



Preparation and Characterization of Polyvinyl Alcohol/Carboxymethyl Cellulose Films with Citric Acid and Activated Carbon for Active Food Packaging

Redzuan M. S. James ^a, Paik San H'ng,^{a,b,*} and Norwahyuni Mohd Yusof ^{c,*}

Carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVOH) composite films incorporated with glycerol and citric acid were examined for development of biodegradable films with improved water resistance properties. Addition of citric acid at 30% effectively reduced water solubility of the film. To prepare functional active packaging films for storage of perishable products, the role of activated carbon (AC) at different percentages was also investigated. Various physical, mechanical, thermal, and functional properties of these films were then characterized. The study found that the inclusion of AC at 0.25, 0.5, and 0.75% did not affect the tensile strength (TS), elongation at break, and thermal properties, resulting in stronger films. Fourier transform infrared analysis suggested intermolecular interactions within the polymer matrix after incorporation of citric acid and activated carbon. The antimicrobial activity test revealed no inhibition zone; however, there was no noticeable increase or spread of bacteria during the testing period.

DOI: 10.15376/biores.21.3.6163-6178

Keywords: Carboxyl methyl cellulose; Poly(vinyl alcohol); Bio-active film; Biomass; Palm kernel shell activated carbon

Contact information: a: Institute of Tropical Forestry and Forest Products, Universiti Putra Malaysia (UPM), 43400 Serdang, Selangor, Malaysia; b: Faculty of Forestry and Environment, Universiti Putra Malaysia (UPM), 43400 Serdang, Selangor, Malaysia; c: Rimba Ilmu, UM Agroforestry, Universiti Malaya, 50603 Kuala Lumpur, Malaysia;

* Corresponding authors: ngpaiksan@upm.edu.my; norwahyuni_my@um.edu.my

INTRODUCTION

The extensive use of synthetic films in food packaging has rapidly increased, causing significant environmental problems due to their resistance to degradation. This has led to growing consumer demand for biodegradable alternatives (Cazón *et al.* 2017). Environmental and food safety issues have become major public concerns, attracting researchers to green chemistry solutions (Wang *et al.* 2018). The food packaging sector is a significant part of the global plastic market. Packaging materials contribute greatly to the total plastic waste, leading to severe environmental issues. These materials are non-biodegradable, have lower costs, durability, excellent barrier properties, strength, and the inclusion of additives like printing inks, adhesives, and colorants exacerbates environmental contamination, their petroleum-based composition leads to severe environmental pollution, known as white pollution (Chen *et al.* 2019). A sustainable solution to this issue is to provide bio-based packaging materials. Polysaccharides, protein, lipids, and polyester have been used to form biopolymer packaging films (Khalid *et al.* 2024). Because a single biopolymer may not have all the desirable film characteristics,

polymer blending is one of the main strategies employed to develop packaging films that will have a wide range of application potential (Muthuraj *et al.* 2018).

The present study investigated the biodegradable polymers poly(vinyl alcohol) and carboxymethyl cellulose for use in the food packaging industry. Carboxymethyl cellulose (CMC) is a versatile cellulose derivative that has garnered significant attention in the food packaging sector. Synthesized through the alkylation and etherification of cellulose, CMC possesses unique physical and chemical properties that enhance the integrity and sustainability of food packaging materials. Its utility arises primarily from its excellent film-forming capability, biocompatibility, and favorable mechanical and gas barrier characteristics, making it a preferred choice in both food processing and packaging applications (Sayanjali *et al.* 2024; Biswas *et al.* 2023). As food safety and sustainability become increasingly paramount, CMC's biodegradable nature offers an eco-friendly alternative to traditional plastic packaging materials, due to its renewability and biodegradability (Wang *et al.* 2024; Zafar *et al.* 2022). However, despite these advantages, CMC presents several limitations that can hinder its effectiveness in specific applications. Potential drawbacks of CMC include its poor water resistance, its tendency to dissolve quickly when exposed to water, and its demonstrated limited mechanical properties such as tensile strength and flexibility (Wang *et al.* 2024; Zhang *et al.* 2023).

Polyvinyl alcohol (PVOH) is gaining increasing prominence in the field of food packaging due to its unique properties and advantages. As a biodegradable and water-soluble polymer, PVOH is characterized by its biocompatibility, non-toxicity, and high mechanical strength, making it an attractive option for sustainable packaging solutions (Zhang *et al.* 2023). Despite its beneficial properties, PVOH also has notable drawbacks. The most significant limitation lies in its high-water solubility and susceptibility to moisture absorption, which can impair its mechanical properties and lead to film deterioration in humid environments (Zhang *et al.* 2023; Channa *et al.* 2022; Terzioğlu and Sıcak 2021).

Both CMC and PVOH can benefit from synergistic approaches, wherein they are combined with other materials to overcome individual limitations. Research has shown that blending CMC with PVOH can create composite films that capitalize on the respective advantages of each polymer while mitigating their disadvantages, such as brittleness found in pure CMC films (Zhang *et al.* 2023; Hashmi *et al.* 2021). These blends can optimize mechanical characteristics, moisture resistance, and biodegradability, thereby paving the way for advancements in food packaging solutions. Indeed, to the best of the authors' knowledge, few works have been conducted on edible films based on PVOH/CMC polymers with different antimicrobial agents (Elgharbawy *et al.* 2024; Hosseini *et al.* 2013). Hussain *et al.* (2023) reported on antimicrobial packaging film based on biodegradable PVOH/CMC-ascorbic acid. The films exhibited excellent microbial activity against *Staphylococcus aureus* and *Escherichia coli*. However, a lower percentage of PVOH showed a better result in terms of high mechanical strength, uniform morphology, higher soil burial degradation and lower water transmission rate. Ghaderi *et al.* (2019) developed biodegradable tertiary films based on PVOH, CMC, and fish gelatin. The result showed that adding different ratios of fish gelatin significantly reduced the solubility, tensile strength, as lowest the values of moisture content, contact angle, whiteness index, and water vapour permeability. Meanwhile, Baysal *et al.* (2023) reported that PVOH/CMC films that incorporated with AgNPs from *Plectranthus amboinicus* (PA) displayed better mechanical strength and morphological properties than pure PVOH/CMC film. The film also exhibited significant antibacterial activities against *Bacillus spizizenii*, *Staphylococcus*

aureus, *Salmonella typhi*, and *Escherichia coli*. According to Muppalla *et al.* (2014), 1% CMC exhibited excellent film forming properties; however, the films formed had weak mechanical properties. The mechanical properties of CMC films can be improved by blending with other polymers. Both CMC and PVOH have significant potential in food packaging applications, especially when chemically crosslinked using citric acid. The use of citric acid as a crosslinking agent has demonstrated notable advantages, enhancing the mechanical properties and functional capabilities of the resulting films.

Citric acid has been shown to serve as an effective, non-toxic crosslinker for both CMC and PVOH. Its ability to form ester linkages between hydroxyl groups present in these polymers can enhance the structural integrity of the films, providing improved mechanical strength and resistance to water solubility, which is particularly beneficial in food packaging scenarios where moisture control is crucial (Dong *et al.* 2021; Shi and Yang 2015). Recent studies have shown that citric acid can facilitate the formation of highly crosslinked networks within PVOH films through a thermal curing process. This reaction promotes intermolecular interactions, yielding films with enhanced durability and water resistance (Dong *et al.* 2021; Shi and Yang 2015). Additionally, incorporating citric acid into CMC matrices can also address solubility issues, support the delivery of moisture-sensitive food products while extend shelf life (Reddy and Yang 2010).

This structured study highlights the innovative potential of combining activated carbon with CMC and PVOH in food packaging, addressing consumer needs for sustainable and effective solutions while providing appropriate references for further exploration in this field. Activated carbon is widely recognized for its high surface area, porous structure, adsorption capability, thermal stability, and light barrier properties, thus making it a promising additive for active food packaging.

EXPERIMENTAL

Materials Preparation

Gelatin from cold water fish skin and chitosan (medium molecular weight, 75 to 85% deacetylated) were purchased from Sigma Alderich (St. Louis, MO, USA), glycerol (analytical grade) and food acetic acid were purchased from Merck Chemicals Co. (Darmstadt, Germany). All other reagents used in this study were analytical grade and supplied by (R&M Chemicals).

Preparation of Carbonized Biomass

Lignocellulosic biomass (palm kernel shell) was washed with distilled water to remove dust and other interfering particles and dried in sunlight for a few days. This shell was crushed into a fine powder and had been treated with chemicals prior to two-stage continuous physical activation. The ash forming elements contain high amounts of ash, such as potassium, silica, sodium, *etc.*, and were removed after being impregnated with H₃PO₄ at ratio of 1:1 with distilled water at 80 °C for 2 h. The suspension was washed using distilled water and dried before physical activation. The activated carbon powder was ground and sieved to obtain a uniform particle size of less than 100 µm prior to incorporation into the film-forming solution.

Two stage continuous physical activation

For two-stage continuous physical activation, the chemical pretreated was carbonized continuously in two stages of different carrier gases: air and N₂. For “N₂ > Air” activation, the pretreated samples were carbonized in N₂ before undergo air activation. While for “Air > N₂” activation, samples were carbonized with air and followed by N₂ activation. The activation was set constantly at 700 °C, after which the product was cooled to room temperature by flowing N₂ through carbonized samples and was kept in desiccator for further analysis.

Preparation of the Film

CMC/PVOH film

The CMC/PVOH composite films were prepared *via* solution casting. A 5% (w/v) PVOH solution was dissolved at 95 °C and cooled to room temperature before mixing with a 1% (w/v) CMC solution at a 50:50 weight ratio. Glycerol (1% v/w of polymer) and citric acid (0 to 50% w/w of polymer) were subsequently incorporated, followed by magnetic stirring for 4 h. The homogeneous mixtures were cast into 9-cm-molds and dried at 23 to 25 °C for 72 h, yielding films with an average thickness of 90 ± 12 μm. The authors acknowledge that the drying condition used in the present study may have resulted in limited esterification between citric acid and the polymer matrix. The resulting samples were designated with the labels CMC/PVOH-CA0, CMC/PVOH-CA20, CMC/PVOH-CA30, CMC/PVOH-CA40, and CMC/PVOH-CA50, according to citric acid content. The citric acid concentration was varied to evaluate its influence on film water solubility. Prior to analysis, the films were conditioned at 25 °C and 50 ± 1% relative humidity for 48 h.

CMC/PVOH film with activated carbon (CB)

The CMC/PVOH film with the lowest water solubility was selected to analyze effect of CA addition on the film properties. The CA was added into CMC/PVOH-CA film forming solution at 0.25, 0.50, and 0.75% w/w (weight of polymer) and prepared to a film using the same procedure as CMC/PVOH film, respectively. The films obtained at 0.25, 0.50, and 0.75% of AC were designated as CMC/PVOH-AC0, CMC/PVOH-AC0.25, CMC/PVOH-AC0.50, and CMC/PVOH-AC0.75, respectively.

Characterization of Films

Water solubility of the films was carried out according to the method of Gontard, Guilbert, and Cuq (1992). Three pieces (1 × 4 cm²) of film were weighed (± 0.0001 g) and subsequently dried in an air-circulating oven at 105 °C for 24 h. After this time films were recovered and re-weighed (± 0.0001 g) to determine their initial dry weight (W_i). Afterwards, the samples were immersed in 30 mL of distilled water and the system gently shaken (100 rpm) for 24 h at room temperature (22 to 25 °C). The samples were then passed through a filter paper (Whatman 1). Then, the filter paper together with un-solubilized fraction was dried in a forced-air oven (105 °C, 24 h) and weighed (W_f). The film solubility (FS%) was calculated using the following equation, $FS (\%) = (W_i - W_f) / W_i \times 100$, where W_i was the initial dry film weight (g) and W_f was the weight (g) of the final dry weight.

A universal testing machine (Cometech Model QC-508B1) equipped with a 60 N load-cell was used to measure tensile strength (TS), elongation at break (EA%), and elastic modulus (EM) according to the standard method ASTM D882-09 (2009). The test was performed in the controlled room at 25 °C and 50 ± 1 RH. Ten film samples (2 cm × 4 cm) with the initial grip length of 3 cm were used for testing. The film samples were clamped

and deformed under tensile loading with the cross-head speed of 30 mm/min until the samples were broken. The maximum load and the final extension at break were used for calculation of TS, EA%, and EM, respectively.

Thermo-gravimetric analysis was conducted using TGA-1 (Mettler Toledo Instrument) from room temperature to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere. Prior to testing, the films were conditioned in a desiccator containing dried silica gel for two weeks at room temperature at 23 to 25 °C to ensure complete dehydration.

The thermal transitions of the films were analyzed using a DSC 200-F3 Maia (Netzsch, Germany). Approximately 10 mg of pre-dried sample was sealed in an aluminum pan and scanned from -50 °C to 150 °C at a heating rate of 10 °C/min, with an empty aluminum pan as the reference. Before DSC measurement, the samples were conditioned in silica-gel desiccator for two weeks at 23 to 25 °C to remove residual moisture.

The film samples were dried in a desiccator containing silica gel for 2 weeks before analysis. Pieces of film 2 cm in diameter were sandwiched between two KBr disks. The FTIR spectra were recorded from wave 400 to 4000 cm⁻¹ in a Bruker Equinox 55 spectrometer (Bruker Banner Lane, Coventry, Germany).

Antimicrobial activity of films was carried out against *Staphylococcus aureus* (Gram-positive) and *Escherichia coli* (Gram-negative) according to Disc diffusion method. Paper discs coated with 50 mg/mL of penomycin and distilled water were used as the positive and negative controls, respectively. The active films were aseptically cut into 6 mm diameter size, and five samples were placed on a Petri dish containing Nutrient Agar (Merck, Germany). Then, the Petri dish was incubated at 37 °C for 24 h, and the inhibition zone surrounding the film was measured in mm by using a digital micrometer. All experiments were conducted in triplicate unless otherwise stated. Data were analyzed using one-way analysis of variance (ANOVA), and significant differences between mean values were determined at $p < 0.05$.

RESULTS AND DISCUSSION

Characterization of CMC/PVOH Films Incorporated with Citric Acid

To select a suitable film composition for analyzing the effect of activated carbon on film properties, different concentrations of citric acid (CA) in CMC/PVOH films were comparatively evaluated based on their water solubility and physical characteristics. The film properties with different CA concentrations were characterized focusing on a lower water solubility of film.

The opacity of packaging films is a critical factor influencing both consumer preference and food quality preservation. In contemporary food packaging, consumers often favor visually transparent films that allow them to see the packaged products. However, an overly transparent film permits light transmission that can accelerate photo-oxidative reactions, particularly in lipid-rich foods, leading to adverse effects on food safety and quality (Flueck 2022).

In the present study, the CMC and PVOH films, modified with varying concentrations of CA, demonstrated a clear and uniform optical appearance. However, an increasing concentration of CA affected the films' optical properties; specifically, the opacity tended to increase with higher CA concentration. This phenomenon can be attributed to the role of CA in modifying the polymer matrix's structure.

Citric acid, with its multiple hydroxyl and carboxyl functional groups, can serve to enhance the interchain bonding within the CMC/PVOH blend. As a crosslinker, CA may disrupt the efficient packing of polymer chains, leading to a more loosely organized matrix. Consequently, this structural alteration results in increased scattering of light, thereby increasing the opacity of the films (Sutharsan *et al.* 2022; Zhang *et al.* 2018). This increase in opacity suggests that the films formed at higher concentrations of CA could potentially offer enhanced barrier properties against light, which is especially beneficial for packaging lipid-rich foods that are sensitive to photo-oxidation.

Film thickness is a critical parameter in food packaging due to its influence on barrier and mechanical properties. In this study, the standardized CMC/PVOH ratio (50:50) ensured consistent thickness across samples, allowing the effect of CA as a crosslinker to be isolated. While CA concentration did not alter thickness, it enhanced mechanical strength, stiffness, and thermal stability *via* ester linkage formation, while preserving effective moisture and gas barrier performance. Table 1 shows that CMC/PVOH films formulated without citric acid achieved the lowest film thickness when compared to those with varying concentrations of citric acid (20%, 30%, 40%, and 50%). This can be attributed to several interrelated factors associated with the chemical and physical interactions. According to Wilpiszewska *et al.* (2019) and Sonker *et al.* (2017), increased concentrations of citric acid can lead to a higher crosslinking density within the film matrix. This denser network effectively restricts the mobility of polymer chains, which typically results in films with enhanced mechanical properties, but less flexibility compared to films with lower citric acid concentrations. Moreover, the presence of citric acid may alter the evaporation rate of the solvent during film formation. With lower concentrations of citric acid (such as 0%), there might be less interaction within the matrix, resulting in thinner films because of a lack of structure that retains water or engages it differently during the drying process (Wu *et al.* 2017).

The CMC/PVOH films with 30% citric acid exhibit the lowest water solubility compared to those with the 0% or 20% levels, but they showed an increase in solubility at 40% and 50% citric acid. This can be attributed to the interplay between crosslinking density, molecular interactions, and the plasticizing effect of citric acid. Although the curing conditions were too mild to expect development of ester linkages in the present work, it is possible that calcium ions bridges were formed between adjacent carboxylate groups. At lower concentrations of citric acid (0% to 20%), there may be insufficient crosslinking to improve mechanical stability while maintaining low solubility. At 30% citric acid, the crosslinking might reach an optimal point where the polymer network is sufficiently dense, inhibiting water uptake and leading to the observed lower water solubility (Huang *et al.* 2023). At 40% and 50% citric acid, it could be suggested that an excess amount causes different interactions within the polymer matrix. Although more crosslinking typically means lower solubility, high concentrations of citric acid may also introduce increased hydrophilicity due to the surplus of carboxyl groups, potentially leading to greater water solubility as the film interacts more with water molecules (Wilpiszewska *et al.* 2019). At 40% and 50% citric acid, additional citric acid can disrupt the intermolecular hydrogen bonds between CMC and PVOH, while simultaneously enhancing interaction with water, resulting in a film that can absorb more moisture and exhibit higher solubility. This scenario contrasts with the 30% concentration, where the film's rigidity may prevent effective water penetration (Li *et al.* 2018). Among the tested formulations, the film containing 30% citric acid exhibited the lowest water solubility while maintaining acceptable film integrity and appearance. Therefore, this formulation

was selected for subsequent incorporation of activated carbon and further characterization studies.

Table 1. Effect of CA Incorporation on the Physical Properties of CMC/PVOH Films

CMC/PVOH Film	Transmittance (%)	Film Thickness (mm)	Water Solubility (%)
CMC/PVOH-CA0	High (90%)	0.019	100% (fully soluble)
CMC/PVOH-CA20	Slightly lower (80%)	0.158	80% (lower than CA0)
CMC/PVOH-CA30	Lower (70%)	0.159	Lowest
CMC/PVOH-CA40	Lower (60%)	0.161	Higher than CA30
CMC/PVOH-CA50	Likely even lower (50%)	0.165	Higher than CA40

Values are expressed as mean \pm standard deviation (n = 3). Different superscript letters within the same column indicate significant differences at $p < 0.05$.

The CMC/PVOH incorporated with 30% CA revealed the lowest percentage of water solubility and was consequently chosen to study the effect of the addition of AC on packaging film properties. The properties of the CMC/PVOH-CA30 with various AC content were studied.

Characterization of CMC/PVOH Films with Activated Carbon

FTIR spectroscopy

FTIR spectroscopy is a powerful analytical technique used to identify chemical functionalities and characterize interactions of polymer chains in various materials, including polymer blends. The FTIR spectra of CMC, PVOH, and their blended films are presented in Fig. 1. Notably, all the peaks observed in CMC and PVOH films also appeared in the CMC/PVOH blend, although with slight shifts in their wavenumber values, indicating possible interactions between the polymer chains.

In the FTIR analysis, PVOH exhibited a broad absorbance band between 3200 and 3530 cm^{-1} , corresponding to -OH stretching vibrations. Specific peaks for -CH stretching, -CH bending, and -C-O stretching were found at 2973, 1406, and 1055 cm^{-1} , respectively (Mali *et al.* 2018). Similarly, CMC displayed a strong broad band for -OH stretching at 3200-3510 cm^{-1} , along with -CH asymmetric stretching and -COO ester asymmetric stretching peaks at 2906 and 1590 cm^{-1} (Mali *et al.* 2018). Additionally, peaks for CH_2 and -OH bending were evident at 1417 and 1325 cm^{-1} , respectively, revealing the rich functional group profile of CMC.

The role of citric acid (CA) within the CMC/PVOH films is noteworthy, as its incorporation appreciably influenced the characteristic peak at 1710 cm^{-1} , possibly associated with carbonyl-related intermolecular interactions within the polymer matrix. Additionally, a sharp absorbance band at 1752 cm^{-1} , characteristic of the C=O group in CA, was observed, which was insignificant in the CMC/PVOH film lacking CA. This spectral change may indicate partial intermolecular interactions and limited crosslinking effects within the polymer matrix under the present drying conditions (Yuan *et al.* 2024). On the other hand, the absence of an absorbance band at 1752 cm^{-1} suggests that there was no significant development of ester linkages. Citric acid, often used as a non-toxic crosslinking agent, showcases its potential in modifying physiochemical properties while promoting effective interchain bonding (Yuan *et al.* 2024).

Analysis of CMC/PVOH films with varying concentrations of activated carbon (AC) demonstrated that the addition of AC did not appreciably alter the FTIR spectra. This

lack of change indicates that AC was incorporated effectively into the film matrix without initiating chemical reactions with CMC or PVOH (Ianchiș *et al.* 2023). The stability of the spectra reinforces the notion that AC serves primarily as a filler or reinforcing agent, rather than as a reactive component, thus preserving the structural integrity of the blended films.

In summary, FTIR spectroscopy effectively revealed chemical interactions and functionalities of CMC/PVOH films, elucidating the impact of citric acid and affirming the compatibility of activated carbon within the polymeric matrix. These findings align with related literature that highlights the ability of citric acid to enhance the properties of various biopolymer blends while maintaining a favorable interaction with other components (Azeredo *et al.* 2015).

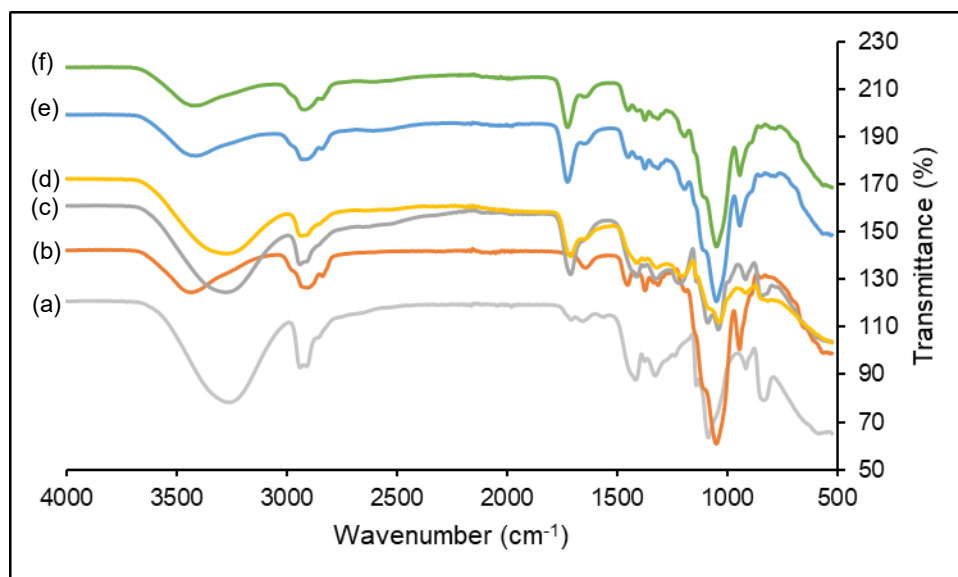


Fig. 1. FTIR spectra of the (a) CMC, (b) PVOH, (c) CMC/PVOH, (d) CMC/PVOH-AC0.25, (e) CMC/PVOH-AC0.50, and (f) CMC/PVOH-AC0.75

Mechanical performance test

The mechanical properties of the CMC/PVOH films exhibited noticeable variation depending on their composition, as presented in Table 2. Pure CMC films typically exhibit a relatively high tensile strength; however, the CMC films tend to show a low elongation at break, highlighting a brittle nature typical of polysaccharide-based films. This brittleness is attributed to strong intermolecular hydrogen bonding.

The blending of CMC and PVOH without activated carbon led to a notable reduction in tensile strength, which should be accurately presented with specific experimental values from relevant studies. The increase in elongation at break to 682.44% indicates pronounced plasticization effects, likely stemming from molecular interactions between CMC and PVOH that disrupt crystalline domains, thereby enhancing chain mobility. Wang *et al.* (2017) provide insights into this behavior, supporting the assertion regarding the effects of molecular interactions on mechanical properties (Zafar *et al.* 2022).

It is worth mentioning that the addition of activated carbon at a loading of 0.25% resulted in a decline in tensile strength and elongation at break. This reduction is likely due to particle agglomeration and suboptimal interfacial adhesion, which can create stress concentration points. Zhou *et al.* (2016) support the notion of how filler materials can adversely affect mechanical performance (Zhang *et al.* 2023). At a higher carbon black

loading of 0.75%, there was a slight improvement in tensile strength, while elongation at break decreased. This trend suggests that although some reinforcement effects arise from the carbon filler, it also restricts polymer chain mobility. This observation aligns with findings from Mark *et al.* (2019) and Ismail and Shafiq (2014), which highlight the correlation between increased filler loading and enhanced tensile strength on composite, but then reduction in elongation due to the stiffening effect caused by the less compatible hydrophobic matrices. The notion is supported by Huang and Zhang's research, which concluded that incorporating wood fillers into high-density polyethylene composites led to a significant decrease in elongation at break while enhancing rigidity, aligning with the general behavior of composite materials containing high-stiffness fillers (Huang and Zhang 2008; Leite-Barbosa *et al.* 2024).

These findings emphasize that blending CMC and PVOH can enhance film flexibility, whereas the incorporation of activated carbon requires careful optimization of dispersion and interfacial bonding to improve tensile performance without compromising ductility. However, additional comparative studies involving films prepared without citric acid under identical conditions would provide further clarification regarding the specific contribution of citric acid to the mechanical performance of the developed films.

Table 2. Tensile Strength, Elongation at Break of the CMC/PVOH Film Incorporated with Various AC Contents

Films	Mechanical Properties	
	Tensile strength (MPa)	Elongation at break (%)
CMC	31.40	12.26
PVOH	35.93	327.94
CMC/PVOH-AC0	12.29	682.44
CMC/PVOH-AC0.25	6.36	134.96
CMC/PVOH-AC0.50	12.94	105.80
CMC/PVOH-AC0.75	17.42	62.06

TGA and DTG

The thermal degradation behaviour of the neat and composite films exhibited multiple stages, as commonly observed in polysaccharide-based blends (Fig. 2). The initial weight loss below 150 °C was attributed to the removal of physically bound moisture, while the second major decomposition stage between 250 and 350 °C corresponded to the breakdown of PVOH and CMC polymer backbones. Similar thermal events have been reported for PVOH/CMC-based films, approximately 65% of the polymer may degrade, resulting in mass loss and a deterioration of mechanical properties (Manne *et al.* 2025; Hussain *et al.* 2023).

Incorporation of activated carbon at increasing loadings (0.25 to 0.75%) influenced both the onset and maximum degradation temperatures, with films containing higher activated carbon showing slightly enhanced thermal stability. Well-dispersed carbon fillers in polymer matrices can effectively protect polymer chains from external thermal radiation, thereby increasing the maximum temperature of thermal decomposition and slowing polymer degradation, while the presence of carbon microspheres further enhances this effect by catalyzing the formation of crosslinked carbon structures that protect the matrix from heat and oxygen (Rybiński *et al.* 2021; Xue *et al.* 2017).

The char residue at 600 °C also increased in proportion to the activated carbon content, indicating the formation of thermally stable carbonaceous structures. Such

improvements are consistent with prior reports where carbonaceous fillers improved the high-temperature resistance of polymer composites (Lim *et al.* 2024; Rybiński *et al.* 2021; Xue *et al.* 2017).

Overall, the TGA and DTG results suggest that although the fundamental degradation mechanisms of PVOH/CMC remain dominant, the presence of activated carbon enhanced thermal stability and residual yield. This provides further evidence of the reinforcing role of activated carbon in bio-based films, which may be advantageous for packaging applications requiring improved heat resistance and dimensional stability (Lim *et al.* 2024).

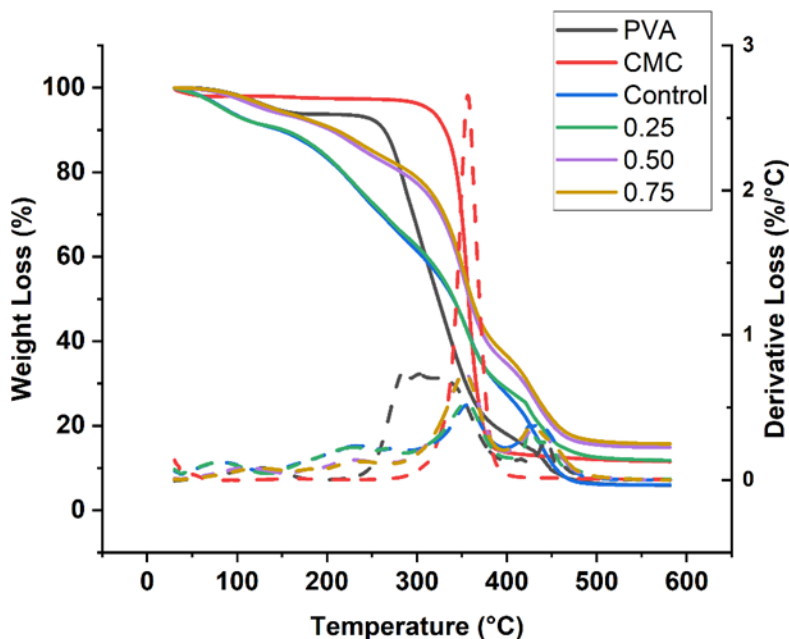


Fig. 2. TGA and DTG of the CMC, PVOH, CMC/PVOH, CMC/PVOH-AC0.25, CMC/PVOH-AC0.50, and CMC/PVOH-AC0.75

Digital scanning calorimetry

The DSC thermograms (Fig. 3) of neat and composite films revealed distinct transitions associated with glass transition (T_g) and melting (T_m). Neat PVOH/CMC films exhibited a clear T_g followed by a broad endothermic peak, reflecting partial miscibility and semi-crystalline domains. With the incorporation of activated carbon, a slight increase in T_g and a decrease in melting enthalpy (ΔH_m) were observed, suggesting restricted chain mobility and disruption of crystalline packing. This reduction in crystallinity is consistent with filler–matrix interactions where activated carbon serves as a physical barrier to polymer chain alignment (Lim *et al.* 2024).

These DSC findings complement the TGA/DTG analysis, which demonstrated enhanced thermal stability of the activated carbon–reinforced composites. The decreased mobility of the polymer chains facilitates enhanced stability during heat exposure. This effect has been corroborated by the findings of Xue *et al.* (2017), who note that restricted molecular motion protects functional groups within the polymer chain from thermal degradation pathways, resulting in improved thermal resistance. The presence of activated carbon not only disrupts crystallization but also promotes the formation of thermally stable residues, thereby improving the overall resistance to degradation (Xu *et al.* 2017).

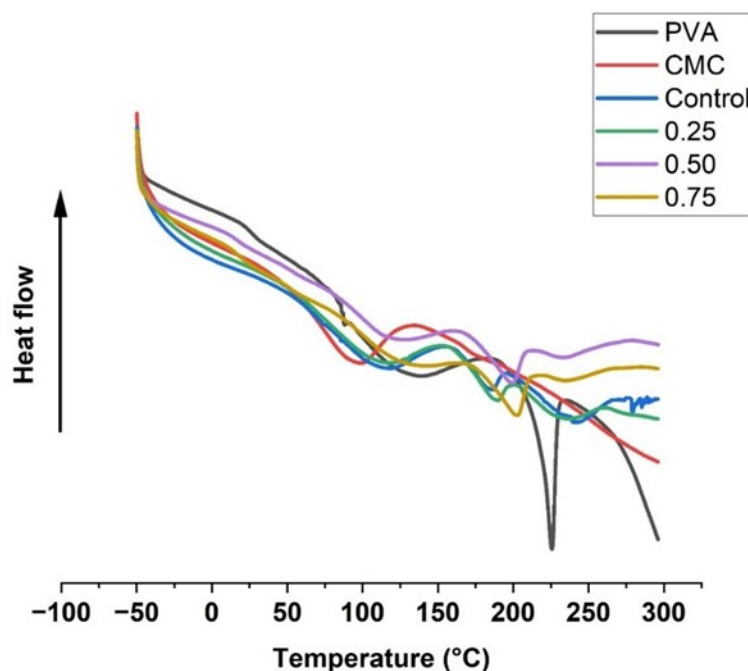


Fig. 3. DSC of the CMC, PVOH, CMC/PVOH, CMC/PVOH-AC0.25, CMC/PVOH-AC0.50, and CMC/PVOH-AC0.75

Antimicrobial activity

The antibacterial evaluation of the four prepared films, namely PVOH/CMC (control), PVOH/CMC with 0.25% activated carbon, PVOH/CMC with 0.50% activated carbon, and PVOH/CMC with 0.75% activated carbon, against *Staphylococcus aureus* and *Escherichia coli* revealed no inhibition zones for any sample. The antimicrobial evaluation was conducted based on previous studies suggesting that activated carbon-containing materials and citric acid may contribute to microbial suppression through adsorption effects and acidic interactions. However, the concentrations incorporated in the present study were insufficient to produce measurable inhibition zones. This result demonstrates that neither the base PVOH/CMC matrix nor the incorporation of low concentrations of activated carbon imparted antimicrobial properties.

The absence of inhibition zones in the control PVOH/CMC films is consistent with earlier studies that reported no antibacterial effect in pure PVOH/CMC systems without active biocidal agents. For example, Mohammed *et al.* (2022) found that PVOH/CMC films exhibited no growth inhibition against *E. coli* until silver hydroxyapatite nanoparticles were incorporated, after which clear inhibition zones were observed. Similarly, Bahrami and Fattahi (2021) demonstrated that CMC–PVOH films without additives failed to inhibit *S. aureus* and *E. coli*, while the inclusion of *Glycyrrhiza glabra* L. essential oil produced significant antibacterial activity.

Recent work by Manne *et al.* (2025) also supports this trend. They reported that PVOH/CMC films doped with Ag nanoparticles exhibit potent antibacterial activity against strains, such as *Staphylococcus aureus* and *Escherichia coli*, thereby achieving significant bacterial inactivation in short durations.

From a mechanistic perspective, the lack of antibacterial activity in the activated carbon loaded films can be attributed to the inert nature of activated carbon in this context. Activated carbon is widely valued for its high surface area, adsorption capacity and role in

filtration applications (Küçük and Önal 2021), yet it does not release antimicrobial agents nor generate reactive species capable of disrupting bacterial membranes. In contrast, silver-based additives release Ag⁺ ions that interact with bacterial cell walls and proteins, while plant-derived bioactives contain polyphenols, terpenoids and other compounds exhibit antimicrobial properties, which can help prolong the shelf life of food by inhibiting microbial growth (Madian *et al.* 2025; Manne *et al.* 2025).

To develop PVOH/CMC films with dual functional properties, future studies could explore the co-incorporation of activated carbon with known antibacterial agents such as silver nanoparticles, zinc oxide nanoparticles, or essential oils. This approach could potentially combine the barrier and adsorption properties of activated carbon with the bactericidal activity of the added agents.

CONCLUSIONS

This study successfully developed biodegradable CMC/PVOH films containing citric acid and reinforced with activated carbon for potential food packaging applications.

1. Films containing 30% citric acid demonstrated the lowest water solubility, indicating enhanced water resistance compared to other formulations.
2. The incorporation of activated carbon contributed to improved thermal stability and increased residual char formation while maintaining acceptable mechanical performance of the films.
3. Fourier transform infrared (FTIR) was used to evaluate intermolecular interactions and ester linkages within the polymer matrix after incorporation of citric acid and activated carbon. There was no evidence of ester formation, which is consistent with the mild conditions employed (no heating step).
4. Although activated carbon did not exhibit antimicrobial activity against *Staphylococcus aureus* and *Escherichia coli*, the developed films demonstrated potential as sustainable bio-based packaging materials.
5. Future studies should investigate the incorporation of additional antimicrobial agents and evaluate barrier properties to further enhance the multifunctional performance of the developed films for active food packaging applications. In addition, the present work can be extended by work in which films are cured over a range of temperatures and times to increase the opportunity for ester bond formation, leading to possible crosslinking.

ACKNOWLEDGEMENTS

This study was financially supported by the Higher Education Center of Excellence (HICoE) Phase 2 grant (Project title: “Improved micropatterning of palm kernel shell graphite for coating film used in food packaging,” vote number: 5210006 project code: 800-3/8/HICoEF2/2023/5210006) provided by the Malaysian Ministry of Higher Education (MOHE). The authors also express their gratitude to the publication fund provided by the Research Management Centre, Universiti Putra Malaysia to cover the publication fee.

REFERENCE CITED

- ASTM D882-09 (2009). "Standard test method for tensile properties of thin plastic sheeting," ASTM International, West Conshohocken, PA, USA.
- Azeredo, H. M. C. d., Kontou-Vrettou, C., Moates, G. K., Wellner, N., Cross, K., Pereira, P., and Waldron, K. W. (2015). "Wheat straw hemicellulose films as affected by citric acid," *Food Hydrocolloids* 50, 1-6.
<https://doi.org/10.1016/j.foodhyd.2015.04.005>
- Bahrami, A., and Fattahi, R. (2021). "Biodegradable CMC–PVOH composite incorporated with *Glycyrrhiza glabra* L. essential oil: Physicochemical and antibacterial features," *Food Science & Nutrition* 9(9), 4993-5004.
<https://doi.org/10.1002/fsn3.2449>
- Baysal, G., Ateş, K. B., Akbulut, A., and Özpinar, H. (2023). "Shelf Life of Foods and Bioactive Materials Used in the Antimicrobial Food Packaging,"
<https://doi.org/10.20944/preprints202309.0669.v1>
- Biswas, A., Ahmed, T., Rana, M., Hoque, M., Ahmed, M., Sharma, M., Sridhar, K., Ara, R., and Inbaraj, B. S. (2023). "Fabrication and characterization of ZnO nanoparticles-based biocomposite films prepared using carboxymethyl cellulose, taro mucilage, and black cumin seed oil for evaluation of antioxidant and antimicrobial activities," *Agronomy* 13(1), article 147. <https://doi.org/10.3390/agronomy13010147>
- Cazón, P., Velazquez, G., Ramírez, J. A., and Vázquez, M. (2017). "Polysaccharide-based films and coatings for food packaging: A review," *Food hydrocolloids* 68, 136-148. <https://doi.org/10.1016/j.foodhyd.2016.09.009>
- Channa, I. A., Ashfaq, J., Gilani, S. J., Shah, A. A., Chandio, A. D., and Bin-Jumah, M. (2022). "UV blocking and oxygen barrier coatings based on polyvinyl alcohol and zinc oxide nanoparticles for packaging applications," *Coatings* 12(7), article 897.
<https://doi.org/10.3390/coatings12070897>
- Chen, H., Wang, J., Cheng, Y., Wang, C., Liu, H., Bian, H., Pan, Y., Sun, J., and Han, W. (2019). "Application of protein-based films and coatings for food packaging: A review," *Polymers* 11(12), 2039. <https://doi.org/10.3390/polym11122039>
- Dong, Y., Feng, Y., Xu, J., Kong, B., Liu, Q., and Wang, H. (2021). "Fabrication, characterization, and antibacterial properties of citric acid crosslinked PVA electrospun microfibre mats for active food packaging," *Packaging Technology and Science* 34(6), 361-370. <https://doi.org/10.1002/pts.2566>
- Elgharbawy, A. S., Demerdash, A.-G. M. E., Sadik, W. A., Kasaby, M. A., Lotfy, A. H., and Osman, A. I. (2024). "Synthetic degradable polyvinyl alcohol polymer and its blends with starch and cellulose—A comprehensive overview," *Polymers* 16(10), 1356. <https://doi.org/10.3390/polym16101356>
- Flueck, J. A. (2022). "Development of intelligent gelatin films incorporated with sappan (*Caesalpinia sappan* L.) heartwood extract," *Polymers* 14(12), article 2487.
<https://doi.org/10.3390/polym14122487>
- Ghaderi, J., Hosseini, S. F., Keyvani, N., and Gómez-Guillén, M. C. (2019). "Polymer blending effects on the physicochemical and structural features of the chitosan/poly (vinyl alcohol)/fish gelatin ternary biodegradable films," *Food Hydrocolloids* 95, 122-132. <https://doi.org/10.1016/j.foodhyd.2019.04.021>
- Hashmi, M., Ullah, S., Ullah, A., Saito, Y., Haider, M. K., Bie, X., Wada, K., and Kim, I. S. (2021). "Carboxymethyl cellulose (CMC) based electrospun composite nanofiber

- mats for food packaging,” *Polymers* 13(2), article 302.
<https://doi.org/10.3390/polym13020302>
- Hosseini, S. F., Rezaei, M., Zandi, M., and Ghavi, F. F. (2013). “Preparation and functional properties of fish gelatin–chitosan blend edible films,” *Food Chemistry* 136(3-4), 1490-1495. <https://doi.org/10.1016/j.foodchem.2012.09.081>
- Hussain, R., Batool, S. A., Aizaz, A., Abbas, M., and Rehman, M. A. U. (2023). “Biodegradable packaging based on poly(vinyl alcohol) and carboxymethyl cellulose films incorporated with ascorbic acid for food packaging applications,” *ACS Omega* 8(45), 42301-42310. <https://doi.org/10.1021/acsomega.3c04397>
- Ianchiș, R., Alexa, R. L., Gîfu, I. C., Marin, M. M., Alexandrescu, E., Constantinescu, R., Serafim, A., Nistor, C. L., and Petcu, C. (2023). “Novel green crosslinked salectan hydrogels and preliminary investigation of their use in 3D printing,” *Pharmaceutics* 15(2), article 373. <https://doi.org/10.3390/pharmaceutics15020373>
- Ismail, H., and Shafiq, M. D. (2014). “The comparison of properties of (rubber tree seed shell flour)-filled polypropylene and high-density polyethylene composites,” *Journal of Vinyl and Additive Technology* 22(2), 91-99. <https://doi.org/10.1002/vnl.21409>
- Kanatt, S. R., and Makwana, S. H. (2020). “Development of active, water-resistant carboxymethyl cellulose-poly vinyl alcohol-*Aloe vera* packaging film,” *Carbohydrate Polymers* 227, article ID 115303. <https://doi.org/10.1016/j.carbpol.2019.115303>
- Khalid, S., Zahid, M., Chaudhary, K., Naeem, M., Mustafa, M., Onyeaka, H., Hafeez, A., Amin, S., and Raana, S. (2024). “Unveiling the emerging trends of egg components-based biodegradable food packaging development: A comprehensive review,” *Comprehensive Reviews in Food Science and Food Safety* 23(5), e13433. <https://doi.org/10.1111/1541-4337.13433>
- Küçük, İ., and Önal, Y. (2021). “Synthesis, characterization, and adsorption properties of highly microporous structured activated carbon,” *Journal of the Turkish Chemical Society Section A: Chemistry* 8(3), 821-834. <https://doi.org/10.18596/jotcsa.753579>
- Leite-Barbosa, O., Pinto, C., Leite-da-Silva, J. M., Aguiar, E., and Veiga, V. F. da. (2024). “Polymeric composites reinforced with amazonian agro-extractive and timber industry residues: A sustainable approach to enhancing material properties and promoting bioeconomy,” <https://doi.org/10.20944/preprints202410.2379.v1>
- Lim, T., Seo, B. H., Kim, S. J., Han, S., Lee, W., and Suk, J. W. (2024). “Nitrogen-doped activated hollow carbon nanofibers with controlled hierarchical pore structures for high-performance, binder-free, flexible supercapacitor electrodes,” *ACS Omega* 9(7), 8247-8254. <https://doi.org/10.1021/acsomega.3c08952>
- Madian, N. G., Ali, M. M., Ahmed, D., and Boules, E. (2025). “Chitosan films with polyphenols as enhancing agent,” *Journal of Applied Polymer Science* 142(33), article e57326. <https://doi.org/10.1002/app.57326>
- Mali, K. K., Dhawale, S. C., Dias, R. J., Dhane, N. S., and Ghorpade, V. S. (2018). “Citric acid crosslinked carboxymethyl cellulose-based composite hydrogel films for drug delivery,” *Indian Journal of Pharmaceutical Sciences* 80(4), 657-667. <https://doi.org/10.4172/pharmaceutical-sciences.1000405>
- Manne, G. K., Srinivasan, K. V., Gopal, N., Kumar, R., Prathap, P., Hanumanthappa, N., Pitchika, G. K., Battana, S., and Mandala, R. (2025). “PVOH/CMC-Ag polymer blend nanocomposites prepared by doping bio-derived ag nanoparticles and their structural, thermal, optical, antimicrobial, and electrical characterization,” *Journal of Applied Polymer Science* 142(18), article e56811. <https://doi.org/10.1002/app.56811>

- Mark, U. C., Madufor, I. C., Obasi, H. C., and Mark, U. (2019). "Influence of filler loading on the mechanical and morphological properties of carbonized coconut shell particles reinforced polypropylene composites," *Journal of Composite Materials* 54(3), 397-407. <https://doi.org/10.1177/0021998319856070>
- Mohammed, A. A., Ahmed, D. S., and Khadom, A. A. (2022). "Enhancement of physico-chemical, optical, dielectric, and antimicrobial properties of polyvinyl alcohol/ carboxymethyl cellulose blend films by addition of silver-doped hydroxyapatite nanoparticles," *Journal of Polymer Research* 29, 229. <https://doi.org/10.1007/s10965-022-02943-5>
- Muppalla, S. R., Kanatt, S. R., Chawla, S. P., and Sharma, A. (2014). "Carboxymethyl cellulose–polyvinyl alcohol films with clove oil for active packaging of ground chicken meat," *Food Packaging and Shelf Life*, 2(2), 51-58. <https://doi.org/10.1016/j.fpsl.2014.07.002>
- Muthuraj, R., Misra, M., and Mohanty, A. K. (2018). "Biodegradable compatibilized polymer blends for packaging applications: A literature review," *Journal of Applied Polymer Science* 135(24), 45726. <https://doi.org/10.1002/app.45726>
- Reddy, N. and Yang, Y. (2010). "Citric acid cross-linking of starch films," *Food Chemistry* 118(3), 702-711. <https://doi.org/10.1016/j.foodchem.2009.05.050>
- Rybiński, P., Syrek, B., Marzec, A., Szadkowski, B., Kuśmierk, M., Śliwka-Kaszyńska, M., and Mirkhodjaev, U. Z. (2021). "Effects of basalt and carbon fillers on fire hazard, thermal, and mechanical properties of EPDM rubber composites," *Materials* 14(18), article 5245. <https://doi.org/10.3390/ma14185245>
- Sayanjali, S., Lu, Y., and Howell, K. (2024). "Extraction and characterization of cellulose from broccoli stems as a new biopolymer source for producing carboxymethyl cellulose films," *International Journal of Food Science* 2024, 1-15. <https://doi.org/10.1155/2024/7661288>
- Shi, J., and Yang, E. L. (2015). "Green electrospinning and crosslinking of polyvinyl alcohol/citric acid," *Journal of Nano Research* 32, 32-42. <https://doi.org/10.4028/www.scientific.net/jnanor.32.32>
- Sonker, A. K., Teotia, A. K., Kumar, A., Nagarale, R. K., and Verma, V. (2017). "Development of polyvinyl alcohol based high strength biocompatible composite films," *Macromolecular Chemistry and Physics* 218(15), article 1700130. <https://doi.org/10.1002/macp.201700130>
- Sutharsan, J., Boyer, C., and Zhao, J. (2022). "Development and characterization of chitosan edible film incorporated with epoxy-activated agarose," *JSFA Reports* 2(12), 613-622. <https://doi.org/10.1002/jsf2.91>
- Terzioğlu, P., and Sıcak, Y. (2021). "Citrus limon L. peel powder incorporated polyvinyl alcohol/corn starch antioxidant active films," *Iğdır Üniversitesi Fen Bilimleri Enstitüsü Dergisi* 11(2), 1311-1320. <https://doi.org/10.21597/jist.825560>
- Wang, H., Qian, J., and Ding, F. (2018). "Emerging chitosan-based films for food packaging applications," *Journal of agricultural and food chemistry* 66(2), 395-413. <https://doi.org/10.1021/acs.jafc.7b04528>
- Wang, H., Zhang, H., Yang, C., Fei, G., and Xie, P. (2024). "Preparation and properties of transparent, waterproof, and antibacterial composite film materials," *Journal of Applied Polymer Science* 141(18), article 55329. <https://doi.org/10.1002/app.55329>
- Wilpiszewska, K., Antosik, A. K., and Zdanowicz, M. (2019). "The effect of citric acid on physicochemical properties of hydrophilic carboxymethyl starch-based films,"

- Journal of Polymers and the Environment* 27(6), 1379-1387.
<https://doi.org/10.1007/s10924-019-01436-9>
- Wu, Z., Wu, J., Peng, T., Li, Y., Lin, D., Xing, B., Li, C., Yang, L., Zhang, L., Ma, R., *et al.* (2017). "Preparation and application of starch/polyvinyl alcohol/citric acid ternary blend antimicrobial functional food packaging films," *Polymers* 9(3), article 102.
<https://doi.org/10.3390/polym9030102>
- Xue, B., Niu, M., Yang, Y., Wei-ya, W., Peng, Y., Song, Y., and Liu, X. (2017). "Influence of graphitization degree of carbon microspheres on properties of pet flame retardant," *Polymer Engineering & Science* 58(8), 1399-1408.
<https://doi.org/10.1002/pen.24728>
- Xue, B., Niu, M., Yang, Y., Wei-ya, W., Peng, Y., Song, Y., and Liu, X. (2017). "Influence of graphitization degree of carbon microspheres on properties of pet flame retardant," *Polymer Engineering & Science* 58(8), 1399-1408.
<https://doi.org/10.1002/pen.24728>
- Yuan, C., Maitland, E., and Pascall, M. A. (2024). "The effect of citric acid concentrations on the mechanical, thermal, and structural properties of starch edible films," *International Journal of Food Science & Technology* 59(3), 1801-1813.
<https://doi.org/10.1111/ijfs.16933>
- Zafar, A., Khosa, M., Noor, A., Qayyum, S., and Saif, M. (2022). "Carboxymethyl cellulose/gelatin hydrogel films loaded with zinc oxide nanoparticles for sustainable food packaging applications," *Polymers* 14(23), article 5201.
<https://doi.org/10.3390/polym14235201>
- Zhang, H., Su, S., Liu, S., Qiao, C., Wang, E., Chen, H., Zhang, C., Yang, X., and Li, T. (2023). "Effects of chitosan and cellulose derivatives on sodium carboxymethyl cellulose-based films: A study from rheological properties of film-forming solutions," *Molecules* 28(13), article 5211. <https://doi.org/10.3390/molecules28135211>
- Zhang, Y., Huang, Y., Chen, Y., and Qin, Z. (2023). "Multifunctional and pH-responsive dialdehyde cellulose/polyvinyl alcohol composite film reinforced with curcumin," *Journal of Applied Polymer Science* 141(9), article 55035.
<https://doi.org/10.1002/app.55035>
- Zhang, Y., Yi, Z., Wei, L., Kong, L., and Wang, L. (2018). "Modified iron phosphate/polyvinyl alcohol composite film for controlled-release fertilisers," *RSC Advances* 8(32), 18146-18152. <https://doi.org/10.1039/c8ra01843j>

Article submitted: August 20, 2025; Peer review completed: September 18, 2025;
Revised version received and accepted: May 8, 2026; Published: May 20, 2026.
DOI: 10.15376/biores.21.3.6163-6178