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Preparation, characterization and mechanical properties of k-Carrageenan/SiO$_2$ nanocomposite films for antimicrobial food packaging

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Abstract. Kappa-Carrageenan (KCG) films have been formulated as a packaging material. This study has been conducted to investigate the effect of incorporating SiO$_2$ nanoparticles inside the KCG matrix, with the aim of enhancing the mechanical and antimicrobial properties of KCG for reinforcement purposes. Films were prepared by solution casting technique with 1.0, 3.0 and 5.0 wt% of SiO$_2$ nano-filler content taking neat KCG as the reference for the study. Structural characterizations of the prepared nanocomposite films were carried out by Fourier transform infrared, scanning electron microscope (SEM) and transmission electron microscope (TEM) techniques. SEM and TEM showed homogeneous dispersion of SiO$_2$ nanoparticles in the KCG matrix. The tensile strength increased significantly by introducing the SiO$_2$ nanoparticles into the KCG matrix, in which KCG/SiO$_2$ films have greater tensile strength (53.9 MPa) when compared to the KCG polymer (46.8 MPa). The moisture uptake (MU) of nanocomposites decreased when SiO$_2$ was introduced into the polymer matrix. The barrier property of the prepared KCG-based nanocomposite films decreased oxygen transmission rate with loading of different wt% of SiO$_2$. SiO$_2$ nanoparticle-loaded films produced higher zones of inhibition against *Staphylococcus aureus* and *Escherichia coli* strains compared to polymer film. This study was intended to find the applications for KCG films containing SiO$_2$ nanoparticles to enhance the shelf-life of foods in the form of biodegradable wrapper.

Keywords. Nanocomposite; k-Carrageenan; SiO$_2$ nanoparticles; mechanical strength; antimicrobial activity.

1. Introduction

Recently, renewable and natural polymers have been extensively developed due to the growth of environmental concerns on non-biodegradable materials and energy crisis, especially in the area of food packing [1]. Nanocomposites have been widely used as automotive parts, packaging materials, building materials and agricultural materials [2]. Different polymer nanocomposites have been extensively studied, including poly(lactic acid), polyhydroxybutyrate, polyhydroxyalkanoates, poly(ε-caprolactone), poly(butylene succinate), thermoplastic starch, cellulose etc. [3]. Recently, inorganic filler was developed as effective reinforcing nano-filler of nanocomposite to improve the properties of neat polymers [4]. However, most researches on inorganic particles as the nano-filler were mainly focused on the three-dimensional (3D) nanoscale particle, as the nano-fillers for preparing biodegradable polymer-based film materials was rarely concerned. Silicon dioxide (SiO$_2$)-filled polymer matrix composites have received considerable attention in the past few years. It has been reported that SiO$_2$ nanoparticle-filled polymer matrix composites show a significant improvement in mechanical and thermal properties [5–7]. Studies on SiO$_2$ dispersion in polymer matrices like poly (methyl methacrylate) [8,9], high-density polyethylene [10] and poly(ethylene

oxide) [11] have been carried out. In the present study, KCG/SiO$_2$ films were prepared by introducing SiO$_2$ nanoparticles into KCG matrix via solution casting technique. The mechanical properties and MU of nanocomposites were also investigated. Finally, the antimicrobial activity of the nanocomposite film is evaluated against two pathogenic bacteria, including *Staphylococcus aureus* and *Escherichia coli* by using the agar disk diffusion method.

2. Materials and methods

2.1 *Materials*

Tetraethyloxysilane (TEOS) was received from Sigma-Aldrich, India. The test strains, *E. coli* (MTCC-1303) and *S. aureus* (ATCC-6538), were procured from IMTECH, Chandigarh. All experimental materials and other solvents were purchased and were used as received without further purification.

2.2 *Synthesis of SiO$_2$ nanoparticles*

Nanocrystalline SiO$_2$ has been synthesized by sol–gel method using TEOS as a source of silicon. A quantity of 7.4 ml of TEOS was added to 80 ml of methanol and the mixture was

stirred vigorously at 150°C and stirred for further 30 min, resulting in white powder. The powder was annealed in a tubular furnace at 300°C for 1 h to get the SiO_2 nanopowder.

2.3 *Extraction of kappa-Carrageenan*

Kappa-Carrageenan (KCG) isolation procedure is followed as described by Barabanova *et al* [12]. Polysaccharide was extracted from red algae *kappaphycus alvarezii* doty ex Silva. Dried algae (10 g) were suspended in 10% NaOH and the olysaccharides were extracted at 90°C for 2 h in a boiling water bath. The suspensions were centrifuged (1000*g*, 20 min) and the algal residues were re-extracted twice with water for 2 h in a boiling water bath. The supernatants were pooled and concentrated under vacuum to about 100 ml. The polysaccharides were separated into the gelling–KCl insoluble and non-gelling–KCl soluble fractions according to Yermak *et al* [13]. The solutions were exhaustively dialysed against distilled water, lyophilized, and then used without further treatment.

2.4 *Preparation of KCG/SiO$_2$ nanocomposite films*

Two grams of KCG solutions were prepared by dissolving KCG in hot water at 100°C with stirring for 24 h. The prepared SiO_2 nanoparticles was dispersed in the above solution to obtain homogeneous solutions under mechanical stirring for 1 h at 80°C. These nanoparticle dispersions were added slowly to KCG solutions with 1, 3 and 5% (w/w) nanoparticle loadings with respect to the mass of polymer [14,15]. The resulting films were dried in a vacuum oven (at room temperature) for 48 h to remove traces of the solvents. Neat KCG film was prepared according to a similar procedure, except without addition of SiO_2. For quick understanding, the prepared four type of nanocomposite films and their abbreviations used in the entire article are given in table 1.

2.5 *Materials characterization*

Fourier transform infrared (FT-IR) spectra of the films were recorded on a FTIR Spectrophotometer (NEXUS 670) in the range of 4000–400 cm^{-1}. The morphologies of samples were evaluated by scanning electron microscope (SEM; HITACHI S-3000H) and transmission electron microscope (TEM) TECNAI-G2 (model T-30). The mechanical

Table 1. Abbreviations of the newly prepared four types of KCG/SiO$_2$ nanocomposite films.

Nanocomposite films	Abbreviation
KCG/SiO$_2$ (0 wt%)	CS0
KCG/SiO$_2$ (1 wt%)	CS1
KCG/SiO$_2$ (3 wt%)	CS3
KCG/SiO$_2$ (5 wt%)	CS5

properties experiment was performed using a universal material testing system (UTM, H10KS, Tinius Olsen) at room temperature according to ASTM D638-03 method. The MU of the nanocomposite films was determined using samples cut into small pieces (2 cm × 3 cm). The samples were first dried in a vacuum drier at 60°C for 2 days. The water contact angle measurements of samples were performed using a Goniometer (GBX, Digidrop) apparatus at ambient temperature. The antimicrobial activity of KCG, nanocomposite films was tested by an inhibition zone method. Food pathogenic bacteria *S. aureus* and *E. coli* were used for the antimicrobial activity of the films. For qualitative measurement of antimicrobial activity, the film samples were punched to make disks (diameter 10 mm), the antimicrobial activity was determined using agar diffusion assay [16].

3. Results and discussion

3.1 *FT-IR spectroscopy*

FT-IR analysis was performed to examine the interactions between KCG and SiO_2 nanoparticles. Figure 1 shows FT-IR spectra of the KCG nanocomposite films. The spectra of KCG films displayed characteristic peaks in the range of 3360–671 cm^{-1}. The characteristic broad absorption band at about 3360 cm^{-1} was attributed to the stretching of hydroxyl (O–H) groups [17]. The intense peak appeared at 2910 cm^{-1}, which was due to the stretching of C–H associated with the ring of methane hydrogen atoms [18]. However, some of the peaks were shifted to higher and lower wavenumber with addition of SiO_2 nanoparticles. The other peaks appeared in the range 1087–465 cm^{-1}, which were due to Si–O group in the SiO_2. For example, in the FT-IR of KCG-based films peaks at 3360, 2910, 1650 and 1040 cm^{-1} were shifted to 3370, 2935, 1669
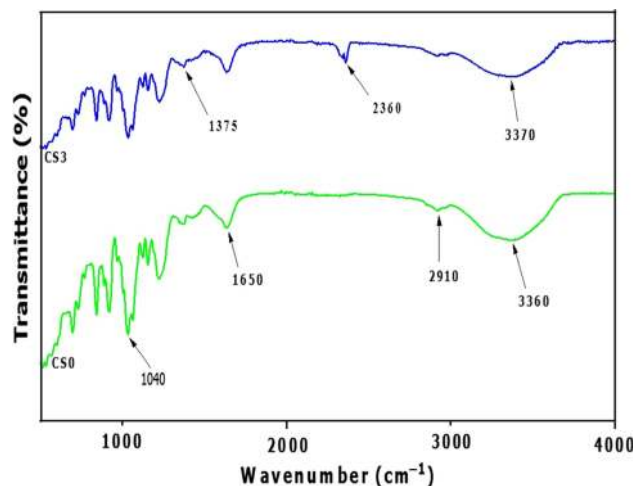

Figure 1. FT-IR spectra of KCG/SiO$_2$ films containing 0 and 3 wt% of SiO$_2$ nanoparticles.

and 1050 cm^{-1}, respectively. Dispersion of the nano-filler is one of the most critical factors in determining the properties of nanocomposites [10].

3.2 *Morphological properties*

Figure 2 shows the SEM and TEM images of synthesized SiO$_2$ nanoparticles, the particle size is 60 nm and shape is like a disk. Figure 3 shows the SEM micrographs of different percentages of SiO$_2$ (1–5 wt%) nanoparticles. The polymers were found immiscible (figure 3a) at the first stage. The smoothness of surface was further improved after the incorporation of SiO$_2$. The surface smoothness was increased up to the addition of SiO$_2$ (5 wt%; figure 3c). The surface of KCG loaded with 5 wt% SiO$_2$ appeared less smoother compared to 3 wt% of SiO$_2$ nanoparticles. The agglomeration occurred at higher
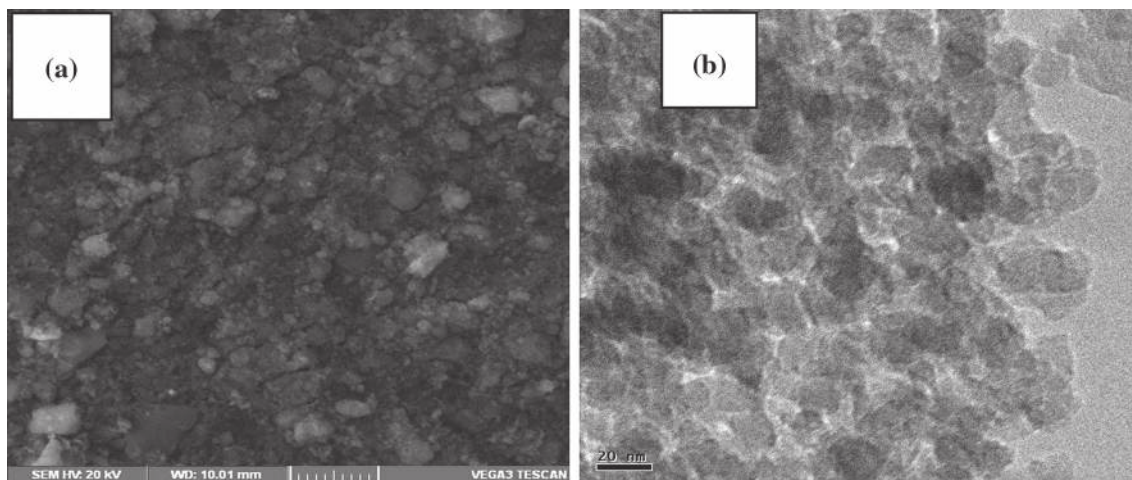

Figure 2. (**a**) SEM and (**b**) TEM images of synthesized SiO$_2$ nanoparticles.
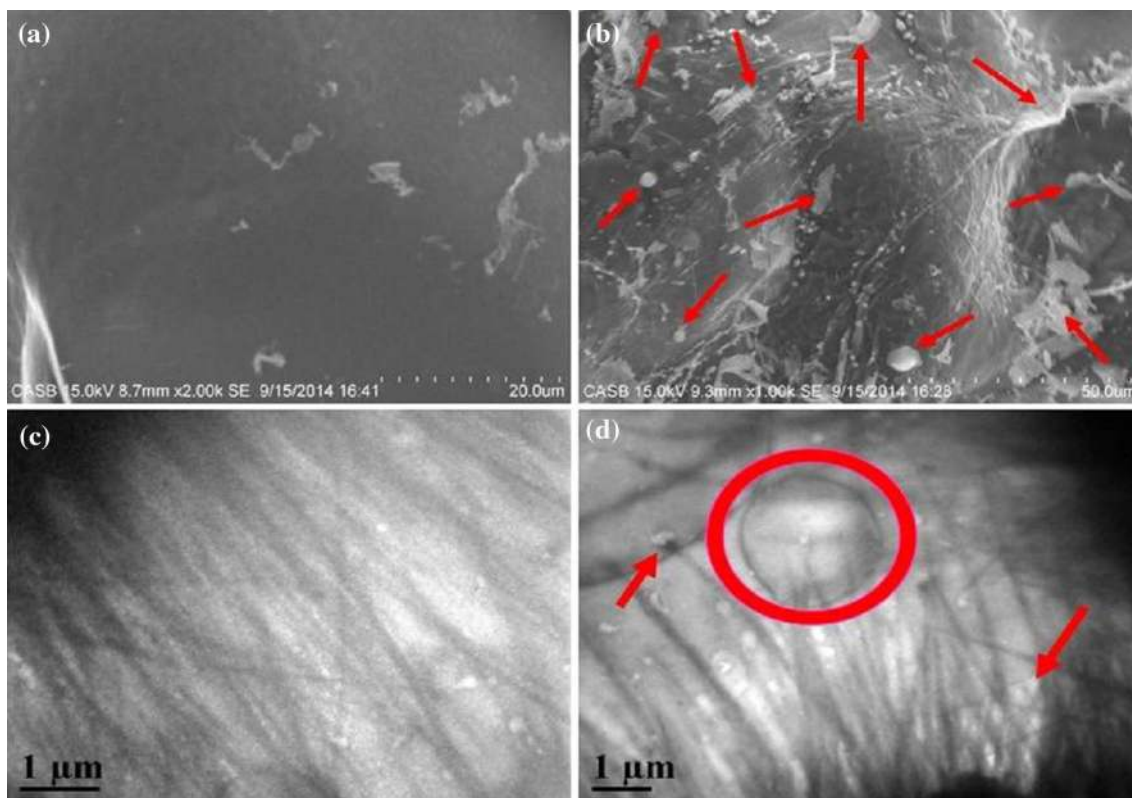

Figure 3. (**a, b**) SEM and (**c, d**) TEM micrographs of KCG/SiO$_2$ NPs containing 0 and 5 wt% of SiO$_2$, respectively.

percentage of SiO$_2$ loading, which might be due to the surface interaction between SiO$_2$ nanoparticles. Similar agglomeration of SiO$_2$ nanoparticles at higher percent of loading was observed. TEM micrographs of polymer blend loaded with KCG different percentages of SiO$_2$ (1–5 wt%) are shown in figure 3. The SiO$_2$ nanoparticles are present as black spots in the figures. At lower percentage of SiO$_2$ loading (1 wt%), a good dispersion of SiO$_2$ nanoparticles was observed. SiO$_2$ nanoparticles were found to disperse well in KCG matrix. At higher percentage of SiO$_2$ (5 wt%) loading, an agglomeration of the nanoparticles was observed. The agglomeration occurred due to the surface interaction among the nanoparticles.

3.3 *MU properties*

The MU at equilibrium and 50% RH is plotted in figure 4a for the nanocomposite films with SiO$_2$ nanoparticles. The influence of SiO$_2$ on the carrageenan moisture absorption was clarified. It was observed that the MU values for pure carrageenan films were 35%, indicating that moisture is absorbed by the hydrophilic biopolymer in the film as well as cavities of the interface. Moreover, when the SiO$_2$ nanoparticle was incorporated, moisture absorption of the carrageenan polymers became lower. This suggested that the addition of SiO$_2$ had an inhibitory effect on the base polymers, which reduced the number of available –OH groups for interaction with migrating water molecules. Another reason for less water

Figure 4. (**a**) Moisture uptake at equilibrium and (**b**) water contact angle of KCG/SiO$_2$ films with different addition of SiO$_2$.

absorption could be the hydrophobic nature of SiO$_2$ nanoparticles.

3.4 *Water contact angle study*

The pure KCG film presented a lower contact angle value of 60.2°, as expected due to the hydrophobic character of KCG. The contact angles increased with the increase of SiO$_2$ nanoparticle contents. However, when the content of SiO$_2$ increased from 0 to 5 wt%, the contact angle increased by only 19°. The dispersion of SiO$_2$ in KCG may explicate the above results. Thus, the surface of nanocomposite films was nearly the same as that of the neat KCG, and the contact angle improved slightly. However, when the content of SiO$_2$ was increased to 5 wt%, some SiO$_2$ nanoparticles were not completely blended with KCG. The water contact angle of nanocomposites increased with the increase of SiO$_2$ nanoparticles content from 1 to 5 wt%, as shown in figure 4b. In addition, the surface hydrophobicity of SiO$_2$ is better than that of the polymers, which probably reduce the diffusion of water molecules in the polymer matrix.

3.5 *Mechanical properties*

To further support the conclusion that SiO$_2$ nanoparticles exhibit strong interactions with KCG chains, the mechanical strength of the KCG/SiO$_2$ nanocomposite films are compared with that of pure KCG film. The obtained tensile strength values are plot with ASTM D638-03 standard deviation, the results are shown in figure 5. It can be seen that with the addition of SiO$_2$ from 0 to 5 wt%, the tensile strength of the carrageenan films sharply increased from 46.3 to 53.9 MPa, while the elongation at the break increased slightly (less than 5%). However, when the SiO$_2$ nanoparticles exceed 5 wt%, the tensile strength decreases with increase in SiO$_2$ wt%. SiO$_2$ nanoparticles agglomerates and disrupts the homogeneity of the materials at higher concentrations [19–22]. It should be noted that all the carrageenan nanocomposite films have a higher tensile strength than pure carrageenan film, as a result of the strong hydrogen bonding interactions between SiO$_2$ nanoparticles and KCG matrix. The increase in the mechanical strength of the composite films is mainly attributed to the physical attraction between the components. It can also be seen that the elongation at break of nanocomposite films increased with an increase in SiO$_2$ loading from 0 to 5 wt%.

3.6 *Oxygen transmission rate*

The oxygen permeability is one of the most important property of a packaging material to check its suitability for different applications. For the KCG/SiO$_2$ films, the oxygen transmission rate (OTR) values were measured and it is represented in figure 6. In a packaging material, oxygen permeability is one of the most important properties for deciding its suitability for various applications. For KCG polymer film, the average OTR value was 2109.74 cc m^{-2} per 24 h.
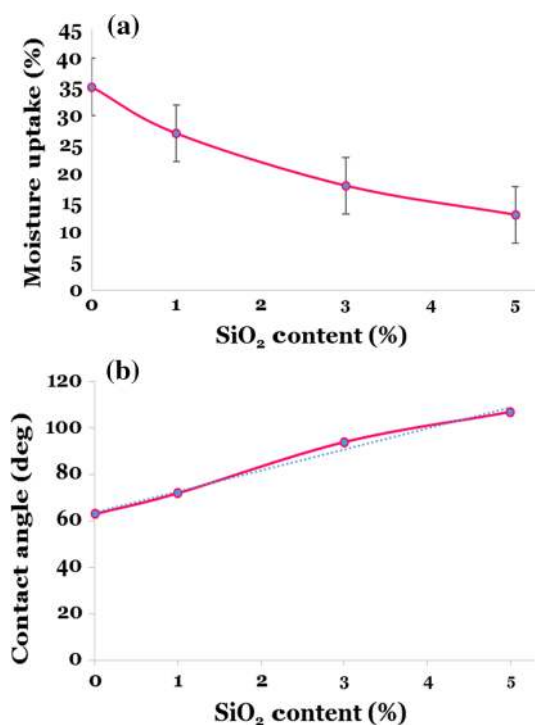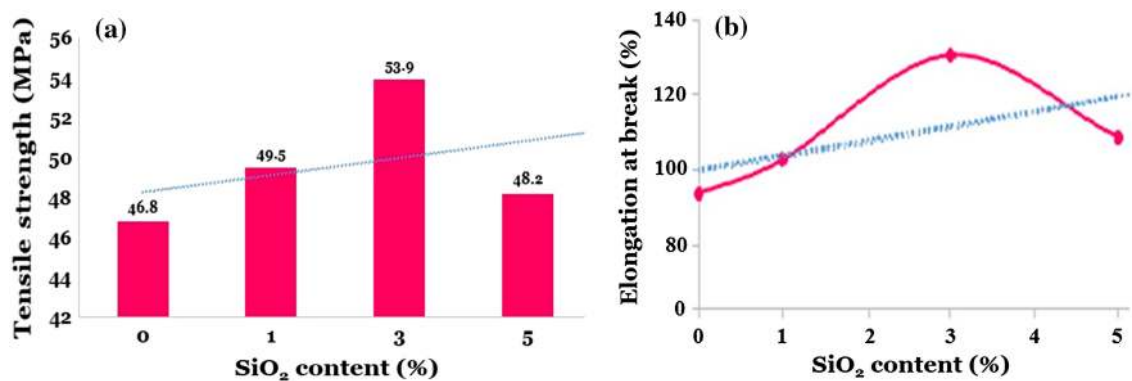
Figure 5. Mechanical strength of KCG/SiO$_2$ films with different wt% of SiO$_2$ nanoparticles.
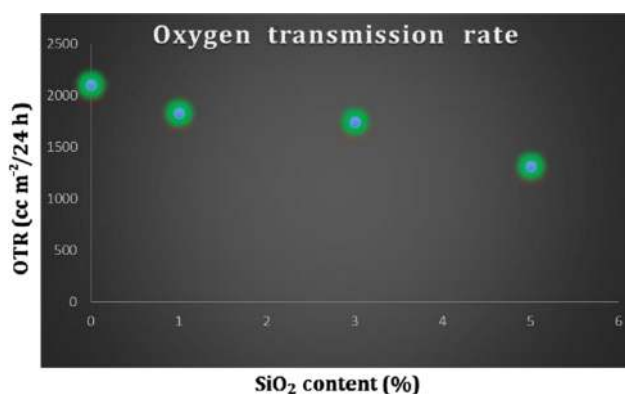

Figure 6. Oxygen transmission rate of the KCG containing (1, 3 and 5 wt%) SiO$_2$ nanoparticles.

The control KCG has high oxygen permeability, but the decrease in OTR of nanocomposite films could be attributed to the generation of tortuous path for the permeation of oxygen molecules in the presence of SiO$_2$ into the KCG biopolymer matrix. The highest value of 2109.74 cc m^{-2} per 24 h was observed in 0 wt% of SiO$_2$ nanoparticles. It was noted that the oxygen transmission rate decreased with increase of SiO$_2$ content (1, 3 and 5 wt%). These results were most important and showed that, if SiO$_2$ nanoparticles were increased the value of oxygen transmission rate also decreased. On the other hand, excess of SiO$_2$ content was a likely cause of phase separation, poor particle fillers distribution and larger agglomerates formation, which led to lower OTR as proven by decreased oxygen transmission rate (1, 3 and 5 wt%).

3.7 *Antimicrobial activities*

The antimicrobial activity of the prepared nanocomposite films by the disk method against two food pathogenic bacteria *E. coli* and *S. aureus* was determined. The KCG film did not show clear microbial inhibition zones for *E. coli* and *S. aureus* (figure 7), reflecting no antimicrobial activity for these materials. The KCG/SiO$_2$ film showed microbial
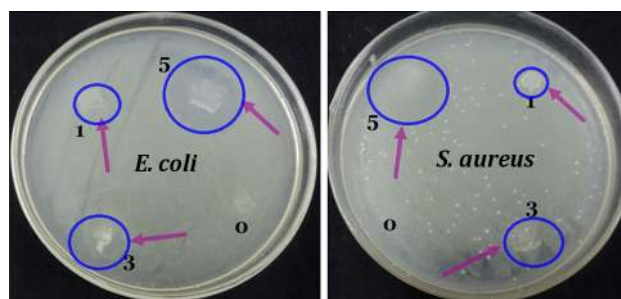

Figure 7. Photograph of antimicrobial test results of KCG/SiO$_2$ nanocomposite films against *E. coli* and *S. aureus*.

Table 2. Effect of SiO$_2$-based antimicrobial films on the inhibition zones.

Strain	Inhabitation zone (mm)			
	CS0	CS1	CS3	CS5
E. coli	—	9.2	11.7	13.0
S. aureus	—	10.1	12.5	13.5

inhibition zones against the two microorganisms in the disk method (table 2) [23,24]. The SiO$_2$ nanoparticle-based films possessed good antimicrobial activity. This property will be very favourable for the applications of the novel antimicrobial packaging material. The mechanism involves the dissociation of the antimicrobial agents from the SiO$_2$ nanoparticles surface and exertion of their antimicrobial effects on bacteria in suspension. Therefore, KCG/5 wt% SiO$_2$ nanocomposite film shows excellent antimicrobial activity against both microorganisms.

4. Conclusions

A novel, homogeneous and reinforced KCG nanocomposite film containing SiO$_2$ nanoparticle was successfully prepared from KCG/SiO$_2$ solutions. Both FT-IR spectra and SEM

images revealed that there was a strong interaction between SiO_2 and KCG chains. The TEM image showed homogeneous dispersion of SiO_2 in the KCG matrix. The results of tensile strength tests demonstrated that the tensile strength of the nanocomposite films was larger than that of pure carrageenan film and showed at first increasing, then decreasing tendency with the increase in SiO_2 content, the maximum value was at 3 wt% SiO_2 content. In addition, the carrageenan nanocomposite films exhibited better hydrophobicity (contact angle) and a lower value of MU than pure carrageenan. This study demonstrates a facile and commercial method to prepare environmentally friendly KCG nanocomposites with high-performance properties with potential for applications in the packaging and functional material fields.

Acknowledgements

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