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Atıflar

1. Shen, J., et al. “Sustainable layer-by-layer films using chitosan decorated with anthocyanins and carboxylated graphene oxide for food packaging applications.” Journal of Polymer Science (2025):1-14.
2. Li, P., et al. “Biosafe Cu-MOF loaded chitosan/gelatin-based multifunctional packaging film for monitoring shrimp freshness.” Food Hydrocolloids 160.1 (2025): 110721

Atıf 1

A.1 Yayının Ünvan Sayfası (Dergi)

A.1 Eserin Başlık Sayfası

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RESEARCH ARTICLE

Sustainable Layer-by-Layer Films Using Chitosan Decorated With Anthocyanins and Carboxylated Graphene Oxide for Food Packaging Applications

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Keywords: bio-based food packaging | carboxylated graphene oxide | chitosan | layer-by-layer self-assembly

ABSTRACT

The abuse of traditional plastic food packaging has caused severe food safety and environmental pollution, urgently necessitating the development of green and sustainable biodegradable packaging materials. Chitosan (CS) belongs to an inexpensive and readily available biopolymer; however, the poor mechanical properties and weak resistance to UV light and water make it unsuitable for the food packaging industry. In this study, a layer-by-layer (LBL) assembly of CS decorated with anthocyanins as a polycationic electrolyte and carboxylated graphene oxide (GO-COOH) as a polyanionic electrolyte is used to fabricate bio-based films with the aim of improving comprehensive properties of CS-based films. The results indicate that the LBL assembly extremely enhanced the UV-blocking ability (the average transmittance in the UV-B region drops to 1.68%), tensile strength (TS) (53.52 MPa), toughness (71.81%), thermal stability, water resistance, hydrophobicity (the water contact angle is up to 109.5°), and antioxidant activities of the films, attributed to hydrogen bonds among CS, anthocyanins, and GO-COOH and electrostatic interactions between GO-COOH and CS along with anthocyanins. In addition, the LBL films show exceptional advantages in the storage application for fresh-cut apples. In general, the study demonstrates that a novel and sustainable CS-based film can be fabricated by the LBL technique for food packaging.

1 | Introduction

Food packaging plays a critical role in various stages of food production, transportation, and consumption, directly impacting consumer health and food safety [1, 2]. Plastic packaging remains dominated by traditional petroleum-based plastics due to their low expense, good mechanical properties, and barrier properties [3, 4]. However, traditional plastics are nonrenewable and nonbiodegradable, offering limited functionality, which imposes significant environmental burdens and threatens human health [5]. Therefore, the development of novel biodegradable bio-based materials is urgent. Currently, the commonly used bio-based plastics primarily include polysaccharides (such as chitin, chitosan [CS], starch, cellulose) [6–9], proteins (such as collagen, gelati, soy protein) [10–12], and polymers synthesized from biological monomers, including polylactic acid, polycaprolactone, and polypropylene carbonate [13, 14].

Among these biopolymers, CS is the second-largest naturally renewable resource with a content second only to cellulose in nature and the only naturally occurring alkaline polysaccharide known, which can be obtained by deacetylating chitin [15, 16]. CS exhibits excellent film-forming properties, biodegradability, biocompatibility, and good gas barrier properties (O_2, CO_2), as well as antibacterial

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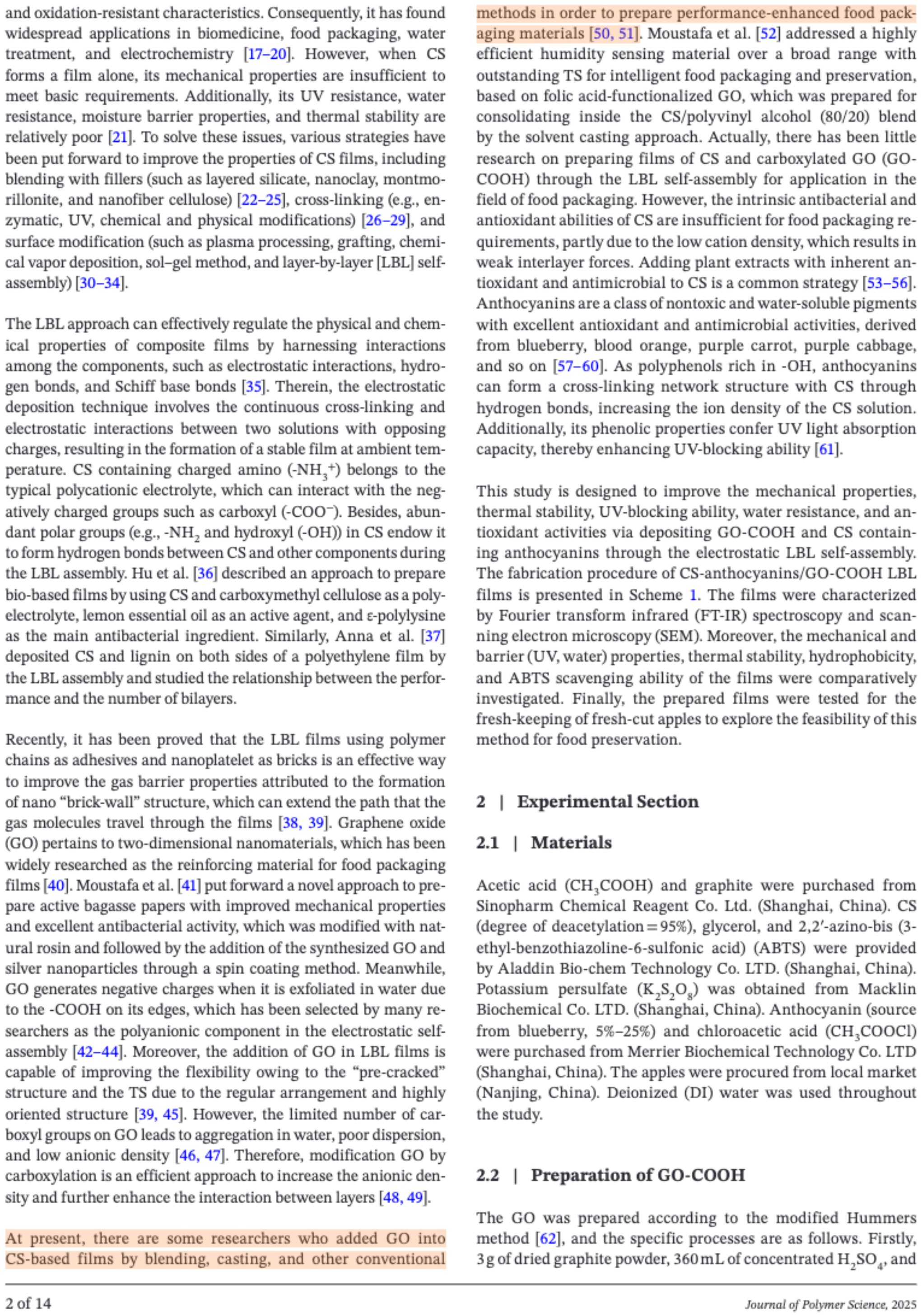
A.1 Eserde ilk atıf yapılan sayfa



and oxidation-resistant characteristics. Consequently, it has found widespread applications in biomedicine, food packaging, water treatment, and electrochemistry [17–20]. However, when CS forms a film alone, its mechanical properties are insufficient to meet basic requirements. Additionally, its UV resistance, water resistance, moisture barrier properties, and thermal stability are relatively poor [21]. To solve these issues, various strategies have been put forward to improve the properties of CS films, including blending with fillers (such as layered silicate, nanoclay, montmorillonite, and nanofiber cellulose) [22–25], cross-linking (e.g., enzymatic, UV, chemical and physical modifications) [26–29], and surface modification (such as plasma processing, grafting, chemical vapor deposition, sol–gel method, and layer-by-layer [LBL] self-assembly) [30–34].

The LBL approach can effectively regulate the physical and chemical properties of composite films by harnessing interactions among the components, such as electrostatic interactions, hydrogen bonds, and Schiff base bonds [35]. Therein, the electrostatic deposition technique involves the continuous cross-linking and electrostatic interactions between two solutions with opposing charges, resulting in the formation of a stable film at ambient temperature. CS containing charged amino (-NH_3^+) belongs to the typical polycationic electrolyte, which can interact with the negatively charged groups such as carboxyl (-COO^-). Besides, abundant polar groups (e.g., -NH_2 and hydroxyl (-OH)) in CS endow it to form hydrogen bonds between CS and other components during the LBL assembly. Hu et al. [36] described an approach to prepare bio-based films by using CS and carboxymethyl cellulose as a polyelectrolyte, lemon essential oil as an active agent, and ε-polylysine as the main antibacterial ingredient. Similarly, Anna et al. [37] deposited CS and lignin on both sides of a polyethylene film by the LBL assembly and studied the relationship between the performance and the number of bilayers.

Recently, it has been proved that the LBL films using polymer chains as adhesives and nanoplatelet as bricks is an effective way to improve the gas barrier properties attributed to the formation of nano "brick-wall" structure, which can extend the path that the gas molecules travel through the films [38, 39]. Graphene oxide (GO) pertains to two-dimensional nanomaterials, which has been widely researched as the reinforcing material for food packaging films [40]. Moustafa et al. [41] put forward a novel approach to prepare active bagasse papers with improved mechanical properties and excellent antibacterial activity, which was modified with natural rosin and followed by the addition of the synthesized GO and silver nanoparticles through a spin coating method. Meanwhile, GO generates negative charges when it is exfoliated in water due to the -COOH on its edges, which has been selected by many researchers as the polyanionic component in the electrostatic self-assembly [42–44]. Moreover, the addition of GO in LBL films is capable of improving the flexibility owing to the "pre-cracked" structure and the TS due to the regular arrangement and highly oriented structure [39, 45]. However, the limited number of carboxyl groups on GO leads to aggregation in water, poor dispersion, and low anionic density [46, 47]. Therefore, modification GO by carboxylation is an efficient approach to increase the anionic density and further enhance the interaction between layers [48, 49].

At present, there are some researchers who added GO into CS-based films by blending, casting, and other conventional methods in order to prepare performance-enhanced food packaging materials [50, 51]. Moustafa et al. [52] addressed a highly efficient humidity sensing material over a broad range with outstanding TS for intelligent food packaging and preservation, based on folic acid-functionalized GO, which was prepared for consolidating inside the CS/polyvinyl alcohol (80/20) blend by the solvent casting approach. Actually, there has been little research on preparing films of CS and carboxylated GO (GO-COOH) through the LBL self-assembly for application in the field of food packaging. However, the intrinsic antibacterial and antioxidant abilities of CS are insufficient for food packaging requirements, partly due to the low cation density, which results in weak interlayer forces. Adding plant extracts with inherent antioxidant and antimicrobial to CS is a common strategy [53–56]. Anthocyanins are a class of nontoxic and water-soluble pigments with excellent antioxidant and antimicrobial activities, derived from blueberry, blood orange, purple carrot, purple cabbage, and so on [57–60]. As polyphenols rich in -OH, anthocyanins can form a cross-linking network structure with CS through hydrogen bonds, increasing the ion density of the CS solution. Additionally, its phenolic properties confer UV light absorption capacity, thereby enhancing UV-blocking ability [61].

This study is designed to improve the mechanical properties, thermal stability, UV-blocking ability, water resistance, and antioxidant activities via depositing GO-COOH and CS containing anthocyanins through the electrostatic LBL self-assembly. The fabrication procedure of CS-anthocyanins/GO-COOH LBL films is presented in Scheme 1. The films were characterized by Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). Moreover, the mechanical and barrier (UV, water) properties, thermal stability, hydrophobicity, and ABTS scavenging ability of the films were comparatively investigated. Finally, the prepared films were tested for the fresh-keeping of fresh-cut apples to explore the feasibility of this method for food preservation.

2 | Experimental Section

2.1 | Materials

Acetic acid (CH_3COOH) and graphite were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). CS (degree of deacetylation = 95%), glycerol, and 2,2′-azino-bis (3-ethyl-benzothiazoline-6-sulfonic acid) (ABTS) were provided by Aladdin Bio-chem Technology Co. LTD. (Shanghai, China). Potassium persulfate ($K_2S_2O_8$) was obtained from Macklin Biochemical Co. LTD. (Shanghai, China). Anthocyanin (source from blueberry, 5%–25%) and chloroacetic acid (CH_3COOCl) were purchased from Merrier Biochemical Technology Co. LTD (Shanghai, China). The apples were procured from local market (Nanjing, China). Deionized (DI) water was used throughout the study.

2.2 | Preparation of GO-COOH

The GO was prepared according to the modified Hummers method [62], and the specific processes are as follows. Firstly, 3 g of dried graphite powder, 360 mL of concentrated H_2SO_4, and

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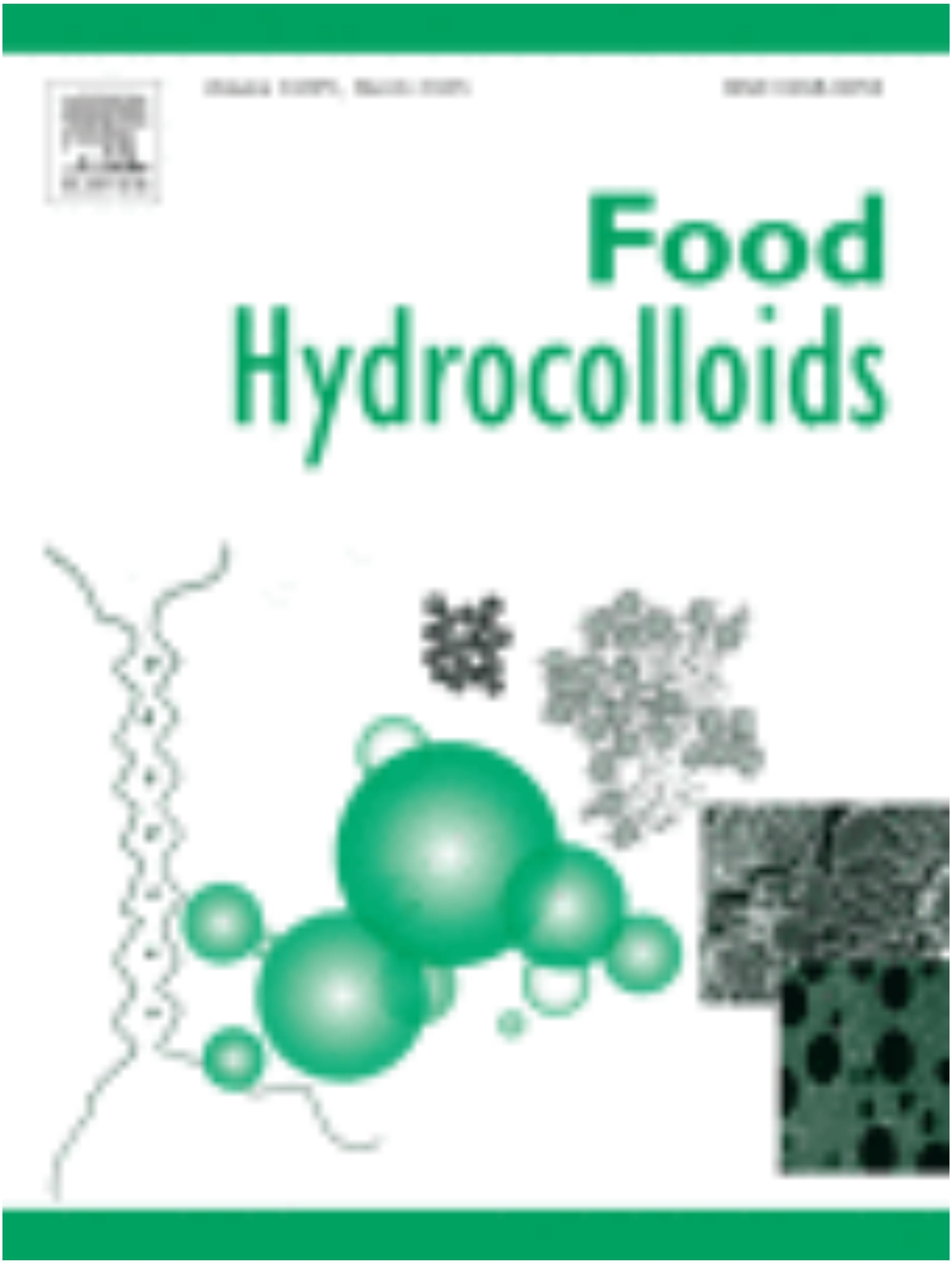
Atıf 2

A.2 Yayının Ünvan Sayfası (Dergi)



Food Hydrocolloids

A.2 Eserin Başlık Sayfası

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Biosafe Cu-MOF loaded chitosan/gelatin-based multifunctional packaging film for monitoring shrimp freshness

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ABSTRACT

As living standards improve, the demand for food freshness has gradually increased. Multifunctional packaging materials that monitor food freshness in real-time, delay spoilage, and are environmentally friendly have emerged as ideal solutions. This study synthesized an ammonia-sensitive copper-based metal-organic framework (Cu-MOF) and incorporated it into a matrix composed of chitosan (CS) and gelatin (Gel). The resulting film exhibits ammonia-sensitive color-changing properties, antibacterial activity, and excellent biodegradability. The effects of Cu-MOF incorporation on the structural, physical, and functional properties of the CS/Gel films were systematically evaluated. Results demonstrated that the Cu-MOF was uniformly distributed within the CS/Gel matrix, significantly enhancing the mechanical properties (tensile strength increased by 68.49%), oxygen/water vapor barrier properties, and UV-blocking capability of the films. Notably, the CS/Gel@Cu-MOF films exhibited excellent antibacterial performance, with sterilization rates of 94.2% against *Escherichia coli* and 99.6% against *Staphylococcus aureus*. Additionally, the films showed good biocompatibility, biodegradability, and a sensitive color response to ammonia. The films were successfully used to monitor shrimp freshness through color change, transitioning from light green to brown as spoilage occurred. These findings indicate that CS/Gel@Cu-MOF films have significant potential for real-time visual freshness monitoring in food packaging, contributing to reduced food safety risks and waste.

1. Introduction

With rising living standards, food safety has become a significant concern. Ensuring the quality and safety of meat products, a crucial part of daily diets, is essential (Hashim et al., 2024; W. Wang et al., 2024). However, during the transportation, storage, and distribution of meat products, spoilage frequently occurs due to microbial activity, enzymatic reactions, and moisture loss (Y. Feng et al., 2024; M. Wu, Xue, et al., 2024). The United Nations Environment Program's Food Waste Index Report (2021)estimates that 931 million tons of food were spoiled or wasted in the global food supply chain in 2019, accounting for approximately 17% of global food production (Karanth, Feng, Patra, & Pradhan, 2023). Traditional plastic packaging materials, such as polyethylene and polypropylene, are widely used for their low cost, good barrier properties, and safety. However, they only possess packaging barrier functions, limiting their further development in food packaging. Moreover, these materials contribute to environment pollution due to their poor biodegradability. To meet these challenges, it is necessary to develop a multifunctional food packaging film that is safe, retains freshness effectively, monitors it in real time, and is biodegradable.

In recent years, research has focused on developing smart packaging films for real-time food freshness monitoring. Typically, natural pigments with pH/ammonia sensitivity, such as curcumin, alizarin, and anthocyanin, are incorporated into biopolymer matrices to create smart packaging films for real-time freshness monitoring (J. Khan et al., 2024a, 2024b, 2024c; Y. Liu, Chen, et al., 2024; J. Zhang et al., 2019). When meat spoils, it releases alkaline gases, such as ammonia and trimethylamine, which cause these natural pigments to change color (Q. Zhang, Zhang, et al., 2024), indicating the freshness of the food. However, the disadvantages of natural pigments are the high cost of the source materials for extraction and the complex and unstable extraction process, which lead to increased costs of the film materials (Elhadef et al., 2024; S. Feng et al., 2023). Therefore, there is an urgent need to develop a pH/ammonia-sensitive antibacterial material for food packaging that is both easy to produce and stable. Combining new multifunctional gas adsorption materials, such as metal-organic frameworks

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A.2 Eserde ilk atıf yapılan sayfa

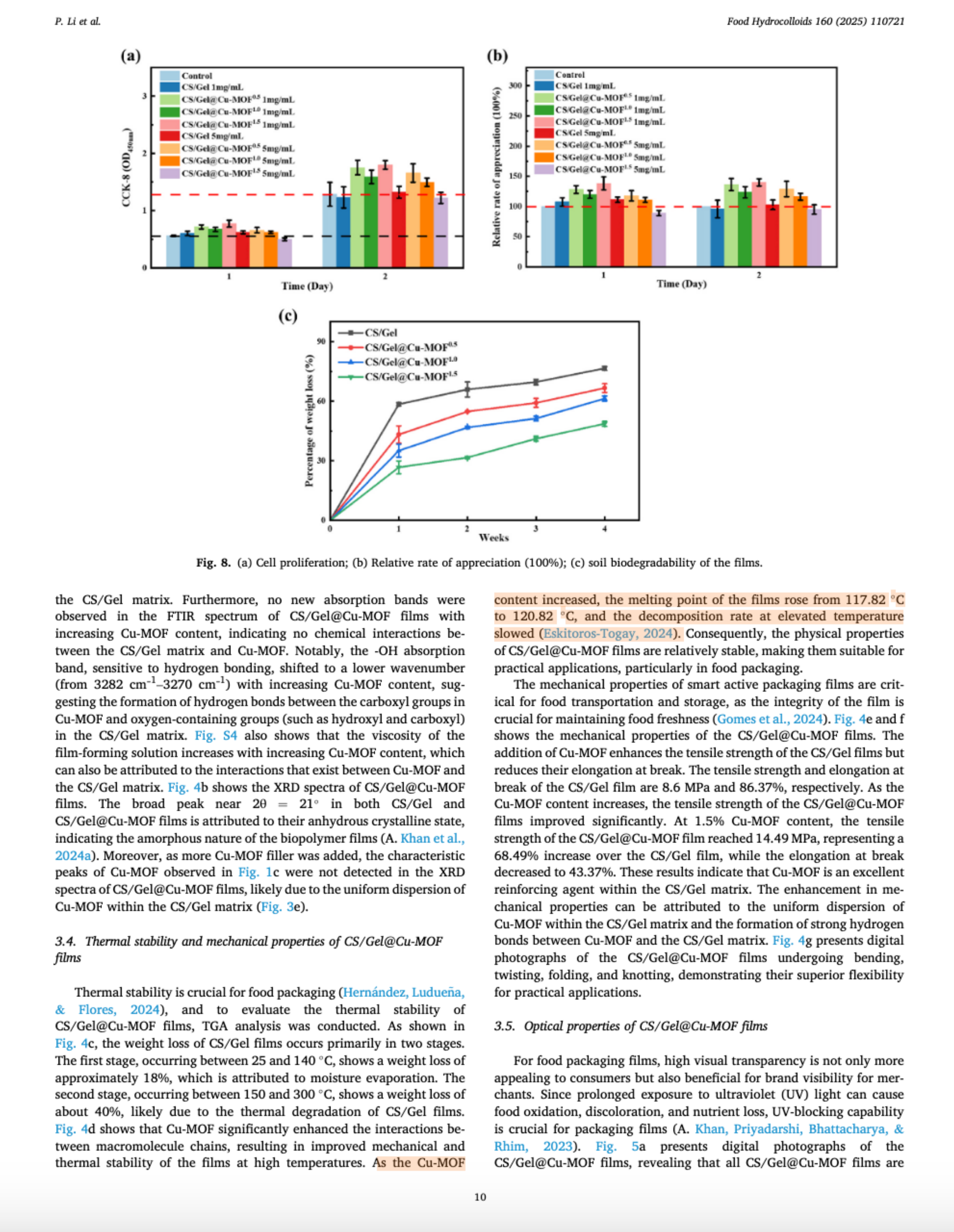

Fig. 8. (a) Cell proliferation; (b) Relative rate of appreciation (100%); (c) soil biodegradability of the films.

the CS/Gel matrix. Furthermore, no new absorption bands were observed in the FTIR spectrum of CS/Gel@Cu-MOF films with increasing Cu-MOF content, indicating no chemical interactions between the CS/Gel matrix and Cu-MOF. Notably, the -OH absorption band, sensitive to hydrogen bonding, shifted to a lower wavenumber (from 3282 cm^{-1}–3270 cm^{-1}) with increasing Cu-MOF content, suggesting the formation of hydrogen bonds between the carboxyl groups in Cu-MOF and oxygen-containing groups (such as hydroxyl and carboxyl) in the CS/Gel matrix. Fig. S4 also shows that the viscosity of the film-forming solution increases with increasing Cu-MOF content, which can also be attributed to the interactions that exist between Cu-MOF and the CS/Gel matrix. Fig. 4b shows the XRD spectra of CS/Gel@Cu-MOF films. The broad peak near $2\theta = 21^\circ$ in both CS/Gel and CS/Gel@Cu-MOF films is attributed to their anhydrous crystalline state, indicating the amorphous nature of the biopolymer films (A. Khan et al., 2024a). Moreover, as more Cu-MOF filler was added, the characteristic peaks of Cu-MOF observed in Fig. 1c were not detected in the XRD spectra of CS/Gel@Cu-MOF films, likely due to the uniform dispersion of Cu-MOF within the CS/Gel matrix (Fig. 3e).

3.4. *Thermal stability and mechanical properties of CS/Gel@Cu-MOF films*

Thermal stability is crucial for food packaging (Hernández, Ludueña, & Flores, 2024), and to evaluate the thermal stability of CS/Gel@Cu-MOF films, TGA analysis was conducted. As shown in Fig. 4c, the weight loss of CS/Gel films occurs primarily in two stages. The first stage, occurring between 25 and 140 °C, shows a weight loss of approximately 18%, which is attributed to moisture evaporation. The second stage, occurring between 150 and 300 °C, shows a weight loss of about 40%, likely due to the thermal degradation of CS/Gel films. Fig. 4d shows that Cu-MOF significantly enhanced the interactions between macromolecule chains, resulting in improved mechanical and thermal stability of the films at high temperatures. As the Cu-MOF content increased, the melting point of the films rose from 117.82 °C to 120.82 °C, and the decomposition rate at elevated temperature slowed (Eskitoros-Togay, 2024). Consequently, the physical properties of CS/Gel@Cu-MOF films are relatively stable, making them suitable for practical applications, particularly in food packaging.

The mechanical properties of smart active packaging films are critical for food transportation and storage, as the integrity of the film is crucial for maintaining food freshness (Gomes et al., 2024). Fig. 4e and f shows the mechanical properties of the CS/Gel@Cu-MOF films. The addition of Cu-MOF enhances the tensile strength of the CS/Gel films but reduces their elongation at break. The tensile strength and elongation at break of the CS/Gel film are 8.6 MPa and 86.37%, respectively. As the Cu-MOF content increases, the tensile strength of the CS/Gel@Cu-MOF films improved significantly. At 1.5% Cu-MOF content, the tensile strength of the CS/Gel@Cu-MOF film reached 14.49 MPa, representing a 68.49% increase over the CS/Gel film, while the elongation at break decreased to 43.37%. These results indicate that Cu-MOF is an excellent reinforcing agent within the CS/Gel matrix. The enhancement in mechanical properties can be attributed to the uniform dispersion of Cu-MOF within the CS/Gel matrix and the formation of strong hydrogen bonds between Cu-MOF and the CS/Gel matrix. Fig. 4g presents digital photographs of the CS/Gel@Cu-MOF films undergoing bending, twisting, folding, and knotting, demonstrating their superior flexibility for practical applications.

3.5. *Optical properties of CS/Gel@Cu-MOF films*

For food packaging films, high visual transparency is not only more appealing to consumers but also beneficial for brand visibility for merchants. Since prolonged exposure to ultraviolet (UV) light can cause food oxidation, discoloration, and nutrient loss, UV-blocking capability is crucial for packaging films (A. Khan, Priyadarshi, Bhattacharya, & Rhim, 2023). Fig. 5a presents digital photographs of the CS/Gel@Cu-MOF films, revealing that all CS/Gel@Cu-MOF films are

A.2 Kaynakça Sayfası

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodhyd.2024.110721.

Data availability

Data will be made available on request.

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