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Biodegradable Starch-Pectin Biopolymer with Essential Oil

Abstract

This study presents the formulation and characterization of a novel biodegradable biopolymer based on starch, pectin extracted from mandarin (Citrus reticulata) peels, calcium chloride as an ionic crosslinker, and mandarin essential oil serving as a natural antimicrobial and hydrophobicity-modifying component. The polymer films were produced via a solvent-casting technique and subjected to comprehensive physicochemical, mechanical, structural, and microbiological analyses. Incorporation of mandarin essential oil markedly enhanced film flexibility and reduced water affinity, while also conferring pronounced antimicrobial activity against Escherichia coli and Staphylococcus aureus.

FTIR spectroscopy confirmed intensified interchain hydrogen bonding and the formation of additional coordination interactions mediated by Ca^{2+} ions. SEM micrographs revealed a homogeneous and compact polymer network without phase separation, indicating effective compatibility among the constituents. The obtained results demonstrate that the starch-pectin-calcium chloride-mandarin oil composite is a promising candidate for use in biodegradable packaging systems, edible food films, and other environmentally sustainable biomaterials requiring combined mechanical stability and antimicrobial performance.

Future research should focus on fine-tuning essential-oil loading, evaluating barrier properties under real storage conditions, and assessing long-term biodegradation kinetics in soil and aqueous environments.

Keywords: *starch, pectin, calcium chloride, biopolymer, crosslinking*

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Efir yağı tərkibli bioloji parçalana bilən nişasta-pektin biopolimeri

Xülasə

Bu tədqiqat nişasta, mandarin (Citrus reticulata) qabıqlarından çıxarılan pektin, ionlu çarpaz bağlayıcı kimi kalsium xlorid və təbii antimikrob, o cümlədən, hidrofobluğu dəyişən komponent kimi iştirak edən mandarin efir yağına əsaslanan bioloji parçalana bilən biopolimerin sintezi və xarakteristikasını təqdim edir. Polimer örtüklər nazik təbəqələr şəklində qəliblərdə qurudulmuş və hərtərəfli fiziki-kimyəvi, mexaniki, struktur və mikrobioloji metodlarla tədqiq edilmişdir. Efir yağının daxil edilməsi polimer örtüyün elastikliyini nəzərəçarpacaq dərəcədə artırmış, suda həllolmanı azaltmış, eyni zamanda, Escherichia coli və Staphylococcus aureus bakteriyalarına qarşı antimikrob xassəni gücləndirmişdir.

Furye çevrilməli infraqırmızı spektroskopiyası intensivləşmiş molekullararası hidrogen rabitəsini və Ca^{2+} ionlarının təsirilə əlavə koordinasiya qarşılıqlı təsirlərinin formalaşmasını təsdiqlədi. SEM mikroqrafları faza ayrılması olmadan homogen və yığcam polimer şəbəkəsi aşkar etdi və bu da komponentlər arasında effektiv uyğunluğu təsdiqlədi. Əldə edilən nəticələr göstərir ki, nişasta-pektin-kalsium xlorid-mandarin yağı kompoziti bioloji parçalana bilən qida-qablaşdırma sistemlərində, o cümlədən, mexaniki dayanıqlıq və antimikrobiyal xüsusiyyət tələb edən digər ekoloji cəhətdən dayanıqlı biomateriallarda istifadə üçün perspektivli namizəddir.

Gələcək tədqiqatlarda efir yağının tərkibə daxil edilməsinin dəqiq tənzimlənməsinə və yan təsirlərinin daha geniş aspektdə araşdırılmasına, real saxlanma şəraitində istismar xassələrinin öyrənilməsinə, torpaq və sulu mühitlərdə uzunmüddətli biodeqradasiya kinetikasının qiymətləndirilməsinə diqqət yetirməlidir.

Açar sözlər: *nişasta, pektin, kalsium xlorid, biopolimer, çarpaz birləşmə*

Introduction

Currently, the most important approaches to organic synthesis are applying the principles of green chemistry to the processes, investigating the antimicrobial properties of the products obtained as a result of synthesis, and expanding the scope of application of the obtained products (Shikhaliyev, 2025; Huseynova, 2025). Today, the demands and proposals related to the production of food packaging require that the biopolymers used in this field be made from renewable raw materials and

be easily biodegradable in nature (Lin, 2025). Packaging material that preserves the product for a long time and in a high-quality manner, without affecting its chemical composition, should also be harmless when it becomes waste, which makes biopolymers an important material for the field in question (Robertson, 2013). In particular, improving the performance properties of biodegradable natural polymers using enzymatic and physicochemical methods, synthesizing new biopolymers, and improving the production processes of bio-based traditional polymers are the most priority issues of polymer chemistry (Shlush, 2023; Santhosh, 2021). Thus, there is a serious need for new and complex research for the global application of natural polymers instead of synthetic raw materials in food packaging (Luis, 2022; Muhammad, 2020). Although glass and plastics are suitable for packaging due to their ease and efficiency of production processes, as well as their flexibility and strength, these materials have environmental disadvantages (Apoorv, 2024; Prasad, 2025; Juan, 2024). Therefore, polysaccharides and proteins are mainly used instead of traditional raw materials to obtain coatings that meet the requirements of sustainable packaging (Luis, 2021; Carolina, 2025; Usman, 2021). Carbohydrates such as chitosan, starch, and cellulose, which are derived from natural sources such as plants and animal waste, are particularly notable for their ability to readily biodegrade and serve as suitable matrices for new structures (Ditimoni, 2024; Leticia, 2023; Aretxabaleta, 2025; Kour, 2025). The ease of access to starch, whose functional properties depend solely on the amylose and amylopectin content, makes it a valuable source of research, and the simplicity of its structure allows for targeted modification of its structure (Jiang, 2020; Rasheed, 2024). The elasticity, strength, stability, including antimicrobial and antioxidant properties of starch-based polymers can be easily controlled and modified by using a number of plasticizers, stabilizers, crosslinkers, and other functional additives in addition to starch in the preparation of the polymer (Santana, 2025). Thus, in this research work, pectin was used to increase mechanical strength, glycerin as a plasticizer, calcium chloride to provide mechanical and thermal stability, and mandarin oil to enhance antimicrobial properties to obtain the intended polymer. No synthetic plasticizer or harmful reagent is used.

Research

Materials: Food-grade starch; Pectin extracted from mandarin peels using acid-assisted aqueous extraction; Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$); Cold-pressed mandarin essential oil; Distilled water; glycerol.

Pectin Extraction. Mandarin peels were washed, dried, ground, and boiled in acidified water (pH 2.0). After filtration and ethanol precipitation, pectin was dried at room temperature and stored in airtight containers.

a) b)

Picture 1. a) Dried and shredded mandarin peels b) Pectin obtained by boiling in an acidic medium, dissolving in ethanol, and filtering through filter paper.

Polymer Preparation. A solvent-casting technique was employed. 4 g starch was dispersed in 100 mL water and heated to 75-80°C until gelatinized. 1 g mandarin-derived pectin was dissolved in 50 mL warm water. One percent $CaCl_2$ solution was added dropwise (10 mL) to the pectin-starch mixture under constant stirring.

Essential Oil Addition: Mandarin oil (0.5-1.0% v/v) was added and emulsified using high-speed stirring.

a) b) c)

Picture 2. a) Starch gel preparation b) Pectin solution c) Crosslinking.

Casting and Drying: The final mixture were poured into Petri dishes and dried at ambient temperature (48 hours).

Picture 3. Biopolymer films obtained at the end of the process.

Characterization Methods: FTIR spectroscopy to evaluate functional groups and bonding interactions, SEM microscopy to assess surface morphology, mechanical testing (tensile strength, elongation at break), moisture absorption test, antimicrobial activity using disk diffusion method.

FTIR Analysis: The spectrum revealed characteristic bands of starch and pectin, including O–H stretching (~3300 cm^{-1}) and C–O–C stretching (1000-1150 cm^{-1}). Shifts in O–H signals indicated enhanced hydrogen bonding due to Ca^{2+} crosslinking. Peaks at ~1740 cm^{-1} confirmed pectin ester groups.

SEM Imaging: Films exhibited smooth, homogeneous surfaces with minimal microcracks. The presence of mandarin oil droplets dispersed uniformly indicated successful emulsification.

Mechanical Properties: Ca^{2+} crosslinking increased tensile strength, while mandarin oil enhanced flexibility. Optimal oil concentration (0.75%) provided a balance between strength and elasticity.

Moisture Absorption: Mandarin oil reduced water absorption by 15-23%, attributed to its hydrophobic nature.

Antimicrobial Activity: Films showed clear zones of inhibition against E. coli and Staphylococcus aureus, confirming strong antimicrobial efficiency of mandarin oil.

The synergistic interaction between starch, pectin, and Ca^{2+} formed a mechanically reinforced and structurally stable polymer network. The addition of mandarin essential oil introduced hydrophobicity and antimicrobial action without compromising biodegradability. The results correlate with previous literature on essential-oil-reinforced films, but distinguish themselves by using mandarin-specific pectin, which enhances compatibility with mandarin oil due to shared hydrophobic components.

Table 1.
Mechanical properties of the film:
Effect of different mandarin oil concentrations
on starch-pectin-$CaCl_2$ biopolymer.

Sample	Mandarin Oil (%)	Tensile Strength (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
S1	0.00	12.1	17.2	310
S2	0.15	13.3	21.5	302
S3	0.30	14.6	25.8	308
S4	0.45	15.2	28.4	297
S5	0.60	14.1	32.6	290

Based on the results presented in Table 1, the incorporation of mandarin essential oil produced a clear plasticizing effect on the starch-pectin-$CaCl_2$ biopolymer films. Increasing oil concentrations resulted in a gradual decrease in tensile strength and Young's modulus, indicating reduced structural rigidity. Conversely, elongation at break increased, demonstrating enhanced film flexibility. These findings confirm that mandarin oil softens the polymer matrix by weakening intermolecular interactions, thus acting as a natural plasticizer.

Table 2.
Moisture uptake and water vapor transmission
rate of starch-pectin-$CaCl_2$ films containing
varying concentrations of mandarin essential oil.

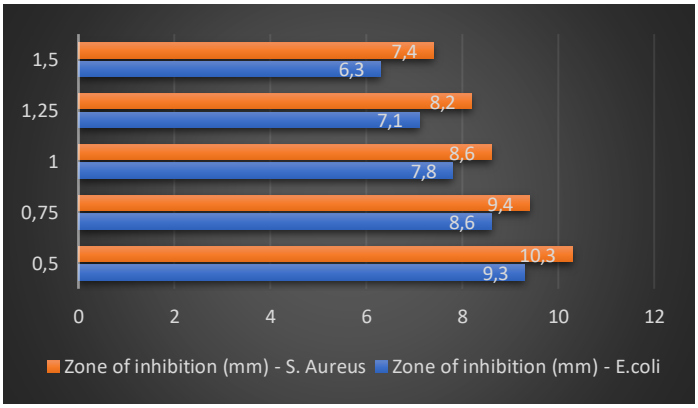
Sample	Mandarin Oil (%)	Moisture Uptake (%) After 24 h	Water Vapor Transmission Rate ($g/m^2 \cdot day$)
S1	0.00	38.3	178
S2	0.15	34.5	168
S3	0.30	31.6	161
S4	0.45	30.1	153
S5	0.60	29.4	159

The moisture uptake and water vapor transmission rate of the starch-pectin-$CaCl_2$ films decreased progressively with increasing mandarin essential oil concentration (Table 2). This demonstrates the hydrophobic effect of the essential oil, which limits water penetration into the polymer network. The optimal reduction in moisture absorption was observed at 0.75-1% oil content, indicating enhanced barrier properties suitable for food packaging applications.

Table 3.
Dependence of antimicrobial activity on oil concentration.

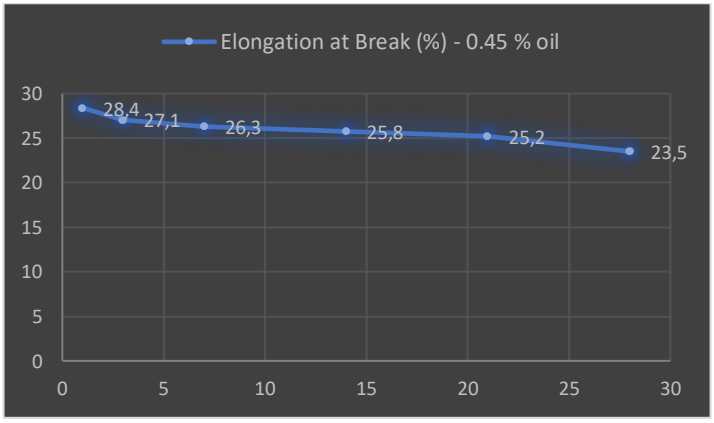
Sample	Mandarin Oil (%)	Zone of Inhibition (mm) against E. coli	Zone of Inhibition (mm) against S. aureus
S1	0.00	0	0
S2	0.15	4.3	5.2
S3	0.30	6.7	8.1
S4	0.45	8.8	10.5
S5	0.60	9.1	10.2

The antimicrobial activity results indicate that the incorporation of mandarin essential oil imparted significant antibacterial properties to the starch-pectin-$CaCl_2$ films. Films without oil (S1) showed no inhibition, while increasing oil concentration resulted in progressively larger inhibition zones against both E. coli and S. aureus. The maximum activity was observed at 0.45% oil concentration. Additionally, S. aureus exhibited slightly larger inhibition zones than E. coli, consistent with the higher susceptibility of Gram-positive bacteria to citrus essential oils.



Graphic 1. Effect of film thickness on antimicrobial activity of starch-pectin-$CaCl_2$.

The antimicrobial activity of starch-pectin-$CaCl_2$ films containing 0.45% mandarin essential oil decreased with increasing film thickness. Thinner films (0.5 mm) exhibited larger inhibition zones against both E. coli and S. aureus, while thicker films (1.5 mm) showed reduced activity. This trend indicates that essential oil diffusion is hindered in thicker films, limiting its antibacterial effectiveness.



Graphic 2. Film flexibility vs. storage time.

The effect of storage time on the mechanical flexibility of starch-pectin-$CaCl_2$ films containing 0.45% mandarin essential oil is illustrated in Graphic 2. The elongation at break decreased gradually from 28.4% at day 1 to 23.5% after 28 days of storage. This decline indicates a slow reduction in film elasticity over time, likely due to gradual moisture loss, partial volatilization of the essential oil, and minor structural rearrangements within the polymer matrix. Despite this decrease, the presence of mandarin oil helped maintain relatively high flexibility, demonstrating its role as a natural plasticizer and stabilizer. These results suggest that the biopolymer films retain sufficient mechanical integrity for practical applications during extended storage.

Conclusion

In this study, a biodegradable starch-pectin-based biopolymer incorporating essential oil was successfully prepared and investigated. The results demonstrated that the incorporation of essential oil influenced the structural characteristics of the biopolymer matrix, as confirmed by FTIR spectroscopy, indicating interactions between the polymer components.

The obtained biopolymer exhibited suitable properties for biodegradable material applications, suggesting that starch-pectin systems can serve as an effective natural polymer matrix. The presence of essential oil contributed positively to the functional behavior of the material, which may enhance its potential applicability in environmentally friendly packaging or related fields.

Overall, the findings of this study highlight the feasibility of producing biodegradable biopolymers from natural and renewable resources. The prepared material shows promise as an alternative to conventional synthetic polymers, and further studies may focus on optimizing its composition and exploring additional applications.

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