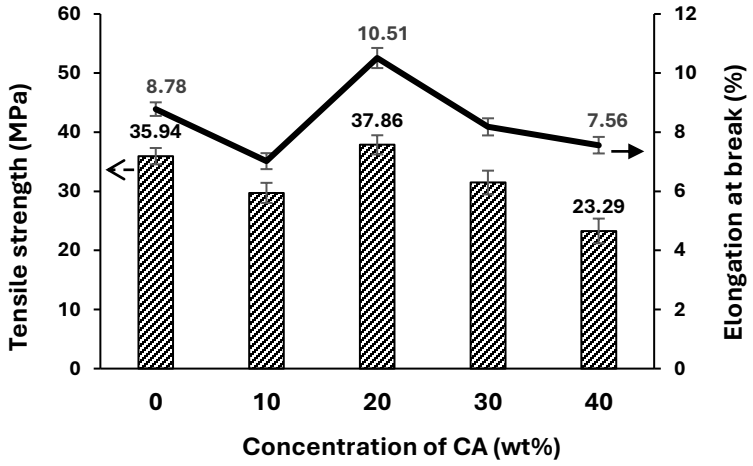


Fig. 3 Mechanical durability of the crosslinked CMC/CA films as a function of CA concentration

Having established the ideal polymer-to-crosslinker formulation (2.25 wt% CMC and 20 wt% CA), the subsequent phase focused on tuning the thermal curing conditions to maximise esterification efficiency while minimising the required energy input.

Kinetic activation: Optimisation of reaction temperature and curing time

Esterification efficiency strongly depends on balancing thermodynamic and kinetic parameters [32,35,36]. Insufficient energy limits crosslinking, whereas excessive heat causes severe moisture loss and structural embrittlement. Thus, the thermal processing parameters were systematically optimised.

Effect of reaction temperature on crosslinked CMC/CA films

Using the optimal formulation (2.25 wt% CMC and 20 wt% CA) with a constant 1-min curing time, the reaction temperature-dependent mechanical durability of the crosslinked films was investigated (**Fig. 4**). The optimum performance was achieved at 80 °C, yielding a maximum TS of 45.88 MPa and an EAB of 14.09%. This success at a relatively low temperature relies on a synergistic kinetic-thermodynamic mechanism. Unlike conventional high-temperature curing, our protocol separates the crosslinking stages. The initial 80 °C treatment provides kinetic activation, supplying sufficient energy to initiate the esterification process between CA and the polymer CMC chains [27,30,37,38]. This aligns with Konwar et al. (2016), who demonstrated that esterification thermodynamics are more favourable at moderately lower temperatures [39]. Subsequently, the prolonged 40 °C drying phase acts as a thermodynamic driver; continuous solvent evaporation shifts the equilibrium forward via Le Chatelier's principle, thereby consolidating a stable ester network. Furthermore, **Fig. 4** confirms that when the activation temperature was elevated to 100 °C and 145 °C, both TS and EAB declined. Chemically, this deterioration likely stems from excessive thermal energy degrading the polymer backbone rather than promoting ester crosslinking. This observation aligns with previous studies indicating that excessively high-temperature curing drives the thermal decomposition of CA, undesirable discolouration, and matrix embrittlement [16,20].

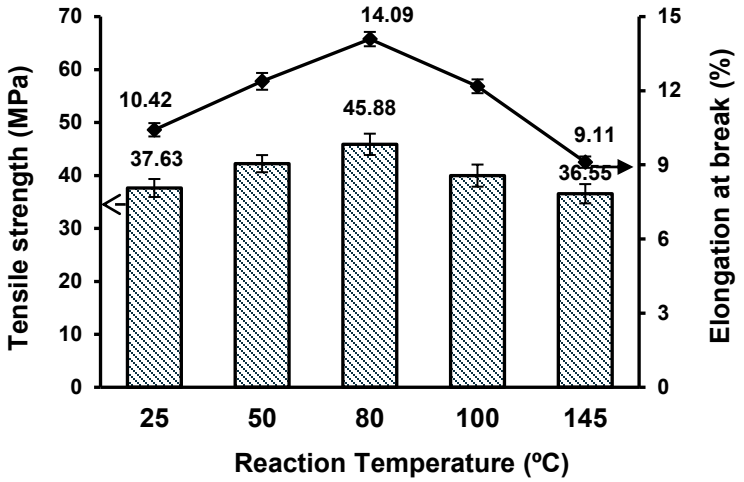


Fig. 4 Effects of reaction temperature on the mechanical durability of the crosslinked CMC/CA films

Effect of curing time on crosslinked CMC/CA films

Based on the optimised temperature of 80 °C, the effect of curing time was evaluated (**Fig. 5**). The results revealed improved mechanical properties after just 3 minutes of curing, with a peak EAB of 41.25% and a robust TS of 45.21 MPa. However, extending thermal exposure beyond 5 minutes led to a significant decline in both TS and EAB ($p < 0.05$), a trend consistent with a previous study on CA-crosslinked films [40].

This mechanical deterioration at prolonged curing times is driven by two main factors. First, extended heating in the acidic solution induces acid-catalysed hydrolysis of the CMC backbone, thereby weakening its structure. Second, excessive heating triggers premature crosslinking in the solution state, severely reducing its strength and flexibility [41]. Therefore, a brief 3-minute activation is optimal to facilitate crosslinking.

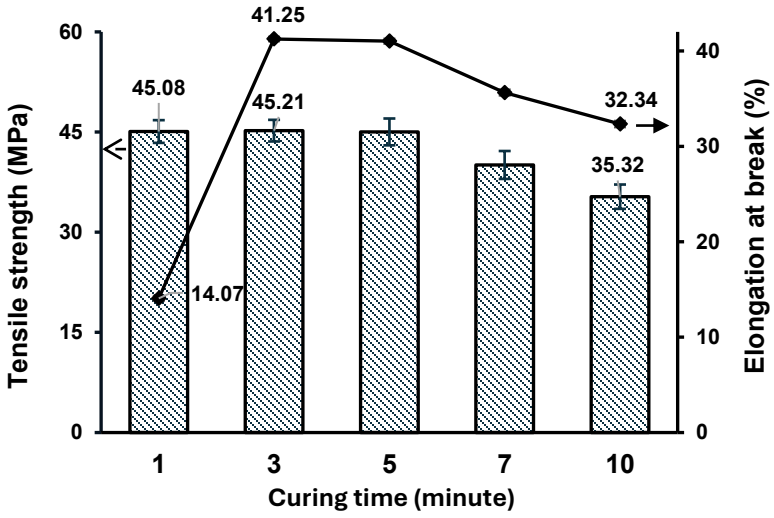


Fig. 5 Effects of curing time on the mechanical durability of the crosslinked CMC/CA films

Chemical validation of the low-energy crosslinking via ATR-FTIR

To demonstrate the efficacy of the low-energy crosslinking strategy and validate the formation of covalent ester linkages, the chemical structures of the films were analysed using ATR-FTIR spectroscopy. First, films with varying CA concentrations (0 – 40 wt%) cured under the optimised conditions (80 °C, 3 min) were evaluated (**Fig. 6**). Unlike pristine CMC, which exhibits a characteristic carboxylate (COO^-) peak at approximately 1587-1589 cm^{-1} but

completely lacks signals in the 1700-1750 cm^{-1} region [42], the crosslinked CMC/CA films reveal the distinct emergence of a new C=O, ester stretching band at 1715-1730 cm^{-1} [43,44]. The systematic increase in the intensity of this C=O, ester peak, proportional to higher CA concentrations, definitively confirms the successful esterification between the hydroxyl groups (CMC) and the carboxyl groups (CA). Concurrently, the precursor COO^- signals progressively attenuate, reflecting their consumption during film formation.

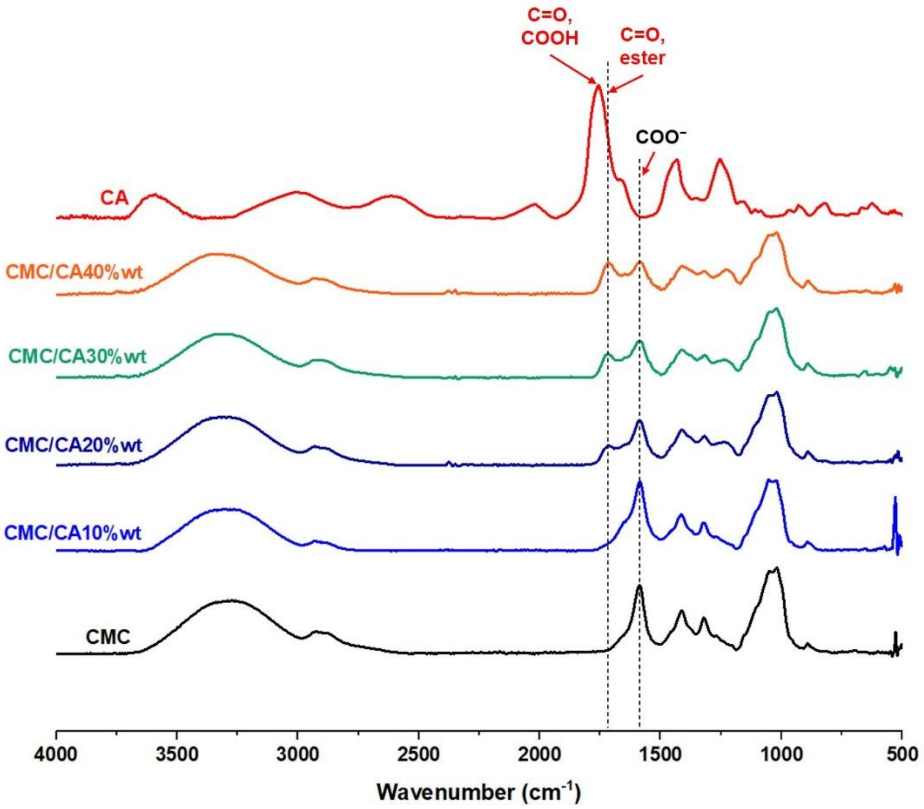


Fig. 6 ATR-FTIR spectra of the pristine CMC and crosslinked CMC/CA film at varying CA concentrations

Subsequently, to validate the necessity of brief kinetic activation in driving esterification, the spectra of unactivated (0 min) and thermally activated (80 °C for 3 min) mixtures at the optimal formulation (2.25 wt% CMC, 20 wt% CA) were compared (**Fig. 7**). The 0-minute sample, which only underwent drying without high-temperature curing, exhibited a peak corresponding to the free acid (C=O, COOH) at approximately 1761 cm^{-1}. This confirms the presence of physically blended, unreacted CA [42]. The complete absence of the C=O bond at approximately 1716 cm^{-1}, ester signal demonstrates that water evaporation during drying is insufficient to initiate the esterification reaction. Conversely, the 3-minute activated spectrum revealed critical structural changes. The emergence of the C=O, ester stretching peak at approximately 1716 cm^{-1} provided direct evidence of successful covalent crosslinking [43,44]. Concurrently, a decrease in the COO^- peak (at ~1580 cm^{-1}) confirmed the consumption of reactive groups on the CMC backbone. Together, these spectral transitions validate that brief thermal activation supplies the essential kinetic energy to readily form stable covalent ester linkages with the CMC matrix.

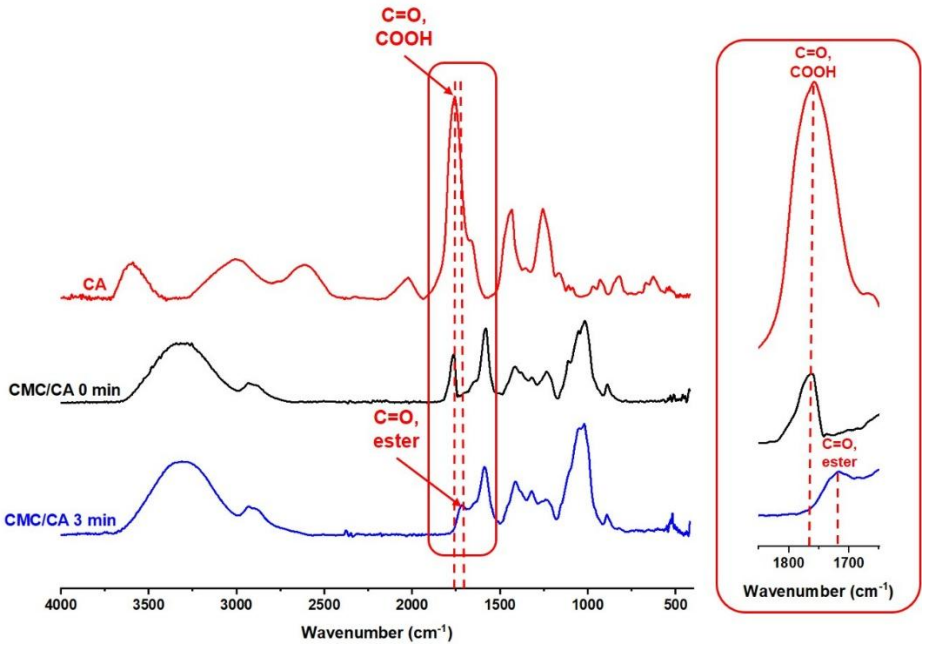


Fig. 7 Comparative ATR-FTIR spectra of the unactivated (0 min) and optimally activated (80 °C for 3 min) CMC/CA films

Comparison with the literature on CA-crosslinked films

A comparison with recent literature (Table 1) highlights the advantages of the proposed low-energy crosslinking strategy. Conventional protocols rely on high-energy, prolonged curing conditions [21,27,37,45]. While these harsh conditions drive the esterification process, they induce over-crosslinking and thermal degradation of the polysaccharide backbone. As evidenced by the literature, prolonged thermal exposure compromises the elasticity and mechanical strength of the resulting matrices.

In contrast, our optimised protocol (2.25 wt% CMC, 20 wt% CA, 80 °C for just 3 min) completely prevents this structural deterioration. This mild approach yields a 1.3-fold increase in TS and a 4.7-fold enhancement in EAB compared to pristine CMC. This superior mechanical performance is attributed to a synergistic two-phase strategy: the brief 3-minute thermal treatment provides precise kinetic activation for esterification without causing polymer chain scission, while the subsequent drying phase thermodynamically drives the reaction equilibrium forward via continuous solvent evaporation. Ultimately, this protocol successfully achieves effective crosslinking while preserving the elasticity of the biopolymer matrix.

Table 1. Mechanical performance of the low-energy crosslinked CMC/CA film compared with recent literature

Reference	Materials	CA Concentration (wt%)	Curing Conditions (Temp. & Time)	TS (MPa)	EAB (%)
This Study (Optimised)	CMC/CA	20	80 °C, 3 min	45.21	41.25
Sabzevari et al. (2025) [27]	CMC/CS/CA	24	80 °C, 30 min	7.09	36.76
Morais et al. (2024) [21]	CMC/GG/CA	20	140 °C, 30 min	Not reported	Not reported

Ghorpade et al. (2019) [45]	CMC/PVA/CA	20	140 °C, 5 min	34.72	Not reported

Morphological and thermal characterisation

Surface morphology characterisation

FE-SEM of freeze-dried films was employed to elucidate the structural basis for the mechanical enhancements achieved via low-energy crosslinking (**Fig. 8**).

The pristine CMC film (**Fig. 8a**) exhibits a highly porous, heterogeneous network with large macropores. This architecture not only facilitates rapid water diffusion, thereby increasing moisture sensitivity, but also compromises robustness. In contrast, the crosslinked CMC/CA film (**Fig. 8b**) retains its porous framework but becomes a denser, more compact network. Covalent ester linkages draw the polymer chains together, thickening the polymeric walls and reducing the average pore size. This compact morphology corroborates the improvements in both mechanical durability and moisture-barrier properties.

These transformations align with previous studies on CA-crosslinked cellulosic networks. Covalent crosslinking has been shown to compact the porous architecture, thicken structural walls, and minimise free volume within the matrix [28,46]. Furthermore, such CA-induced pore-size reduction is confirmed as the mechanism that restricts water diffusion and enhances the moisture stability of CMC-based matrices [17].

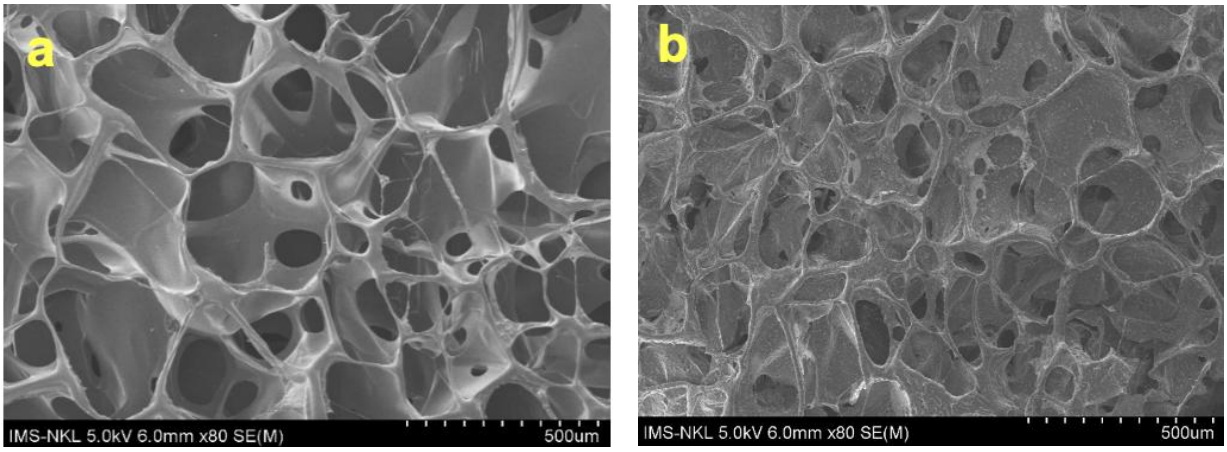


Fig. 8 FE-SEM images of the freeze-dried (a) pristine CMC and (b) optimised CMC/CA films

Thermal stability (TGA/*d*TG) characterisation

Thermogravimetric and derivative thermogravimetric (TGA-*d*TG) analyses (**Fig. 9**) were employed to evaluate the thermal stability of the polymer matrices. The results revealed a multi-stage thermal degradation profile for both films. The process commenced with an initial dehydration stage (derivative peak at ~91 °C), corresponding to the evaporation of free and hydrogen-bonded water molecules. Notably, the crosslinked CMC/CA film exhibited reduced water-binding capacity because the hydrophobic ester network restricted the availability of free hydroxyl groups [32]. This reduced water affinity aligns with previous studies on CA-crosslinked polysaccharides and provides a chemical basis for the enhanced moisture resistance described in subsequent sections [47,48].

During the next degradation stage (T_{max} ≈ 324 - 327 °C), which represents the thermal decomposition of the CMC backbone [31], the pristine CMC film suffered a mass loss of 73.22%. In contrast, the crosslinked matrix demonstrated enhanced thermal stability with a lower mass loss of 67.94%. This thermal reinforcement is consistent with our ATR-FTIR and mechanical analyses [49]; the covalent ester linkages serve as structural anchors, restricting polymer chain mobility.

The final weight loss stage, extending up to 900 °C, is associated with the progressive carbonisation of residual organic matter [50]. Overall, the TGA-*d*TG findings provide thermodynamic evidence that CA-induced crosslinking fortifies the thermal and structural durability of the films, rendering them suitable for packaging applications.

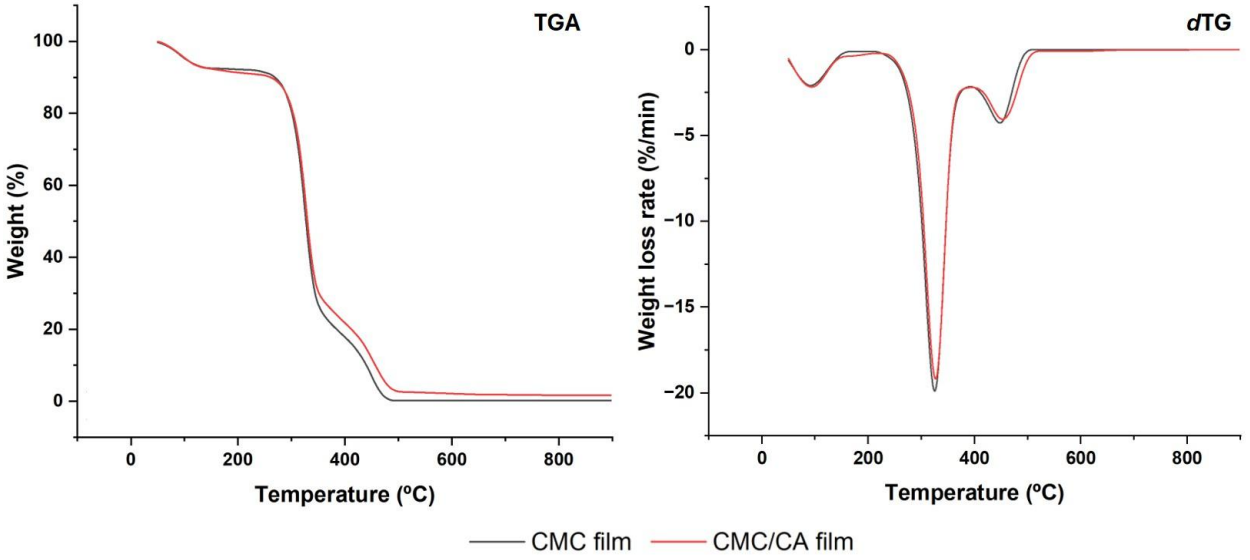


Fig. 9 Comparative TGA and *d*TG thermograms of the CMC film and the optimally crosslinked CMC/CA film

Moisture stability of the crosslinked CMC/CA films

Despite the enhancements in mechanical and thermal robustness, the limitation of CMC-based packaging remains its inherent high hydrophilicity [51,52]. To address this, chemical crosslinking via esterification is required. Although a CA concentration of 20 wt% has been established as the optimum for mechanical durability, a systematic investigation of moisture stability across the CA concentration range (0-40 wt%) remains essential. Evaluating this continuum elucidates the structure-property relationship of the crosslinked film. Specifically, the crosslinker concentration directly dictates the crosslinking density, which governs two anti-moisture mechanisms: (1) the chemical depletion of water-affinity sites (hydroxyl and carboxylate groups) and (2) the physical reduction of free volume within the film. Therefore, the impact of varying CA concentrations on moisture content (MC), water vapour transmission rate (WVTR), and Water immersion stability was evaluated [53].

Moisture content (MC)

As illustrated in **Fig. 10**, the CMC film exhibited a high MC (7.28%) due to its affinity for ambient moisture [51]. However, the incorporation of CA resulted in a statistically significant decrease in MC ($p < 0.05$), declining to 3.98% at a CA concentration of 40 wt%. This reduction is chemically driven by esterification. As previously corroborated by the ATR-FTIR results, increasing the crosslinker concentration consumes a larger fraction of the hydrophilic hydroxyl and carboxylate groups on the CMC backbone, converting them into more hydrophobic covalent ester linkages [21]. Consequently, the material's affinity toward water molecules is severely diminished, reducing its capacity to absorb and retain moisture within the matrix [54]. Furthermore, prior to complete crosslinking, the unreacted carboxyl groups of CA can form strong hydrogen bonds with the polysaccharide chains, further masking any residual hydrophilic sites and enhancing the overall water resistance [55].

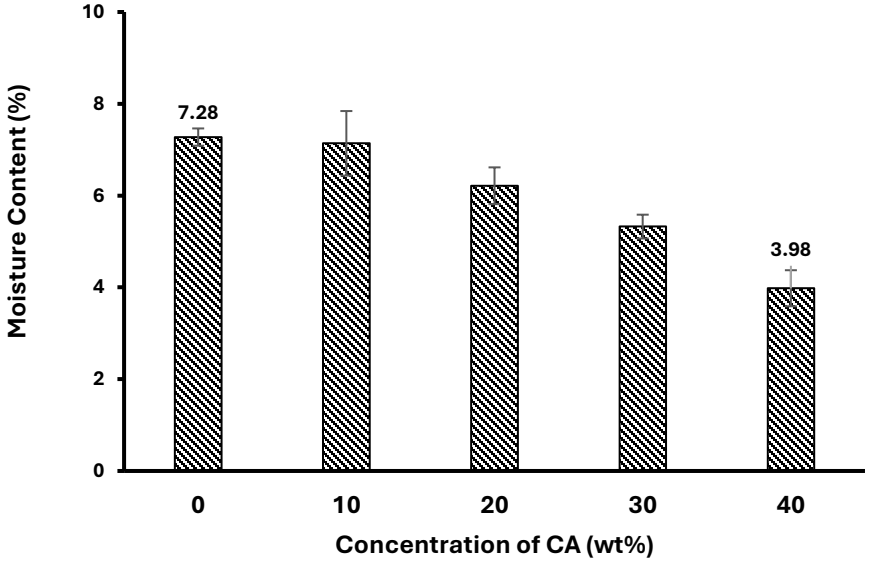


Fig. 10 MC of the CMC and CMC/CA films with various concentrations of CA

Water vapour transmission rate (WVTR)

Building on the restricted water affinity demonstrated by the MC results, further evaluation of the WVTR further elucidates the films' protective capabilities. WVTR not only assesses practical barrier performance - a critical parameter for protective coatings to suppress microbial growth, prevent oxidation, and extend product shelf life - but also serves as a crucial indicator of crosslinking efficiency [25]. As shown in **Fig. 11**, the WVTR decreased by a factor of 2.8, from 225.50 g/m²/day in the uncrosslinked CMC film to 80.03 g/m²/day at the highest crosslinker concentration (40 wt% CA).

This remarkable reduction in permeability is the direct culmination of the chemical and structural transformations confirmed earlier. Specifically, the conversion of hydrophilic precursor groups into hydrophobic ester linkages (ATR-FTIR) and the subsequent crosslinking-induced structural densification (FE-SEM) minimises the free volume available for water-molecule diffusion [21]. This establishes tortuous pathways that severely restrict vapour permeation [27,56]. Consequently, this enhanced barrier behaviour mirrors the increased crosslinking density and aligns with recent literature, including a 1.5-fold reduction in CA-crosslinked CMC films reported by Sabzevari et al. (2025) [27], as well as similar barrier improvements documented in CA-modified starch elastomers [57], and CMC/guar gum blends [21]. Ultimately, this ability to restrict the diffusion of water vapour establishes a robust physical shield, laying the groundwork for the films' resistance to swelling and disintegration when subjected to direct water, as evaluated in the subsequent immersion stability tests.

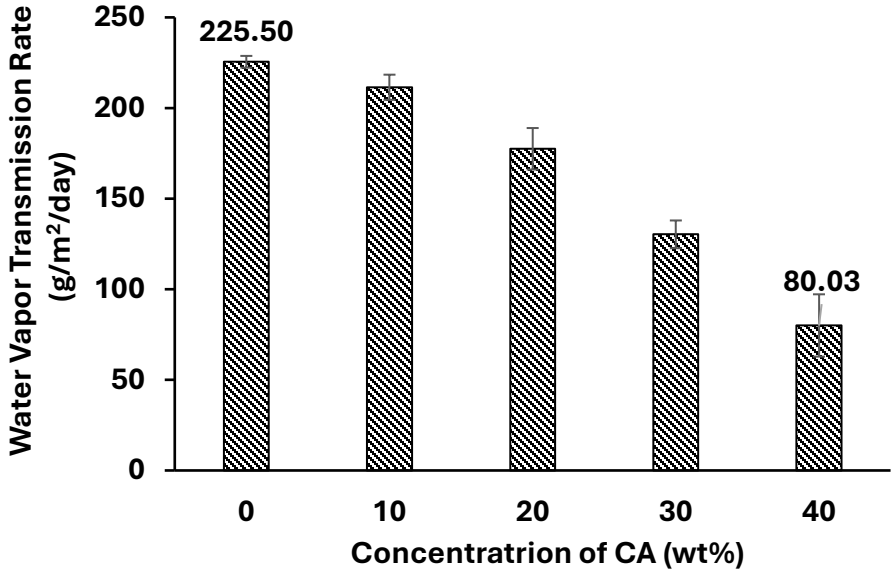


Fig. 11 WVTR of the CMC and CMC/CA films with various concentrations of CA

Water immersion stability

Building upon the restricted water diffusion demonstrated by the aforementioned MC and WVTR results, the films' dimensional stability in aqueous environments was visually validated through immersion tests (**Fig. 12**). The pristine CMC film rapidly swelled and completely dissolved upon immersion, due to unhindered water-molecule penetration and the rapid disruption of intermolecular hydrogen bonds. Conversely, the crosslinked film maintained dimensional stability, retaining its structural integrity even after 15 minutes of direct immersion. This water resistance confirms that the dense covalent ester network successfully acts as a physical shield, restricting solvent-polymer interactions and hindering solvent diffusion into the matrix [58]. Similar anti-swelling and anti-solubility behaviours have been reported in CA-crosslinked potato starch/CMC composites [59]. and partially substituted guar gum films [60], confirming that the conversion of -OH groups into a crosslinked network effectively shields the biopolymer backbone from rapid aqueous solvation.

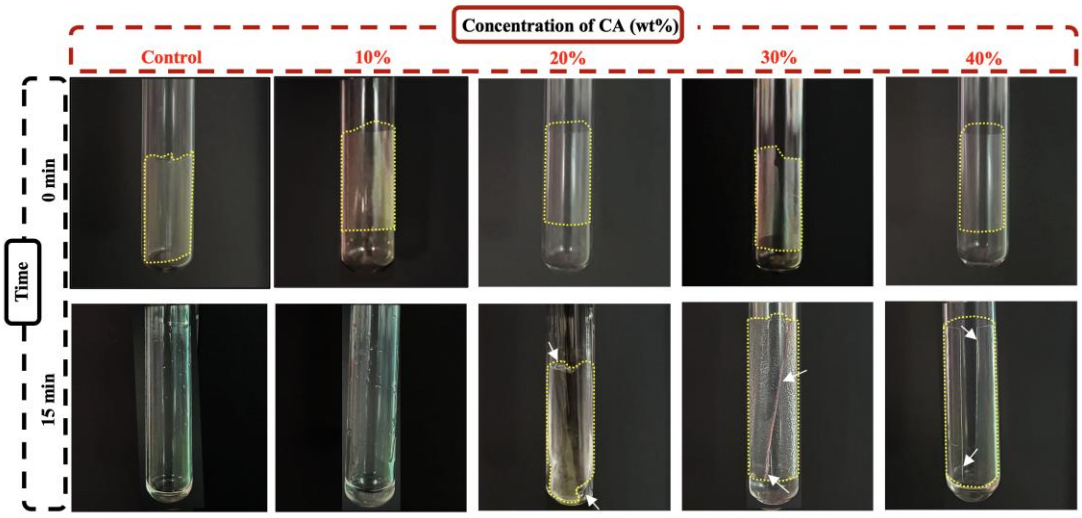


Fig. 12 Visual demonstration of the water immersion stability and structural disintegration of the pristine CMC versus crosslinked CMC/CA films (Yellow arrows indicate structural disintegration and dissolution in the uncrosslinked films).

Practical application in cherry tomato preservation

Comprehensive evaluations establish the optimal "low-energy" crosslinking parameters: 2.25 wt% CMC and 20 wt% CA, kinetically activated at 80 °C for just 3 min. The 20 wt% CA concentration represents a threshold that maximises covalent ester linkages for structural reinforcement, while preventing the matrix embrittlement associated with over-crosslinking and unreacted acid. At this optimum, CA consumes hydrophilic precursors to reduce water affinity and matrix free volume, successfully balancing mechanical flexibility with an outstanding moisture barrier. By overcoming the inherent fragility and high hydrophilicity of pristine CMC, this biodegradable coating demonstrates immense potential for packaging, as practically validated by its excellent performance in the *in vivo* cherry tomato preservation trial.

To practically validate the immense packaging potential of the optimised "low-energy" CMC/CA matrix, an *in vivo* preservation trial was conducted on fresh cherry tomatoes. The physiological changes of the packaged fruits were continuously monitored over a 21-day period under ambient conditions (27-28 °C, 70-80% RH).

As illustrated in **Fig. 13**, visual evaluations demonstrated the superior protective capability of the crosslinked films. The control group exhibited rapid physiological deterioration, characterised by severe shrinkage, loss of turgidity, and localised fungal decay by day 7, culminating in complete structural collapse by day 21. Similarly, while the pristine CMC-wrapped samples provided initial protection, they ultimately failed to prevent surface wrinkling and fruit dehydration due to their inherent hydrophilicity and high moisture permeability.

In contrast, tomatoes packaged with the optimised CMC/CA film successfully maintained their dimensional integrity, turgidity, and glossy skin appearance throughout the entire 21-day trial, with no visible microbial proliferation.

This postharvest performance is the direct consequence of the CMC/CA barrier enhancements established earlier. Specifically, the reduced WVTR of the crosslinked film mitigates fruit transpiration and subsequent cellular dehydration [21,27]. Furthermore, by restricting moisture permeation, the hydrophobic coating prevents the formation of a humid environment at the fruit-film interface [25]. Consequently, this CMC/CA shield translates improvements into practical performance, significantly prolonging storage time duration and maintaining the postharvest quality of easily spoiled agricultural products.

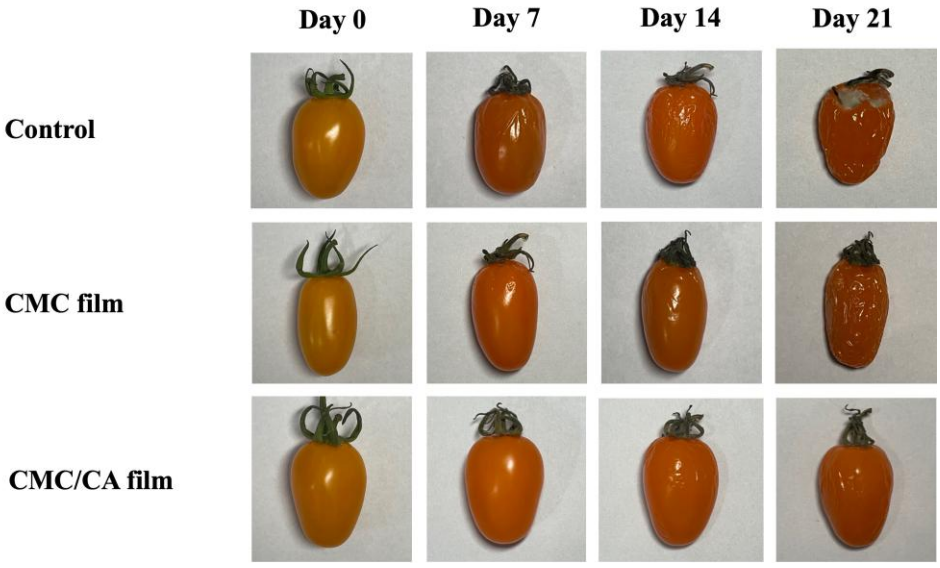


Fig. 13 Visual quality and physiological preservation of cherry tomatoes packaged with pristine CMC and optimised crosslinked CMC/CA films over a 21-day storage period under ambient conditions

Conclusion

This study successfully developed a low-energy crosslinking strategy to overcome the inherent brittleness and moisture sensitivity of Carboxymethyl cellulose (CMC) films. By systematically optimising the formulation to 2.25

wt% CMC and 20 wt% CA, a brief kinetic activation (80 °C for 3 minutes) coupled with a thermodynamically driven drying phase established a robust covalent ester network. This low-energy protocol effectively bypassed thermal degradation, substantially enhancing the films' mechanical durability, as evidenced by a 1.3-fold increase in tensile strength (to 45.21 MPa) and a remarkable 4.7-fold improvement in elongation at break (to 41.25%). Furthermore, the densely crosslinked matrix notably improved moisture stability. This was quantitatively demonstrated by a 1.3-fold reduction in water vapour transmission rate (from 225.50 to 177.50 g/m²/day) and a significant decrease in moisture content (from 7.28% to 6.21%), granting the films excellent structural integrity even upon direct water immersion. Ultimately, the optimised CMC/CA films, functioning as highly effective sacrificial moisture barriers, successfully preserved the physiological and sensory quality of fresh cherry tomatoes over a 21-day storage period. These findings confirm the potential of this low-energy crosslinked network as a high-performance, sustainable packaging solution for preserving fresh fruit.

CRediT authorship contribution statement

Khanh Quang Tran: Conceptualisation, investigation, and writing – original draft. Son Anh Pham: Formal analysis, and data curation. Khai Dinh Do: Software, experimental support, and data interpretation. Son Thi Nguyen: Experimental support, and data interpretation. Hanh Thi My Luong: Formal analysis. Oanh Thi Kim Vuong: Methodology. Vuong Duy Nguyen: Validation, resources, and visualisation. Ngoc Thi Bich Vu: Laboratory investigation, sample preparation, and result verification. Supakij Sutirueingwong: Formal analysis, Methodology, Writing. Thu Hong Anh Ngo: Supervision, project administration, writing – review & editing.

Declaration of competing interest

The authors have declared no conflict of interest.

Funding declaration

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