Rheological and Antimicrobial Properties of Silica and silver Nanoparticles-reinforced K-carrageenan/hydroxyethyl Cellulose Composites for Food Packaging Applications

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Abstract

Sustainable food packaging films were developed using a combination of k-Carrageenan (C), hydroxyl ethyl cellulose (H), silicon dioxide (SiO\textsubscript{2}), and silver (Ag) nanoparticles. The CH-SiO\textsubscript{2}/Ag nanocomposites showed promising results, mainly due to their transparency, flexibility, low cost, and environmental friendliness. The structure and uniform morphology of the CH-SiO\textsubscript{2}/Ag nanocomposites were determined by FT-IR, XRD, and SEM analysis. Barrier properties (water vapor permeability-WVP), thermal properties (T\textsubscript{5%} loss, char yield), and mechanical properties determined for the CH and CH-SiO\textsubscript{2}/Ag nanocomposites, which improved by 3.3–1.9 \times 10^{-9} \text{gm/m}^2 \text{Pas (WVP)}, 59.1-115.7 °C (T\textsubscript{5%}), 13.4–29.3 % (char yield), 23.8–41.5 MPa(tensile strength), and 22.3–28.9 (EB), respectively. The contact angles of the CH-SiO\textsubscript{2}/Ag nanocomposites were in the range of 60.1–76.4. The UV transmittance of the CH composites decreased with the addition of SiO\textsubscript{2} and Ag nanoparticles. However, the transparency of the composites was not affected, and it inhibited UVA and UVB rays by the addition of Ag nanoparticles.

The viscosity of the CH composites increased with the SiO\textsubscript{2} content and decreased with the shear rate. All the composites exhibited shear-thinning behavior. The storage modulus of the prepared composites is higher than the loss modulus in the entire frequency region. Overall, SiO\textsubscript{2} and Ag nanoparticles improved the hydrophilic nature of the CH-SiO\textsubscript{2}/Ag films and showed significant activity against six common food pathogens, \textit{Staphylococcus aureus, Bacillus cereus, Listeria monocytogenes, Bacillus subtilis, Salmonella typhi, and Cronobacter sakazakii}. The synergistic combination of CH-SiO\textsubscript{2}/Ag nanocomposite has potential for packaging and other biomedical applications.

Introduction

These days there is a great attention on the terms environment friendly, green synthesis, sustainable, biocompatible and biodegradable, in the area of material science research. Particularly, in polymers and plastics being used in many sectors for packaging (Castro-Mayorga et al. 2016; Gholam et al. 2013; Yoldas et al. 2014; Tippabattini et al. 2013). However, it is damaging our ecosystem, human and animal health, due to unrealizable utilization (Zhili et al. 2017; Rhim et al. 2014). Owing to the above concerns, biopolymer-based composites are an immediate alternative with reasonable parameters such as low cost, biodegradability, biocompatibility, and low toxicity, and are available from sustainable natural resources.

Carrageenan is a linear and high molecular weight biopolymer derived from red seaweed (\textit{Eucheuma spinosum}) and is available in different structures such as kappa, iota, and alpha carrageenan. It was classified based on the composition of 3, 6 –anhydro-galactose and ester sulfate groups. Kappa-carrageenan contains the lowest content of sulfate ester groups, which has better film-forming ability than others. Carrageenan is used in many foods and cosmetic and pharmaceutical applications (Yunpeng et al. 2019; Zineb et al. 2019; Bianca-loana et al. 2020; Afsaneh et al. 2018; Maria et al. 2010; Joana et al. 2013; Hou et al. 2019).

Hydroxyethyl cellulose is the most important non-ionic water-soluble cellulose derivative. It is a biodegradable material that is widely used in food, coating, medicine, and papermaking industries (Zhili et al. 2017).
However, both k-Carrageenan and hydroxyethyl cellulose are mechanically weak and have poor barrier properties (Mithilesh et al. 2019; Cristina et al. 2010; Márcia et al. 2012; Jéssica de et al. 2020; Andong et al. 2013).

To overcome these disadvantages, the incorporation of two more biopolymers and the addition of inorganic additives is the best method (Lokesh et al. 2014; Maria et al. 2010). The above disadvantages are easily overcome by the preparation of two or more biopolymers based on the addition of inorganic additives such as TiO$_2$, ZnO, GO, MTT clay, SiO$_2$, and Ag nanoparticles (Ivan et al. 2020; Rhim 2013; Izabela et al. 2008; Guanzheng et al. 2019). Silica has attracted great attention because of its chemical inertness, morphology, availability, low cost, easy surface functionalization, and well-defined particle size (Merve et al. 2019). Silica nanoparticles have been used in various applications such as drug delivery systems, absorbents for bioactive compounds, molecular imaging, sensors, and optical devices (Iñigo et al. 2018). On the other hand, the reinforcement of Ag nanoparticle-based polymer composites help to develop active packaging materials. The antimicrobial properties of the Ag nanoparticles improve or maintain the self-life, safety, and quality of the food product (Castro-Mayorga et al. 2016; Márcia et al. 2012; Li et al. 2011; Mahdieh et al. 2018). Both the synergistic combination of Ag and SiO$_2$ nanoparticles help to develop active materials with improved barrier, mechanical, thermal, and antimicrobial properties of the polymer composites.

In this work, we prepared a synergistic composition based on k-carrageenan, hydroxyethyl cellulose, Ag, and SiO$_2$ nanoparticles. We focused and thoroughly studied the rheological properties of the CH-SiO$_2$/Ag nanocomposites. In addition, the effect of Ag and SiO$_2$ on the water barrier, contact angle, and mechanical properties were systematically explored.

**Materials And Methods**

K-Carrageenan (Ash content 40.0% and viscosity min 10.0 in 0.30% in water at 25$^\circ$ C), 2-hydroxyethyl cellulose (molecular weight M$_v$ ~ 1,300,000), and SiO$_2$ (particle size 50 nm, BET) were purchased from Sigma Aldrich, South Korea and used as received. Glycerin, sodium citrate, epichlorohydrin, and citric acid were purchased from Dajang Chemicals, South Korea. A silver colloid (Nanomix-silver 30 000 ppm) was obtained from Meiji Nanotech (Seoul, Korea). All reagents were used as received.

**Preparation of CH-SiO$_2$/Ag nanocomposite films**

CH with various concentrations of SiO$_2$ (0, 2.5, 5, 7.5, and 10 wt%) and Ag nanoparticles were prepared by the solvent evaporation method. First, k-carrageenan (0.5g) and hydroxyethyl cellulose (0.5g) were dispersed in glycerin (3g) to ensure that there was no particle agglomeration. Then, 75 mL of distilled water was added with continuous stirring and the temperature was increased to 80 $^\circ$C for 15 min. The crosslinking agent of epichlorohydrin (4 wt%) was added to the above solution. Subsequently, citric acid (0.5g) and sodium citrate (0.5g) were mixed one by one in the reaction mixture at same condition. SiO$_2$ was dispersed in ethanol separately in sonicated for 60 min at 50 $^\circ$C. The dispersed SiO$_2$ was mixed with the hydrogel reaction mixture and continuously stirred for another 60 min. The temperature was reduced to 50 $^\circ$C and 0.25 mL of silver
colloid solution was added with vigorous stirring. Finally, the CH-SiO$_2$/Ag nanocomposite hydrogel was spread on the glass plate and dried at ambient temperature, and then removed from the glass plate, under dried conditions. Similarly, the same procedure was followed for all the (a) CH (b) CH-SiO$_2$-2.5 wt% (c) CH-SiO$_2$-5 wt% (d) CH-SiO$_2$-7.5 wt% (e) CH-SiO$_2$-10 wt% (f) CH-SiO$_2$-10 wt% /Ag nanocomposite preparations.

Result And Discussion

FT-IR

The FT-IR spectra of the CH-Ag composites are shown in Fig. 1. The characteristic absorption peaks at 2961, 2865 (CH stretching), 3349 (O-H stretching), 1222 (O = S = O asymmetric), 918 (C-O-C stretching), and 843 (O-SO$_3$ stretching vib of β-D-galactose). The C-O of 3, 6-anhydro-D-galactose and C-O-SO$_3$ of D-galactose-4-sulfate presence in k-carrageenan exhibited characteristics at 922 and 846 cm$^{-1}$. A broad band at 3356 and 1404 attributed to, or belongs to the OH stretching vibration and OH bending vibration of hydroxylethyl cellulose. The aliphatic C-H stretching, C-O-C stretching vibration, and C-O stretching vibration are represented at 2876, 1036, 1010, and 1108 cm$^{-1}$, respectively (Zhili et al. 2017; Márcia et al. 2012; Li et al. 2011). In the spectrum of CHSiO$_2$ nanocomposites in the region of 800–1200 cm$^{-1}$, shoulder peaks appear at 899 cm$^{-1}$ (Si-OH) (Cristina et al. 2010). In addition, there are two absorption bands around 900–1100 cm$^{-1}$ due to the stretching vibration of Si-O-Si and Si-O-C bonds, whose intensity increases upon increasing the SiO$_2$ content (Joana et al. 2013; Bo et al. 2018). The absorption near 1062 cm$^{-1}$, 965 cm$^{-1}$, and 792 cm$^{-1}$ were attributed to the asymmetric stretching vibration, symmetric stretching vibration, and bending vibration of Si-O-Si, respectively. This indicates the intermolecular interactions between the components in the CH-SiO$_2$ nanocomposites.

XRD

The XRD patterns of CH and CH-SiO$_2$/Ag composites are shown in Fig. 2. The broad and clear diffraction peaks appeared at 23.1° for the CH composites, indicating the amorphous structure of the composites. Further, w by the addition or increasing content of SiO$_2$ nanoparticles, this peak shifted slightly, and the intensity of the peak for the CH-SiO$_2$-10 wt% composites increased. The XRD patterns of the CH-SiO$_2$-10 wt% /Ag nanocomposites all the materials dispersed well, and the amorphous structure of k-C was not affected and altered by the incorporation of HEC, SiO$_2$, and Ag nanoparticles.

UV

UV-VIS spectroscopy is a very important technique for studying the transmittance and absorption of food packaging composite films. Figure 3 and Table 1 show that the transmittance of the CH and CH-SiO$_2$-10 wt% /Ag nanocomposites are in the ranges of 92.2–89.7 and 91.5–89.5 % at 800 nm and 600 nm, respectively. There was no significant reduction in their transmittance. However, at 280 nm, the transmittance decreased to 71.7–56.6 % for CH and CH-SiO$_2$-10 wt% /Ag composites, respectively. The transmittance of the CH composites decreased from 800 to 280 nm from 92.2% to 71.7 %, and for the CH-SiO$_2$-10 wt% composite is 90.7% to 64.1 %. The addition of SiO$_2$ nanoparticles gradually decreased the transmittance, but the addition of
Ag decreased the transmittance by 56.6 %, at 280 nm. Both these nanoparticles improved the light barrier properties of the CH composites and blocked UV light transmission. The thermal, mechanical, and FT-IR results support the uniform dispersion of SiO$_2$ and Ag nanoparticles. CH-SiO$_2$-10 wt% /Ag nanocomposites are the perfect composition for food oxidative deterioration (Hou et al. 2019; Mahdieh et al. 2018). The color parameter is very important in packaging films and is affected by the addition of SiO$_2$ and Ag nanoparticles. The lightness (L), redness (a), and yellowness (b) of the CH composites were not significantly affected by the addition of SiO$_2$ nanoparticles. But the CH-SiO$_2$/Ag nanocomposites color values reduced significantly. The above results indicate that the CH-SiO$_2$/Ag nanocomposites have the highest UV barrier property, without significant sacrifice to the transparency of the neat CH composite films.

Table 1
UV-transmittance, thickness, and color values of CH and CH-SiO$_2$/Ag nanocomposite films.

| Sample             | Thickness (mm) | T (%) at 600 nm | Lightness (L$^*$) | Redness (a$^*$) | Yellowness (b$^*$) | Water vapor permeability ($\times 10^{-9}$ gm/m$^2$ Pas) | Water contact angle (°) |
|--------------------|----------------|-----------------|-------------------|-----------------|-------------------|-----------------------------------------------|------------------------|
| CH                 | 0.04           | 91.5            | 85.87             | 1.22            | -3.13             | 3.3                                           | 60.1                   |
| CH-SiO$_2$-2.5 wt% | 0.04           | 91.0            | 85.72             | 1.18            | -2.96             | 3.1                                           | 63.5                   |
| CH-SiO$_2$-5 wt%   | 0.05           | 90.7            | 85.66             | 1.16            | -2.95             | 2.7                                           | 68.2                   |
| CH-SiO$_2$-7.5 wt% | 0.05           | 90.5            | 85.18             | 1.16            | -2.86             | 2.5                                           | 70.5                   |
| CH-SiO$_2$-10 wt%  | 0.05           | 90.3            | 84.73             | 1.14            | -2.84             | 2.1                                           | 73.6                   |
| CH-SiO$_2$-10 wt% /Ag | 0.05        | 89.5            | 83.04             | 1.09            | -1.77             | 1.9                                           | 76.4                   |

WVP

Generally, biopolymers are highly sensitive to moisture, which restricts their application in several fields. To overcome these disadvantages, preparing nanocomposites or incorporating hydrophobic additives is the best solution. This restricted the water molecules to cross the nanocomposite films and decreased the WVP values. The prepared CHSA nanocomposites are shown in Table 1. The WVP values of CH composites $3.3 \times 10^{-9}$ gm/m$^2$ Pas, which reduced to $3.1, 2.7, 2.5$ and $2.1 \times 10^{-9}$ gm/m$^2$ Pas, by the addition of $2.5, 5, 7.5, 10$ wt % of SiO$_2$ nanoparticles respectively and it further reduced to $1.9 \times 10^{-9}$ gm/m$^2$ Pas by the addition of Ag nanoparticles respectively. This improvement is mainly due to the fact that the HEC is slightly more crystalline than k-C, and it restricts k-C to swell in water upon reinforcement. The reinforcement effect of HEC restricted the k-C materials to swell in water because HEC is slightly more crystalline than k-C (Mithilesh et al. 2019). The improvement or reduction in WVP value is mainly due to the hydrophobic nature of SiO$_2$ nanoparticles, homogeneously dispersed in the CH matrix, and it also provided strong intermolecular interactions between or
with the polymer matrix (Jéssica de et al. 2020). Furthermore, Ag nanoparticles reduced the intermolecular spacing within the CHS nanocomposites, thus significantly reducing their WVP values (Márcia et al. 2012).

**CA**

Surface hydrophilic/hydrophobic properties and wettability are interesting and important parameters for polymer composite films measured by CA. The CA of the CH and CH-SiO2-10 wt% /Ag nanocomposite films is shown in Table 1. The CA of neat CH composite film is 60.1, then it increased significantly to 63.5, 68.2, 70.5 and 73.6° CH-SiO2-2.5 wt%, CH-SiO2-5 wt %, CH-SiO2-7.5 wt%, and CH-SiO2-10 wt% nanocomposites respectively. It further increased (76.4°) upon incorporation of Ag nanoparticles. This is mainly attributed to the surface cohesiveness and interaction between the components.

**TGA**

The rate of decomposition and thermal stability of the CH and CH-SiO2-10 wt% /Ag nanocomposites were studied by TGA under nitrogen atmosphere (Table 2 and Fig. 4). The initial thermal degradation of the CH composites is very low. The 5% gravimetric loss of the CH composites was 59.1 °C, which increased slowly with increasing the content of SiO2. The addition of SiO2 increased the T5% and T10% loss values from 69.1-115.7 °C and 81.1-150.4 °C, which is nearly 48.9 % (T5%) and 46 % (T10%). The main reason for the significant improvement in the thermal stability of the CH-SiO2-10 wt% /Ag nanocomposites is (mainly due to the) SiO2 nanoparticles forming continuous protective solid layers, so that oxidation degradation becomes slower. It also increased the char yield of the nanocomposites, which increased by 13.4 % (CH) to 29.3 % (CH-SiO2-10 wt% /Ag). Moreover, incorporation of Ag nanoparticles increased the thermal stability to the next level. It significantly increased T5% and char yield to 115.7 °C and 29.3 %, respectively. These results are encouraging for CH-based SiO2 and Ag composites, and the results are comparable with previously reported nanocomposites (Yunpeng et al. 2019; Mithilesh et al. 2019; Andong et al. 2013; Mahdieh et al. 2018). Overall, the results suggest that the inorganic SiO2 and Ag nanoparticles are uniformly dispersed and distributed on the polymer surface and stabilize the organic matrices.

**DSC**

The DSC thermogram is a very important thermal analysis (in polymer nanocomposites) to determine the effect of nanoparticles on the polymer composite structures, such as Tg and Tm (Table 2). The Tg and Tm of the CH composites improved from 146.7 to 149.5 °C by the incorporation of SiO2 and Ag particles. These changes were even more pronounced for the CH-SiO2-10 wt% /Ag composites, which showed higher Tg and Tm values. The dispersion of SiO2 disturbs the Tg and Tm of polymer composites by hydrogen bonding interactions between the polymer chains. This formation of bonds reduces the segmental mobility in the polymer chain and hence increases Tg [28]. This result is consistent with the TGA and mechanical properties of the CH-SiO2-10 wt% /Ag composites (Castro-Mayorga et al. 2016; Jéssica de et al. 2020; Lokesh et al. 2014; Mahdieh et al. 2018).

**SEM**
SEM micrographs of CH and CH-SiO$_2$-10 wt% /Ag nanocomposites are shown in Fig. 5. The neat CH composites exhibited a smooth, uniform structure, suggesting compatibility and dispersion of k-C and HEC polymers when increasing the SiO$_2$ nanoparticles in the CH composites. There are no structural changes at low concentrations of SiO$_2$, but at high concentrations, it is very slightly agglomerated on the surface, without any cracks. The roughness of the CH surface was slightly enhanced by the addition of SiO$_2$ (10 wt %). In the CH-SiO$_2$-10 wt% /Ag nanocomposites, the Ag nanoparticles were not observed in the SEM images, even in the cross-section images. The smooth and homogeneous cross section of the prepared composites was not affected by the inorganic SiO$_2$ and Ag nanoparticles (Castro-Mayorga et al. 2016; Joana et al. 2013; Jéssica de et al. 2020; Maria et al. 2010; Mahdieh et al. 2018). The EDX analysis of CH-SiO$_2$-10 wt% /Ag reveals the presence of elements such as C, O, Na, and Cl along with Si and Ag in the CH-SiO$_2$ composites. These data confirm the homogenous distribution of C, O, Si, S and Ag in CH-SiO$_2$-10 wt% /Ag nanocomposites and displays a well-defined compositional profile of the hybrid.

**Mechanical properties**

CH with SiO$_2$ and Ag nanocomposites were measured for tensile strength (TS) and elongation at break (EB) to evaluate the effect of SiO$_2$ and Ag nanoparticles. TS and EB (Table 2) were evaluated for the effect of SiO$_2$ and Ag nanoparticles on the CH composites. The TS of neat CH composites increased gradually and reached the highest value of 41.5 MPa for the CH-SiO$_2$-10 wt% /Ag nanocomposites. It almost improved by 42.6 % of TS. Initially, the TS values of the CH-SiO$_2$-2.5 wt% nanocomposites were slightly higher than those of the CH composites. Then, SiO$_2$ increased to 5 wt% (CH-SiO$_2$-5 wt%) to 29.5 MPa. The CH-SiO$_2$-10 wt% nanocomposites were also significantly higher than those of the CH-SiO$_2$-7.5 wt% nanocomposites. However, the same concentration of SiO$_2$ with Ag nanocomposites demonstrated superior TS values (41.5 MPa). The observed improvement in the TS is mainly due to the reinforcement effect of homogeneously dispersed inorganic nanoparticles and intermolecular adhesion and interaction between the polymers and SiO$_2$ and Ag inorganic nanoparticles [15]. The EB of CH and CH-SiO$_2$-10 wt% /Ag nanocomposites are in the range of 22.3–28.9 %. At low concentrations of SiO$_2$, EB increased drastically, but at high concentrations, it improved or increased slightly to higher values. By the addition of Ag nanoparticles, it improved from 27.5% to 28.9 %. This may be due to the greater interaction between CH and SiO$_2$/Ag nanoparticles. The extreme rigidity of these composites restrict their EB to a considerable extent (Afsaneh et al. 2018; Cristina et al. 2010; Maria et al. 2010; Mahdieh et al. 2018).
Table 2
Thermal, mechanical, water vapor permeability, and contact angle properties of the CH and CH-SiO2/Ag nanocomposite films.

| Sample          | TGA  | DSC  | Tensile strength (MPa) | Elongation at break (%) |
|-----------------|------|------|-------------------------|-------------------------|
|                 | T5% | T10% | CY (%)                  | Tg (°C)                 | Tm (°C)              |
| CH              | 59.1| 81.1 | 13.4                    | 146.7                   | 221.5               | 23.8                | 22.3                |
| CH-SiO2-2.5     | 69.1| 91.5 | 19.1                    | 146.5                   | 222.1               | 26.2                | 23.5                |
| CH-SiO2-5       | 83.9| 102.7| 24.0                    | 147.4                   | 222.6               | 29.5                | 24.8                |
| CH-SiO2-7.5     | 94.7| 129.5| 26.1                    | 148.2                   | 223.3               | 33.2                | 26.4                |
| CH-SiO2-10      | 107.3| 142.1| 26.7                    | 148.9                   | 225.7               | 37.1                | 27.5                |
| CH-SiO2-10/Ag   | 115.7| 150.4| 29.3                    | 149.5                   | 2264                | 41.5                | 28.9                |

**Rheology**

The storage modulus (G') and loss modulus (G'') were studied for the 3D structure and coordination bonds between k-C, HEC, SiO2, and Ag nanocomposites. G' and G'' of CH-SiO2-10 wt% /Ag nanocomposites are characterized in the form of angular frequency (0–100 rad/s), as shown in Figs. 6 and 7. The G' increased and G'' decreased continuously with increasing frequency. G' is almost independent of the entire frequency range. At high frequencies, G' is dependent on the frequency. Both the addition of SiO2 and Ag nanoparticles significantly improved on G' and G''. The continuous increase in G' from low to high frequency is mainly due to the interaction and concentration of SiO2 and Ag nanoparticles. It improved the fine structure and gelling network (Pinheiro et al. 2011).

However, the rate of increase of G' shows that the elastic properties of the gelling hydrogel dominate. Figure 7 shows the loss modulus of the CH composites. It was observed as very steep in the low frequency region. When the frequency is increased, it minimizes the slippage level and maintains a reasonable level. In the high-frequency region (20–100 rad/s), G'' increased, which indicated that the nanocomposites exhibited a more elastic behavior for the materials. The concentrations of SiO2 and Ag played an important role in the G' and G'' of the CH composites.

The complex viscosity versus frequency of the CH and CH-SiO2-10 wt% /Ag nanocomposites is shown in Fig. 8. The nanocomposites exhibited shear-thinning behavior. The molecular entanglements and the interactions disrupt at or up to certain initial or low angular frequencies. The addition of SiO2 increased the sensitivity and increased the complex viscosity even at low concentrations of SiO2 nanoparticles. These results suggest that a significant amount of SiO2 and Ag nanoparticles diffused into the polymer interlayers.
From the dynamic viscoelastic results of $G'$ and $G''$ and the complex viscosity of CH and CH-SiO$_2$-10 wt% /Ag nanocomposites showed strong interactions between CH and SiO$_2$ and Ag nanoparticles.

Figure S4 shows the shear dependent viscosity results for the CH-SiO$_2$-10 wt% /Ag nanocomposites. The viscosity of the CH composites decreased at a low shear rate. This shear thinning or non-Newtonian behavior of composites is due to the molecular disentanglements in their structure and aligned with the flow direction (Hadi et al. 2020).

The viscosity of the CH composites was 51.2 Pas, which increased to 261.0 Pas by the addition of 10 wt% of SiO$_2$ nanoparticles at a 1/s shear rate (Fig. 9). The highest viscosity of the CH-SiO$_2$-10 wt% composites was further improved by the Ag nanoparticles. CH-SiO$_2$-10 wt% /Ag exhibited the maximum viscosity in the low-and high-viscosity regions. These results are attributed to the structural characteristics such as size, confirmation, rigidity, and interaction with different concentrations of SiO$_2$ and Ag particles. The CH-SiO$_2$-10 wt% /Ag nanocomposites exhibited high viscosity over the whole shear range as the structure of SiO$_2$/Ag embedded in a continuous matrix on the CH following the deformable fillers in a viscous entangled network, resulting in higher viscosities (Xudong et al. 2017).

At low shear rates, the viscosity of the nanocomposite is higher than that of neat CH, but the high shear rate decreases significantly. This may be attributed to the coalescence of nanoparticles, which leads to a decrease in the surface area and interaction between the nanoparticles and polymer matrices.

The full range of shear stress versus shear rate of CH and CH-SiO$_2$-10 wt% /Ag composites is shown in Fig. 10. The flow properties of the nanocomposites were also described. Similarly, the shear stress increased with increasing the shear rate and concentration of SiO$_2$ and Ag nanoparticles. The neat CH composites showed the lowest shear stress, which may be due to the absence of large attractive forces among the k-C and HEC components. The addition of SiO$_2$/Ag nanoparticles had a positive influence on the viscosity and shear stress of the CH composites. Similar flow and viscosity behaviors of the composites have already been reported. The effect of SiO$_2$ and Ag nanoparticles is more pronounced at low shear rates, and it (or the relative effect) diminishes with increasing shear rates due to shear thinning. Moreover, the trend of the viscosity and shear stress with shear rate is very similar to the reported composites.

**Antimicrobial properties**

The antimicrobial properties of the CH and CH-SiO$_2$-10 wt% /Ag nanocomposites were studied by the well diffusion method and the results of their inhibition zone of the CH-SiO$_2$-10 wt% /Ag nanocomposite films are shown in Table 3. This study was broadly performed using four different gram positive and two different gram-negative pathogens. The neat CH and CH-SiO$_2$-10 wt% based nanocomposites had no considerable antimicrobial effect on the bacteria. However, the combination or incorporation of Ag nanoparticles exhibited more pronounced antimicrobial activity against both gram-positive and gram-negative bacteria. The CH-SiO$_2$-10 wt% /Ag nanocomposite showed a high antimicrobial inhibition zone against Staphylococcus aureus (34 mm) and less activity against Bacillus cereus (15.33 mm). However, the clear antimicrobial mechanism of Ag NP is still not clear because it includes several reasons, such as the outer membrane, degradation of
structural changes, and finally death of bacterial cells (Rhim et al. 2014; Paul et al. 2005). The addition of Ag NPs greatly improved the antimicrobial properties of CH-SiO$_2$-10 wt% nanocomposites and extended their potential applications in packaging films.

Table 3
The antimicrobial activities of the CH and CH-SiO$_2$Ag nanocomposite films.

| Organism                        | Zone of growth inhibition (mm) | Ciprofloxacin (Control) | CH | CH-SiO$_2$-2.5 | CH-SiO$_2$-5 | CH-SiO$_2$-7.5 | CH-SiO$_2$-10 | CH-SiO$_2$-10/Ag |
|---------------------------------|-------------------------------|-------------------------|----|---------------|--------------|---------------|---------------|-----------------|
| Staphylococcus aureus           |                               |                         |    |               |              |               |               |                 |
|                                 |                               |                         | 28.7 | N/D           | N/D          | N/D           | N/D           | 34.0            |
| Bacillus cereus                 |                               |                         | 26.7 | N/D           | N/D          | N/D           | N/D           | 15.3            |
| Listeria monocytogenes          |                               |                         | 22.7 | N/D           | N/D          | N/D           | N/D           | 19.7            |
| Bacillus subtilis               |                               |                         | 35.7 | N/D           | N/D          | N/D           | N/D           | 19.0            |
| Salmonella typhi                |                               |                         | 33.0 | N/D           | N/D          | N/D           | N/D           | 22.3            |
| Cronobacter sakazakii          |                               |                         | 24.7 | N/D           | N/D          | N/D           | N/D           | 25.7            |

N/D- Not detected; mm-millimeter.

Conclusion

Novel synergistic combinations of CH and CH-SiO$_2$-10 wt% /Ag nanocomposites were prepared successfully and studied well for food packaging applications. FT-IR, XRD, and SEM analyses revealed the structure, morphology, and homogenous dispersion of all the materials. All the composites exhibited shear thinning behavior, and their viscosity increased with increasing polyacrylamide content. The storage modulus of the prepared hydrogel composites was in the range of 815.8-1242.7 at 1 rad/s, and it increased continuously throughout the frequency region. The dynamic rheological properties of AP and AP-QAS hydrogels indicated that the prepared hydrogel composites had good mechanical strength. The addition of SiO$_2$ and Ag nanoparticles significantly improved the TS and EB of the CH composites. It increased 42.69 % TS and 23 % EB. The UV-transmittance values of the CH composites reduced gradually with increasing SiO$_2$ and Ag nanoparticles, and these barrier properties are good for food packaging applications. Both inorganic nanoparticles improved the hydrophilic nature of the CH composites, which reduced the WVP values from 3.3 to 1.9 $\times$ 10$^{-9}$ gm/m$^2$ Pas and increased the CA values from 60.1° to 76.4°. From the TGA and DSC results, nanoparticles delayed the thermal degradation of the CH composites. The T$_{5\%}$ are in the range of 59.1-115.7 °C, CY (13.4–29.3 %), T$_g$ (146.7-149.5 °C), and T$_m$ (221.5-226.4 °C), respectively. Finally, the Ag-added CH-SiO$_2$ nanocomposites showed excellent antimicrobial activity against gram-positive and gram-negative pathogens. These developed CH-SiO$_2$-10 wt% /Ag nanocomposites are suitable for active food processing in biomedical applications.
Declarations

Conflicts of interest

There are no conflicts to declare.

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The authors declare no competing financial interest.

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