

Research Article

Novel Karaya Gum Derivatives Produced by Alkaline Hydrolysis and Periodate Oxidation for Active Packaging with Cinnamaldehyde

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This study aims to produce novel derivatives of karaya gum using chemical modification and then apply them for active packaging with cinnamaldehyde as the main active component. Native karaya gum (NKG) was hydrolyzed using sodium hydroxide to yield hydrolyzed karaya gum (HKG), which then was oxidized using sodium periodate to yield hydrolyzed-oxidized karaya gum (HOKG). For comparison, NKG was also directly oxidized using sodium periodate to produce oxidized karaya gum (OKG). FTIR spectra confirmed the removal of acetyl groups after alkaline hydrolysis and the formation of carbonyl groups with subsequent formation of hemiacetal and acetal structures after periodate oxidation. The alkaline hydrolysis and the periodate oxidation resulted in opposite effects on the hydrophilicity of the gum: hydrolysis increased solubility, moisture uptake, and viscosity, while periodate oxidation decreased these properties. We then produced films from corn starch and these gums (5% *w/w* gum/starch) and properties of the films were studied. Hydrolysis of KG resulted in higher tensile strength, higher transparency but lower puncture strength and antifungal activity against of the films, while periodate oxidation exerted the opposite effects. The incorporation of 5% cinnamaldehyde (*w/w* of starch) exerted strong antifungal and antibacterial effects on the films against *Colletotrichum gloeosporioides* and *Escherichia coli*, which are useful in active packaging. The active packages based on the novel derivatives of KG can find applications in the agricultural, food, and pharmaceutical industries.

1. Introduction

Karaya gum is produced from *Sterculia* trees in the form of dried tears. Native karaya gum (NKG) is a natural branched, partially acetylated rhamnogalacturonan-type polysaccharide with molecular masses of 9-16 MDa [1]. Its main structure is made of α -D-galacturonic acid and α -L-rhamnose units bonded alternately by 1 \rightarrow 2 and 1 \rightarrow 4 linkages (Figure 1). There are two types of sidechains on the main structure: (i) β -D-glucuronic acid sidechains linked by 1 \rightarrow 3-bonds to the galacturonic acid and (ii) β -D-galactose sidechains linked by 1 \rightarrow 4-bonds to the rhamnose part

and by 1 \rightarrow 2-bonds to the galacturonic part. Neutral sugars rhamnose and galactose compose 55-60% of NKG, while galacturonic and glucuronic acid sugars compose 37-40%, and acetyl groups—about 8% [2]. NKG exists in the form of calcium and magnesium salts of the sugar acids. The acetyl groups and the 2+ cations make NKG insoluble and highly swellable in water [1]. Alkaline hydrolysis using ammonia or alkali metal hydroxides is a simple way to remove the acetyl groups and precipitate the 2+ cations to increase the solubility of KG and widen its applications [3]. The structure of NKG and hydrolyzed karaya gum (HKG) is presented in Figure 1.

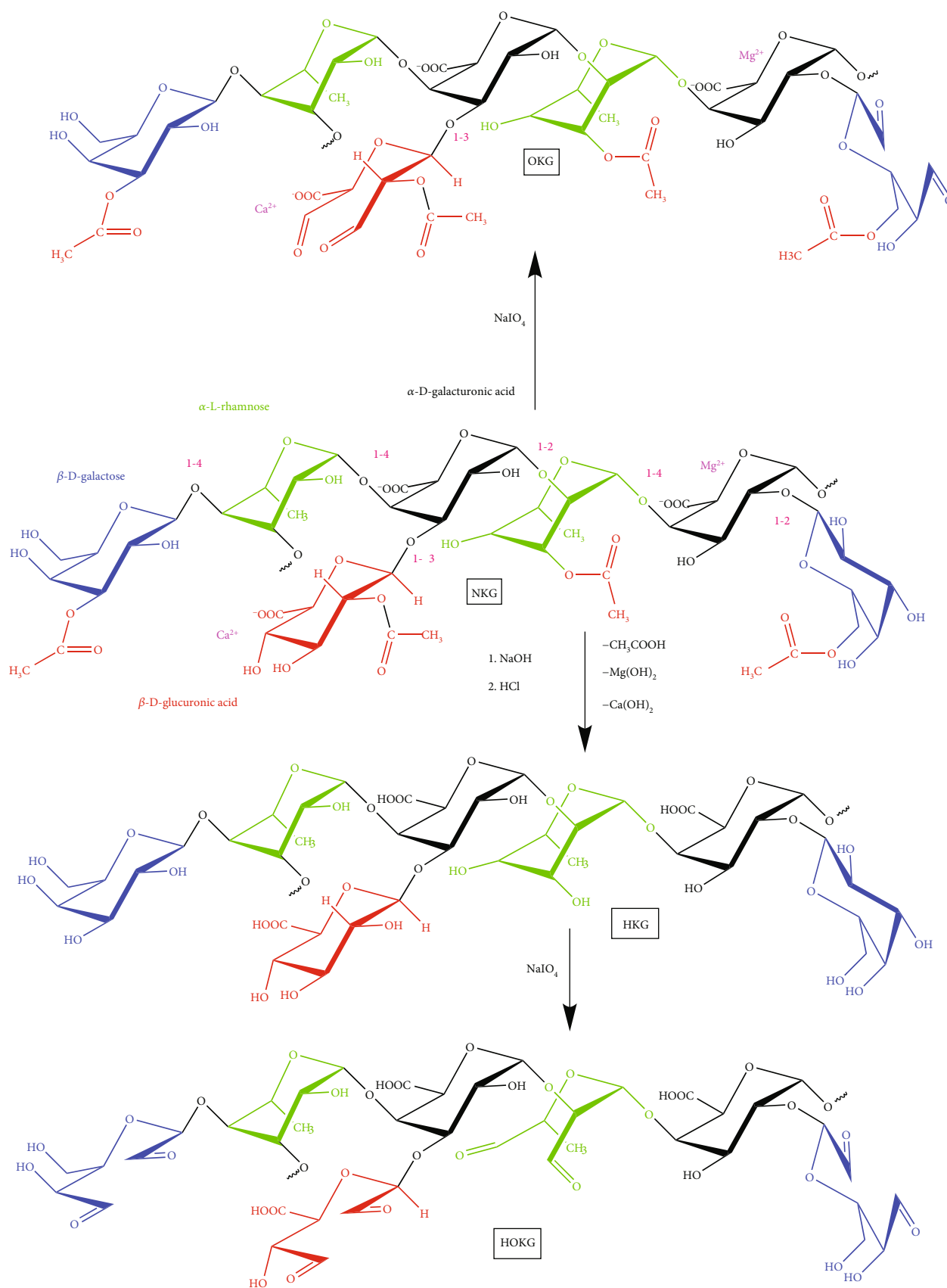


FIGURE 1: Structures of native (NKG), hydrolyzed (HKG), periodate oxidized (OKG), and hydrolyzed-periodate oxidized (HOKG) karaya gums.

Periodate oxidation is a popular method in structural carbohydrate chemistry. In this method, the periodate ion selectively oxidizes 1,2-dihydroxyl groups to paired aldehyde groups without significant side reactions. Sodium periodate NaIO_4 is the most common reagent and has been used to oxidize several polysaccharides such as starch [4, 5], cellulose [6, 7], alginate [8, 9], chitosan [10, 11], and hyaluronic acid [12, 13]. The dialdehyde derivatives of these polysaccharides are commonly used as a crosslinker with other polymers in films and gels. To the best of our knowledge, there was no study using periodate to oxidize karaya gum. Therefore, we used the periodate oxidation to modify the structure of NKG and HKG to convert the vicinal hydroxyl groups to carbonyl groups and obtained oxidized karaya gum (OKG) and hydrolyzed-oxidized karaya gum (HOKG), respectively (Figure 1). Compared to the instinct carboxyl and hydroxyl groups in KG and HKG, the carbonyl groups can participate in more chemical reactions, such as nucleophile addition with a wide range of nucleophiles, oxidation-reduction, and bisulphite reaction. Therefore, OKG and HOKG can be potential intermediates to several derivatives of KG.

This study intended to produce novel derivatives of KG and apply them in active food packaging. Active packaging is a growing research interest in producing packages that have active functions such as antibacterial, antifungal, and antioxidant activities by releasing active components to protect and prolong the shelf life of the packaged food [14]. The active components should be natural, such as essential oils, plant extracts, or compounds isolated from them. Cinnamaldehyde is a yellowish oil extracted from cinnamon oils and is commonly used to give a cinnamon flavour to food, cosmetics, medicines, and perfumes [15]. Cinnamaldehyde inhibits bacterial growth [16], molds [15], and insects [17] by inhibiting ATPase synthesis [18] and cell wall biosyntheses [19] and altering cell wall structure and integrity [20]. Cinnamaldehyde has been incorporated into several natural polymeric films from natural sources such as starch [21], gliadin [22], soy protein isolate [23], and synthetic polymers [24, 25] for antifungal and antibacterial applications.

In this study, after producing hydrolyzed and oxidized KG and incorporating them into starch films, we also added 5% cinnamaldehyde and tested the antibacterial, antifungal, and antioxidant properties of the composite films.

2. Experimental Methods

2.1. Chemicals and Materials. Karaya gum and corn starch were purchased from Xuan Hong Ltd. (Vietnam). Analytical-grade chemicals including NaOH, HCl, NaIO_4 , $\text{NH}_2\text{OH}\cdot\text{HCl}$, and cinnamaldehyde were purchased from Xilong Ltd. (China), 95% ethanol from Chemsol (Vietnam).

2.2. Alkaline Hydrolysis of Karaya Gum. HKG was prepared according to a published procedure [3]. Two grams of NKG were left swelling in 100 mL of distilled water for 24 h. The swelled gum was hydrolyzed and solubilized by adding 33.3 mL of 1 M NaOH solution and stirring the mixture for 30 min. The excess NaOH was then neutralized using 1 M HCl solution until the suspension pH reached approximately

3. To precipitate NKG, 95% ethanol was added to the solution with a 3 : 1 v/v ratio. The precipitated gum was collected using a stirring rod, washed twice using 75% ethanol, dried at 50°C for 24 h, and ground to powder.

2.3. Periodate Oxidation of NKG and HKG. Dialdehyde derivatives of NKG and HKG were prepared based on a method for carboxymethyl cellulose [26]. Each type of gum (1 g) was stirred in 20 mL of distilled water for 24 h. Then, 2 mL of 0.11 g/mL NaIO_4 solution was added, and the pH was adjusted to 3 using 1 M HCl solution. The mixture was stirred for 4 h at room temperature in the dark. The oxidized product was precipitated by adding 95% ethanol with a 3 : 1 v/v ratio. The filtered precipitate was then washed using 75% ethanol until the washing water did not change the color of a solution containing KI and soluble starch. The filtered solid was dried at 50°C for 8 h, ground to powder, and stored for further uses.

2.4. Characterization of Gum Powders

2.4.1. Content of Carbonyl Groups [5]. Each oxidized gum powder (0.2 g) was dispersed in 25 mL of 0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ solution (pH = 5.0) by stirring for 15 min. The mixture was then heated in a water bath at 50°C under stirring and continuously titrated with a standard 0.100 M NaOH solution to maintain the solution pH at 5.0. The same procedure was conducted for the NKG as the control.

The mass percentage (%) of carbonyl groups in the oxidized gum was calculated using the following formula:

$$\% \text{CHO} = \frac{29 \times 0.1 \times (V_s - V_c)}{0.2 \times 1000} \times 100 = 14.5 \times (V_s - V_c), \quad (1)$$

where V_s and V_c (mL) were the volumes of the standard 0.100 M NaOH solution used to titrate the oxidized gum and the NKG control, respectively.

2.4.2. FTIR Spectra. The dried gum powders were pressed on an attenuated total reflection (ATR) support of an FT/IR-4700 spectrophotometer (Jasco, Japan). The spectra were scanned from 400 to 4000 cm^{-1} with a resolution of 2 cm^{-1} .

2.4.3. Solubility. An excess amount of each gum was stirred for 24 h in 100 mL of distilled water for complete solubilization. The mixture was then centrifuged at 3000 rpm for 15 min. The clear supernatant was poured on a Petri dish, weighed, and dried at 105°C for 24 h to obtain the dissolved gum portion. The procedure was triplicated for each gum. The solubility was calculated using the following formula:

$$S\% = \frac{m_{\text{solid}}}{m_{\text{soln}}} \times 100, \quad (2)$$

where m_{soln} was the mass of clear supernatant, and m_{solid} was the mass of remaining solid after complete drying of the supernatant.

2.4.4. Relative Viscosity. The relative viscosity of gum solutions (concentrations from 0.025 to 0.100 g/L) was determined with an Ostwald viscosimeter ($\varnothing = 0.3$ mm) and using distilled water as the reference.

2.4.5. Moisture Uptake. Each dried gum powder was spread on a Petri dish and put in a closed container with 75% relative humidity (by a saturated NaCl solution put inside). The mass of the Petri dish with gum was recorded every hour for 2 days to calculate the moisture of the gum over time.

2.5. Film Preparation. Starch-gum films were prepared based on a published procedure [27]. A dispersion containing 0.1 g of gum and 20 mL water was prepared and left for 24 h. Two grams of corn starch, 0.6 g glycerol, and a predetermined amount of cinnamaldehyde were dispersed in 40 mL of distilled water. The mixture was heated to 95°C and kept for 20 min for complete gelatinization of starch. The swelled gum dispersion was then added to the gelatinized starch solution. This film-forming mixture was stirred for 10 min and then poured into Petri dishes and left 48 h for drying at room temperature. The dried films were then peeled off the Petri dishes and conditioned in a vessel containing a saturated NaCl solution (75% relative humidity) at least 48 h before film characterizations.

2.6. Film Characterization. The thickness of each film was measured at 10 positions using a digital caliper (Mitutoyo, Japan) with an accuracy of 0.01 mm.

2.6.1. Texture Analysis. Puncture and tensile tests for the films were conducted using a CT3 Texture Analyzer (Brookfield, USA) according to a published study [28]. For puncture tests, each film was cut to 40 × 40 mm strips and conditioned in the 75% RH container for at least 48 h before the test. Each strip was gripped and punctured perpendicularly using a 4.0 mm probe with a 1.0 mm/s speed until completely penetrated (Figure 2(a)).

The puncturing penetration stress (MPa) was calculated using the following formula:

$$P = \frac{F}{A}, \quad (3)$$

where F is the maximum resistance force (N), and $A = 12.56$ mm² is the contact area between the film and the penetration probe.

For tensile tests, the films were cut to 120 × 15 mm strips and glued and wrapped around the 17.8 mm probes at an initial distance of 45 mm (Figure 2(b)). The upper probe was then moved upward at a 1.0 mm/s speed until the film is completely broken.

The tensile strength of the films (N/mm²) was calculated using the following formula:

$$P = \frac{F}{S}, \quad (4)$$

where F was the maximum resistance force (N), and S was the initial cross-section area (mm²).

2.6.2. Moisture, Water Uptake, and Solubility of Films. The moisture, water uptake, and solubility of the films were determined based on a published procedure with minor modifications [29]. The films were cut into 30 × 30 mm pieces, weighed (m_0), dried at 105°C for 24 h, and weighed again (m_1). The dried films were then immersed in 20 mL of distilled water for 24 h, dried using a filter paper, and weighed (m_2). The films were subsequently dried at 105°C for 24 h and weighed again (m_3). The moisture content (MC, %), water uptake (WU, %), and solubility in water (S, %) were calculated using the following formulae:

$$\begin{aligned} \text{MC} &= \frac{m_0 - m_1}{m_0} \times 100 (\%), \\ \text{WU} &= \frac{m_2 - m_3}{m_3} \times 100 (\%), \\ \text{S} &= \frac{m_1 - m_3}{m_1} \times 100 (\%). \end{aligned} \quad (5)$$

Water vapor permeability (WVP) of films was determined according to method ASTM E-96.

2.6.3. Antibacterial and Antifungal Activities. Antibacterial and antifungal activities of the films were evaluated based on the disc diffusion method [30]. The bacteria *Escherichia coli* and the mold *Colletotrichum gloeosporioides* were supplied by the Vietnam Type Culture Collection. The culture medium contained 2% agar and 2% nutrient broth. For antifungal tests, the antibiotic chloramphenicol (8 ppm) was used to inhibit the growth of bacteria. The medium was autoclaved, left cooling, and then poured into Petri dishes. When the medium was cooled to room temperature, 100 μL of the microorganism suspension (5 log cfu/mL of *E. coli* or mycelia of *C. gloeosporioides*) was spread onto the medium surface. The films were cut into 10 mm diameter circles and put on the dry contaminated agar surface. The growth of microorganisms was then observed every 4, 48, and 52 h.

2.7. Statistical Analysis. All experiments were triplicated, and the results were analyzed with the one-way analysis of variance (ANOVA) using SPSS software. The differences between mean values were evaluated using Duncan's multiple range test with a 95% significance level.

3. Results and Discussion

3.1. Characterization of Native and Modified Karaya Gum Powders

3.1.1. Carbonyl Content. The carbonyl contents in OKG (5.12 ± 0.44%) and HOKG (4.01 ± 0.33%) determined by titration with hydroxylamine were significantly different ($p < 0.05$). HOKG had a lower free carbonyl content probably because it had a higher content of hydroxyl groups, hence, more readily reacted with carbonyl groups to form hemiacetal and acetal groups and could not react with hydroxylamine [31].

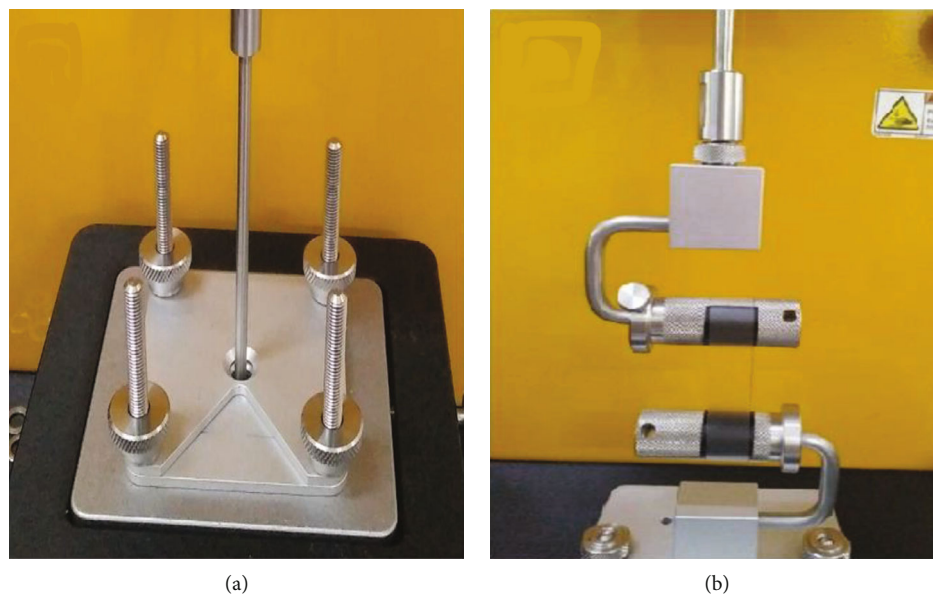


FIGURE 2: Experimental setups for the puncture (a) and tensile (b) strength tests.

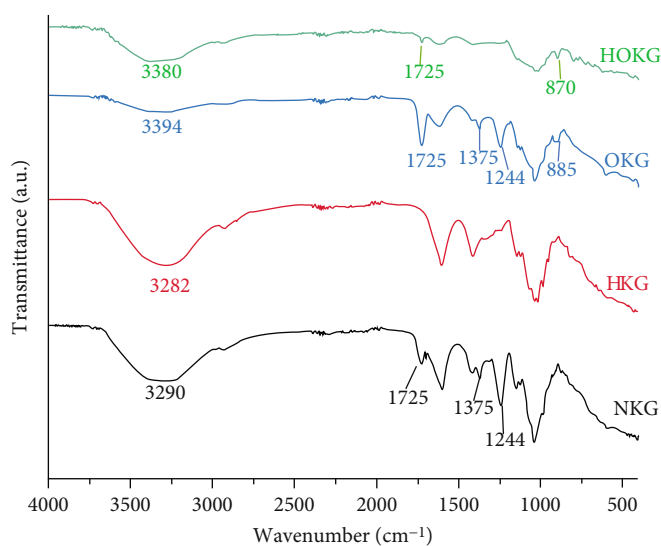


FIGURE 3: FTIR spectra of KG samples.

TABLE 1: Some characteristic peaks in FTIR spectra of the KG types.

| Wavenumber (cm^{-1}) | 3282-3394 | 1725, 1244 | 1375 | 885, 887 |
|---------------------------------|-----------|--------------------|------------|------------------|
| Bond | -OH | Carbonyl/ester C=O | Methyl C-H | (Hemi)acetal C-O |

3.1.2. FTIR Spectra. The FTIR spectra of the four KG types are presented in Figure 3, and their major peaks are listed in Table 1.

The broad peaks at $3282\text{--}3394\text{ cm}^{-1}$ in FTIR spectra of the native and modified KG characterize hydroxyl groups

in KG structure and the absorbed moisture (Figure 3). This peak for oxidized KG was significantly lower, indicating a low content of hydroxyl in its structure. The reason for this low hydroxyl content is the peroxidation that converted the turned adjacent hydroxyl groups to carbonyl groups, which

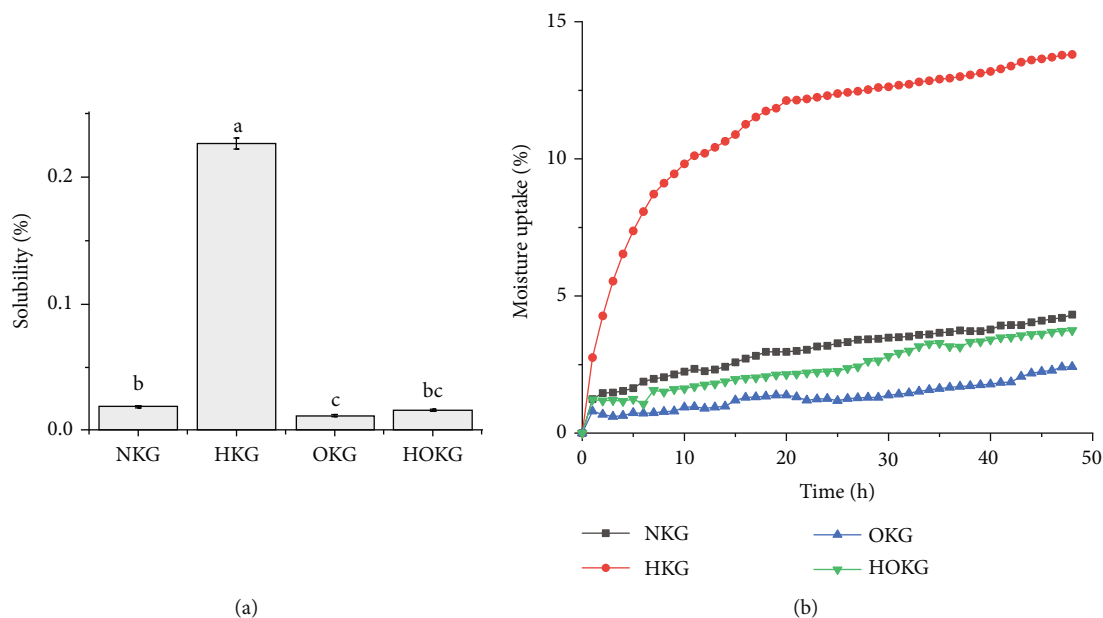


FIGURE 4: Solubility (a) and moisture uptake (b) of KG powders.

could further react with other hydroxyl groups in the KG backbone to form hemiacetal and acetal.

The peaks of C=O bond at 1725 cm^{-1} and 1244 cm^{-1} and methyl C-H at 1375 cm^{-1} groups, which were present in NKG spectrum, disappeared in the spectrum of HKG due to the removal of acetyl groups by alkaline hydrolysis [3]. After periodate oxidation of HKG, the 1725 cm^{-1} peak appeared again in the spectrum of OKG and HOKG due to the formation of carbonyl groups [32]. Moreover, the intensity of this 1725 cm^{-1} peak was significantly lower for HOKG because HOKG has more hydroxyl groups due to the hydrolysis step, thus, facilitating the formation of hemiacetal and acetal groups and lowering the number of free carbonyl groups. The peaks of hemiacetal groups were at 885 cm^{-1} for OKG and 887 cm^{-1} for HOKG [26].

3.1.3. Solubility, Moisture Uptake, and Relative Viscosity.

Because of the presence of acetyl groups and $\text{Mg}^{2+}/\text{Ca}^{2+}$ cations in the structure, NKG has a low aqueous solubility of 0.018% (Figure 4(a)), which is closed to a reported value of 0.02% [3]. After alkaline hydrolysis that replaced the hydrophobic acetyl groups with the hydrophilic hydroxyl ones and 2+ cations with Na^+ , the solubility of HKG increased 10-fold compared to NKG [26]. OKG has a lower solubility (0.011%) compared to NKG because some hydroxyl groups were converted to the carbonyl groups. Interestingly, HOKG has a solubility comparable with that of NKG and significantly lower than that of HKG. This result indicates that the conversion of hydroxyl to carbonyl groups and the formation of hemiacetal and acetal strongly decreased the hydroxyl content and hence lowered the solubility of the gum.

The order of moisture uptake by the gum powders was **HKG** > **NKG** > **HOKG** > **OKG** (Figure 4(b)), which is the same as the order of the aqueous solubility. The explanation of this order remained the same with that for solubility because these two properties are determined by hydrophilicity.

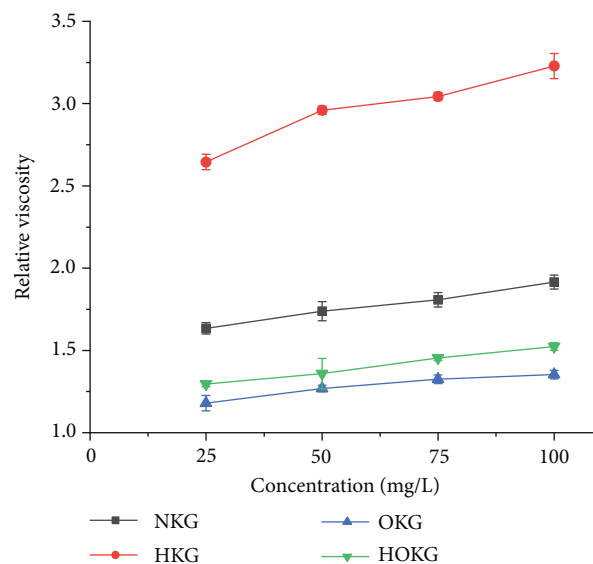


FIGURE 5: Relative viscosity of KG solutions at room temperature.

The order of relative viscosity of KG samples was **HKG** > **NKG** > **HOKG** > **OKG** (Figure 5). This order is the same as the order of aqueous solubility. HKG solution has a high viscosity due to the high content of hydroxyl groups, which increased the hydrogen bonds between its molecules in solution. This result is in line with another report that the viscosity of KG solution increased with higher concentration, lower temperature, and higher deacetylation degree [33].

3.2. Properties of Starch Films Incorporated with Native and Modified KG

3.2.1. Puncture and Tensile Strength. Table 2 shows that starch films containing 5% KG had puncture strengths increasing in the order **HKG** < **NKG** < **HOKG** < **OKG** and

TABLE 2: Results of puncture and tensile tests of the films.

| Starch film with | Elongation at puncture (%) | Puncture strength (N/mm ²) | Elongation-at-break (%) | Tensile strength (N/mm ²) |
|------------------|----------------------------|--|---------------------------|---------------------------------------|
| NKG | 53.29 ± 3.02 ^{bc} | 0.316 ± 0.005 ^c | 36.64 ± 0.46 ^d | 3.00 ± 0.19 ^{bcd} |
| HKG | 47.72 ± 1.47 ^c | 0.279 ± 0.008 ^d | 49.45 ± 1.66 ^b | 3.55 ± 0.31 ^a |
| OKG | 66.67 ± 1.78 ^a | 0.411 ± 0.025 ^a | 19.47 ± 0.07 ^b | 2.60 ± 0.24 ^{de} |
| HOKG | 50.51 ± 0.80 ^c | 0.372 ± 0.011 ^b | 32.65 ± 0.56 ^c | 2.84 ± 0.41 ^{cde} |

Results are expressed as mean ± standard deviation ($n = 3$). Means with different superscripts in a column are significantly different ($p < 0.05$).

TABLE 3: Results of moisture, water uptake, solubility, and moisture permeability of the films.

| Starch film with | Moisture content (%) | Water uptake (%) | Solubility (%) | Moisture permeability ($\times 10^{-10}$ g/Pa.m.s) |
|------------------|----------------------------|----------------------------|---------------------------|---|
| NKG | 21.72 ± 0.54 ^b | 124.80 ± 0.77 ^b | 19.62 ± 1.04 ^b | 1.736 ± 0.066 ^{ab} |
| HKG | 24.90 ± 0.80 ^a | 151.77 ± 2.26 ^a | 21.44 ± 0.24 ^a | 1.882 ± 0.054 ^a |
| OKG | 18.53 ± 0.66 ^c | 104.73 ± 3.56 ^c | 16.78 ± 0.51 ^d | 1.589 ± 0.037 ^{bc} |
| HOKG | 20.15 ± 0.38 ^{cd} | 119.32 ± 2.64 ^b | 18.06 ± 0.70 ^c | 1.670 ± 0.061 ^{bc} |

Results are expressed as mean ± standard deviation ($n = 3$). Means with different superscripts in a column are significantly different ($p < 0.05$).

elongation at break decreasing in the same order. This result means that alkaline hydrolysis plasticized, while periodate oxidation hardened the films. The reason of plasticizing effect of alkaline hydrolysis was possibly the removal of metallic cations crosslinking $-\text{COO}^-$ groups in the KG backbones. Moreover, hydrophilic hydroxyl groups released after hydrolysis of KG attracted more moisture that acted as a plasticizer. The plasticizing effect of alkaline hydrolysis was also observed in another study, in which deacetylation of xanthan gum increased decreased the strength and increase the elongation-at-break of its films [34].

The hardening effect of periodate oxidation on the films was due to the formation of carbonyl groups in KG molecules that can form hemiacetal and acetal crosslinks with hydroxyl groups in the molecules of starch and KG [35]. The crosslinking of carbonyl groups was also observed in collagen films incorporated with glutaraldehyde [36] and eggwhite films incorporated with oxidized starch [37].

Table 2 shows that the puncture strength and tensile strength of the films were inversely related to their EB: films with lower tensile strength/puncture strength had higher EB.

It is interesting to note that the alkaline hydrolysis and periodate oxidation oppositely affected the puncture and tensile strengths of the films: alkaline hydrolysis increased the tensile strength but lowered the puncture strength, while periodate oxidation decreased the tensile strength but increased the puncture strength. These results showed that the action mode of KG along the films in tensile tests was different from the action in the perpendicular direction in the puncture tests.

3.2.2. Hydrophilicity. Table 3 shows that moisture content, moisture permeability water uptake, and solubility of the films incorporated with KG had the same trend: HKG > NKG > HOKG > OKG. These three properties are related with the hydrophilicity of the films. Alkaline hydrolysis of KG produced more hydrophilic hydroxyl groups and hence increased the hydrophilicity of the films [3]. Oppositely, periodate oxidation converted hydroxyl groups to less hydro-

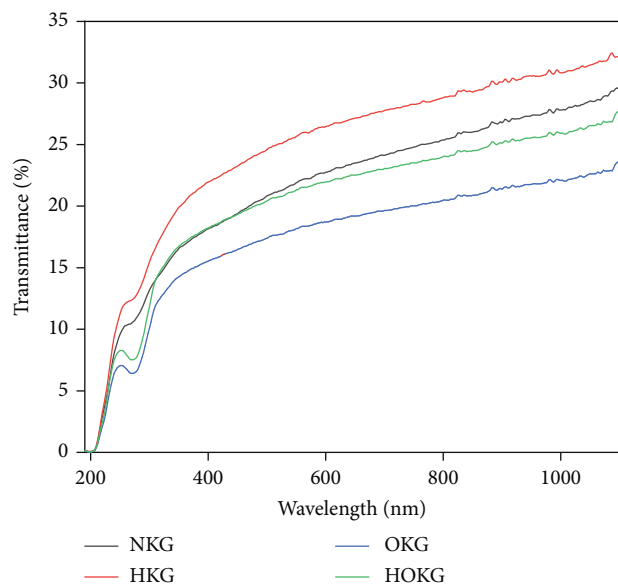


FIGURE 6: UV-vis spectra of starch-KG films.

philic carbonyl groups, which further produced hemiacetal and acetal with other hydroxyl groups [5]. Therefore, periodate oxidation significantly reduced the hydrophilicity of the OKG and HOKG films. Our results are consistent with other studies on dialdehyde starch-gelatin films [38] and dialdehyde carboxymethyl cellulose-gelatin films.

3.2.3. UV-Vis Spectra and Transparency. UV-vis spectroscopy helps evaluate the visible transparency and UV barrier properties of films, which are important for food packaging applications. Figure 6 shows that the order of transparency of the films is the same in three regions (UV, visible, and IR): HKG > NKG > HOKG > OKG. This result indicates that hydrolysis enhanced but periodate oxidation lowered the film transparency.

Films containing OKG and HKG showed a strong absorption peak at 270 nm while the peak was weak for films containing NKG and HKG. This peak is due to the

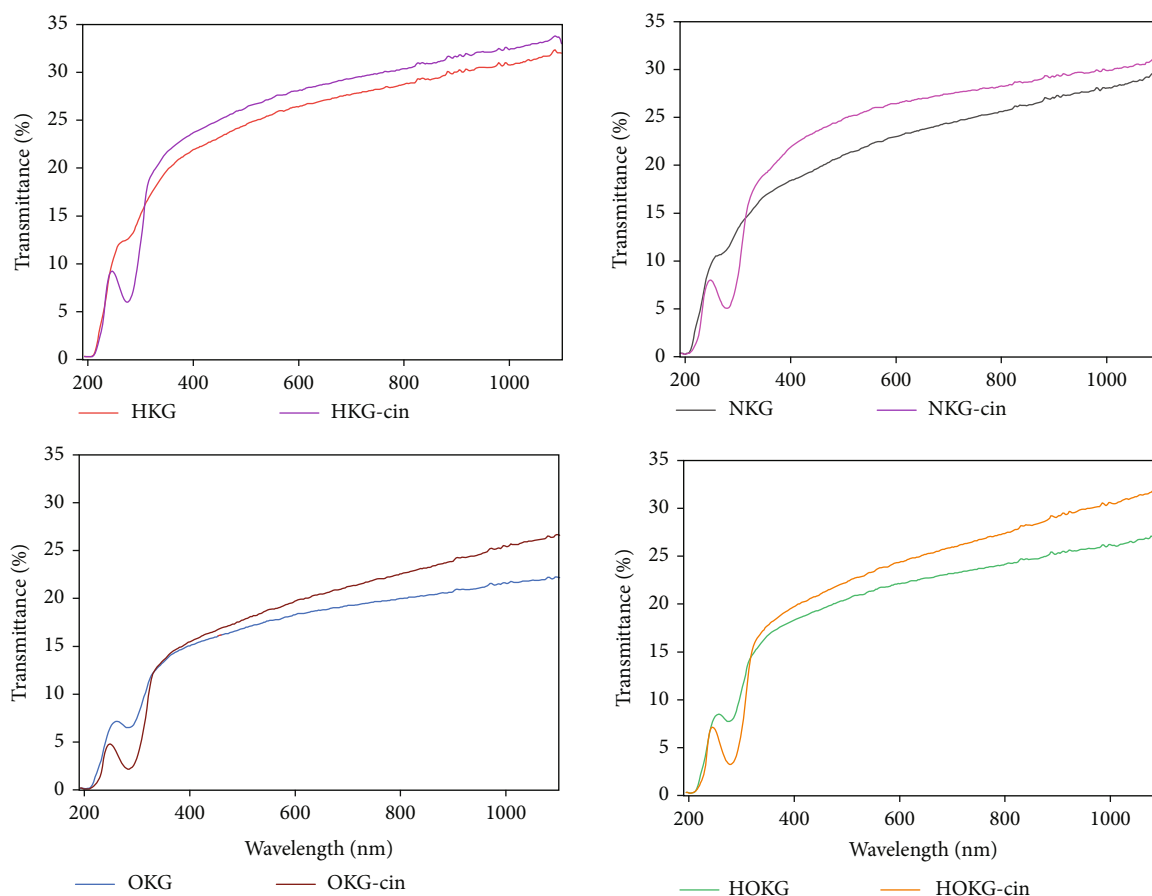


FIGURE 7: UV-vis spectra of starch-KG films with and without 5% cinnamaldehyde.

absorption of the $-C=O$ bond in the aldehyde and ester groups in KG, which was also observed in gelatin films incorporated with dialdehyde CMC [26]. The strong absorption of starch films incorporated with OKG and HOKG can protect the packaged products from UV radiation.

It is interesting to note that when incorporated with 5% cinnamaldehyde, all the four films transmitted slightly more IR and visible radiation, but more strongly absorbed UV light (Figure 7) because the carbonyl group in aldehydes was reported to absorb radiations near 280 nm [39]. Therefore, the incorporation of cinnamaldehyde can enhance the protective effect of the films against UV- light.

3.2.4. Antifungal Activity. Figure 8 shows that *C. gloeosporioides* grew quickly on the Petri dishes with films not containing cinnamaldehyde. Except for OKG, the fungi grew on the surface of starch-KG films. However, the incorporation of 5% cinnamaldehyde significantly inhibited the growth of *C. gloeosporioides*. Several studies have shown the antifungal activity of cinnamaldehyde against several fungi such as *Colletotrichum gloeosporioides*, *Rhizoctonia solani*, *Fusarium solani*, and *Ganoderma austral* [22, 40]. The mechanism of the antifungal activity is related to the decrease of plasma membrane ATPase activity and ergosterol, a vital component of the fungal cell wall [41].

Based on the degree of invasion of fungi on the film surface, the antifungal activity of KG types is $HKG < NKG < HOKG < OKG$. Interestingly, the starch film with HKG (Figure...) facilitated the growth and spore production of *C. gloeosporioides* after even one day. The fact that the fungi strongly developed even outside the film indicates that HKG with high solubility diffused to the agar and promoted the growth of *C. gloeosporioides*. On the opposite side, the fungi grew normally outside the film with OKG but almost could not invade the film after 3 days (Figure 8). This result indicates that OKG can inhibit by direct contact with fungal cells possibly due to the carbonyl groups that can interact with the fungal cell wall.

3.2.5. Antibacterial Activity. Figure 9 shows that after 4 days *E.coli* grew fully on the agar and the films without cinnamaldehyde. Although KG has a slight antibacterial and enzyme degradation activity [42], its content in the films (3.7% on a dry basis) was too low to be effective. The incorporation of 5% cinnamaldehyde in the films resulted in an inhibition zone around each film from day 1 (images not shown), and the diameters of the inhibition zones did not change afterwards.

The antibacterial action of cinnamaldehyde is known to be dose-dependent and can differ for different bacteria. At low concentrations, cinnamaldehyde interacts and damages the bacterial cell walls while at high concentrations, it can

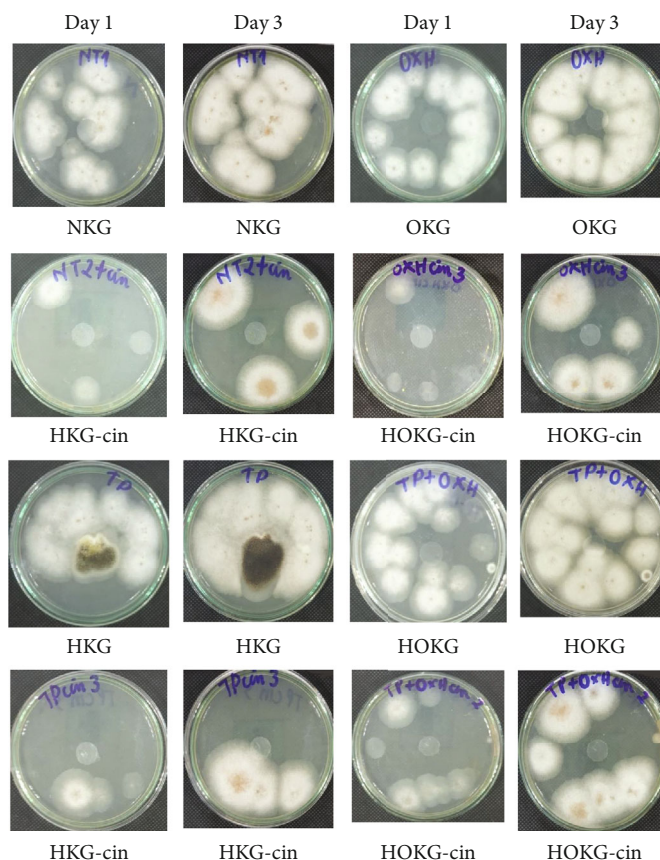


FIGURE 8: Antifungal activity of KG-starch films with and without cinnamaldehyde for 3 days against *C. gloeosporioides*.

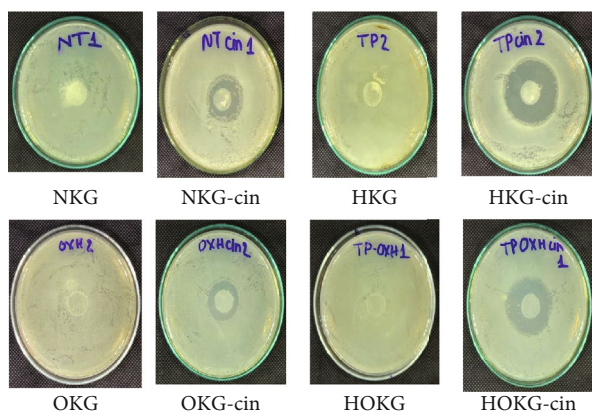


FIGURE 9: Disc diffusion test of KG-starch films with and without 5% cinnamaldehyde after 4 days.

diffuse into the cell and denature proteins in important enzymes in the cytoplasm, leading to cell death [43, 44].

4. Conclusion

This is the first report on periodate oxidation with and without alkaline hydrolysis to chemically modify karaya gum (KG) and develop new products from it. The hydrolysis increases while periodate oxidation decreases the hydrophilicity of KG. The carbonyl groups formed by periodate oxidation can give KG the possibility to be further modified by redox reactions

or coupling with functional groups such as hydroxyl and amine. The modified KG can be blended with different biopolymers and active components to be used as packaging materials in the food and pharmaceutical industries.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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References

- [1] D. Le Cerf, F. Irinei, and G. Muller, "Solution properties of gum exudates from *Sterculia urens* (Karaya gum)," *Carbohydrate Polymers*, vol. 13, no. 4, pp. 375–386, 1990.
- [2] V. Raj, J. H. Lee, J. J. Shim, and J. Lee, "Recent findings and future directions of grafted gum karaya polysaccharides and

- their various applications: a review," *Carbohydrate Polymers*, vol. 258, article 117687, 2021.
- [3] H. Postulkova, I. Chamradova, D. Pavlinak, O. Humpa, J. Jancar, and L. Vojtova, "Study of effects and conditions on the solubility of natural polysaccharide gum karaya," *Food Hydrocolloids*, vol. 67, pp. 148–156, 2017.
 - [4] M. Fiedorowicz and A. Para, "Structural and molecular properties of dialdehyde starch," *Carbohydrate Polymers*, vol. 63, no. 3, pp. 360–366, 2006.
 - [5] J. Yu, P. R. Chang, and X. Ma, "The preparation and properties of dialdehyde starch and thermoplastic dialdehyde starch," *Carbohydrate Polymers*, vol. 79, no. 2, pp. 296–300, 2010.
 - [6] E. Maekawa and T. Koshijima, "Preparation and structural consideration of nitrogen-containing derivatives obtained from dialdehyde celluloses," *Journal of Applied Polymer Science*, vol. 42, no. 1, pp. 169–178, 1991.
 - [7] U.-J. Kim, M. Wada, and S. Kuga, "Solubilization of dialdehyde cellulose by hot water," *Carbohydrate Polymers*, vol. 56, no. 1, pp. 7–10, 2004.
 - [8] Y. Hu, L. Liu, Z. Gu, W. Dan, N. Dan, and X. Yu, "Modification of collagen with a natural derived cross-linker, alginate dialdehyde," *Carbohydrate Polymers*, vol. 102, pp. 324–332, 2014.
 - [9] R. Aston, M. Wimalaratne, A. Brock, G. Lawrie, and L. Grøndahl, "Interactions between chitosan and alginate dialdehyde biopolymers and their layer-by-layer assemblies," *Biomacromolecules*, vol. 16, no. 6, pp. 1807–1817, 2015.
 - [10] X. Liu, N. Dan, W. Dan, and J. Gong, "Feasibility study of the natural derived chitosan dialdehyde for chemical modification of collagen," *International Journal of Biological Macromolecules*, vol. 82, pp. 989–997, 2016.
 - [11] J. Ren, M. Li, R. Yuan, A. Pang, Z. Lu, and L. Ge, "Adherent self-healing chitosan/dialdehyde starch coating," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 586, article 124203, 2020.
 - [12] A. Sionkowska, M. Michalska-Sionkowska, and M. Walczak, "Preparation and characterization of collagen/hyaluronic acid/chitosan film crosslinked with dialdehyde starch," *International Journal of Biological Macromolecules*, vol. 149, pp. 290–295, 2020.
 - [13] R. R. Vildanova, N. N. Sigaeva, O. S. Kukovinets, and S. V. Kolesov, "Preparation and rheological properties of hydrogels based on N-succinyl chitosan and hyaluronic acid dialdehyde," *Polymer Testing*, vol. 96, article 107120, 2021.
 - [14] I. Ahmed, H. Lin, L. Zou et al., "A comprehensive review on the application of active packaging technologies to muscle foods," *Food Control*, vol. 82, pp. 163–178, 2017.
 - [15] S. Shreaz, W. A. Wani, J. M. Behbehani et al., "Cinnamaldehyde and its derivatives, a novel class of antifungal agents," *Fitoterapia*, vol. 112, pp. 116–131, 2016.
 - [16] M. Friedman, P. R. Henika, and R. E. Mandrell, "Bactericidal activities of plant essential oils and some of their isolated constituents against *Campylobacter jejuni*, *Escherichia coli*, *Listeria monocytogenes*, and *Salmonella enterica*," *Journal of Food Protection*, vol. 65, no. 10, pp. 1545–1560, 2002.
 - [17] Y. Huang and S. Ho, "Toxicity and antifeedant activities of cinnamaldehyde against the grain storage insects, *Tribolium castaneum* (Herbst) and *Sitophilus zeamais* Motsch," *Journal of Stored Products Research*, vol. 34, no. 1, pp. 11–17, 1998.
 - [18] J. Usta, S. Kreydiyyeh, P. Barnabe, Y. Bou-Moughlabay, and H. Nakkash-Chmaisse, "Comparative study on the effect of cinnamon and clove extracts and their main components on different types of ATPases," *Human & Experimental Toxicology*, vol. 22, no. 7, pp. 355–362, 2003.
 - [19] K. H. Bang, D. W. Lee, H. M. Park, and Y. H. Rhee, "Inhibition of fungal cell wall synthesizing enzymes by trans-cinnamaldehyde," *Bioscience, Biotechnology, and Biochemistry*, vol. 64, no. 5, pp. 1061–1063, 2000.
 - [20] X. Xie, J. Fang, and Y. Xu, "Study of antifungal effect of cinnamaldehyde and citral on *Aspergillus flavus*," *Food Science*, vol. 25, no. 9, pp. 32–34, 2004.
 - [21] J. Ke, L. Xiao, G. Yu, H. Wu, G. Shen, and Z. Zhang, "The study of diffusion kinetics of cinnamaldehyde from corn starch-based film into food simulant and physical properties of antibacterial polymer film," *International Journal of Biological Macromolecules*, vol. 125, pp. 642–650, 2019.
 - [22] M. P. Balaguer, G. Lopez-Carballo, R. Catala, R. Gavara, and P. Hernandez-Munoz, "Antifungal properties of gliadin films incorporating cinnamaldehyde and application in active food packaging of bread and cheese spread foodstuffs," *International Journal of Food Microbiology*, vol. 166, no. 3, pp. 369–377, 2013.
 - [23] J. Wu, Q. Sun, H. Huang, Y. Duan, G. Xiao, and T. le, "Enhanced physico-mechanical, barrier and antifungal properties of soy protein isolate film by incorporating both plant-sourced cinnamaldehyde and facile synthesized zinc oxide nanosheets," *Colloids and Surfaces B: Biointerfaces*, vol. 180, pp. 31–38, 2019.
 - [24] A. Nostro, R. Scaffaro, M. D'Arrigo et al., "Study on carvacrol and cinnamaldehyde polymeric films: mechanical properties, release kinetics and antibacterial and antibiofilm activities," *Applied Microbiology and Biotechnology*, vol. 96, no. 4, pp. 1029–1038, 2012.
 - [25] A. Srisa and N. Harnkarnsujarit, "Antifungal films from trans-cinnamaldehyde incorporated poly(lactic acid) and poly(butylene adipate-co-terephthalate) for bread packaging," *Food Chemistry*, vol. 333, article 127537, 2020.
 - [26] C. Mu, J. Guo, X. Li, W. Lin, and D. Li, "Preparation and properties of dialdehyde carboxymethyl cellulose crosslinked gelatin edible films," *Food Hydrocolloids*, vol. 27, no. 1, pp. 22–29, 2012.
 - [27] A. Nawab, F. Alam, M. A. Haq, Z. Lutfi, and A. Hasnain, "Mango kernel starch-gum composite films: physical, mechanical and barrier properties," *International Journal of Biological Macromolecules*, vol. 98, pp. 869–876, 2017.
 - [28] A. Farahnaky, B. Saberi, and M. Majzoobi, "Effect of glycerol on physical and mechanical properties of wheat starch edible films," *Journal of Texture Studies*, vol. 44, no. 3, pp. 176–186, 2013.
 - [29] T. L. Cao and K. B. Song, "Effects of gum karaya addition on the characteristics of loquat seed starch films containing oregano essential oil," *Food Hydrocolloids*, vol. 97, article 105198, 2019.
 - [30] N. M. Zain, A. G. Stapley, and G. Shama, "Green synthesis of silver and copper nanoparticles using ascorbic acid and chitosan for antimicrobial applications," *Carbohydrate Polymers*, vol. 112, pp. 195–202, 2014.
 - [31] H. Li, B. Wu, C. Mu, and W. Lin, "Concomitant degradation in periodate oxidation of carboxymethyl cellulose," *Carbohydrate Polymers*, vol. 84, no. 3, pp. 881–886, 2011.
 - [32] S. D. Zhang, Y. R. Zhang, J. Zhu, X. L. Wang, K. K. Yang, and Y. Z. Wang, "Modified corn starches with improved comprehensive properties for preparing thermoplastics," *Starch-Stärke*, vol. 59, no. 6, pp. 258–268, 2007.

- [33] Y. López-Franco, I. Higuera-Ciajara, J. Lizardi-Mendoza, W. Wang, and F. M. Goycoolea, "Other exudates: tragacanth, karaya, mesquite gum, and larchwood arabinogalactan," in *Handbook of Hydrocolloids*, pp. 673–727, Woodhead Publishing Series in Food Science, Technology and Nutrition, 2021.
- [34] P. Veiga-Santos, L. M. Oliveira, M. P. Cereda, A. J. Alves, and A. R. P. Scamparini, "Mechanical properties, hydrophilicity and water activity of starch-gum films: effect of additives and deacetylated xanthan gum," *Food Hydrocolloids*, vol. 19, no. 2, pp. 341–349, 2005.
- [35] S. Veelaert, D. de Wit, K. F. Gotlieb, and R. Verhé, "Chemical and physical transitions of periodate oxidized potato starch in water," *Carbohydrate Polymers*, vol. 33, no. 2-3, pp. 153–162, 1997.
- [36] D. Simmons and J. Kearney, "Evaluation of collagen cross-linking techniques for the stabilization of tissue matrices," *Biotechnology and Applied Biochemistry*, vol. 17, no. 1, pp. 23–29, 1993.
- [37] A. Gennadios, A. Handa, G. W. Froning, C. L. Weller, and M. A. Hanna, "Physical properties of egg white–dialdehyde starch films," *Journal of Agricultural and Food Chemistry*, vol. 46, no. 4, pp. 1297–1302, 1998.
- [38] O. Moreno, J. Cárdenas, L. Atarés, and A. Chiralt, "Influence of starch oxidation on the functionality of starch-gelatin based active films," *Carbohydrate Polymers*, vol. 178, pp. 147–158, 2017.
- [39] A. Asthana, D. Bose, S. Kulshrestha, S. P. Pathak, S. K. Sanghi, and W. T. Kok, "Determination of aldehydes in water samples by capillary electrophoresis after derivatization with hydrazino benzene sulfonic acid," *Chromatographia*, vol. 48, no. 11-12, pp. 807–810, 1998.
- [40] H. C. Lee, S. S. Cheng, and S. T. Chang, "Antifungal property of the essential oils and their constituents from *Cinnamomum osmophloeum* leaf against tree pathogenic fungi," *Journal of the Science of Food and Agriculture*, vol. 85, no. 12, pp. 2047–2053, 2005.
- [41] S. Shreaz, R. A. Sheikh, B. Rimple, A. A. Hashmi, M. Nikhat, and L. A. Khan, "Anticandidal activity of cinnamaldehyde, its ligand and Ni(II) complex: effect of increase in ring and side chain," *Microbial Pathogenesis*, vol. 49, no. 3, pp. 75–82, 2010.
- [42] D. Verbeken, S. Dierckx, and K. Dewettinck, "Exudate gums: occurrence, production, and applications," *Applied Microbiology and Biotechnology*, vol. 63, no. 1, pp. 10–21, 2003.
- [43] F. Mousavi, B. Bojko, V. Bessonneau, and J. Pawliszyn, "Cinnamaldehyde characterization as an antibacterial agent toward *E. coli* metabolic profile using 96-blade solid-phase microextraction coupled to liquid chromatography–mass spectrometry," *Journal of Proteome Research*, vol. 15, no. 3, pp. 963–975, 2016.
- [44] N. Sanla-Ead, A. Jangchud, V. Chonhenchob, and P. Suppakul, "Antimicrobial activity of cinnamaldehyde and eugenol and their activity after incorporation into cellulose-based packaging films," *Packaging Technology and Science*, vol. 25, no. 1, pp. 7–17, 2012.