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Multi-Properties of Chitosan/Montmorillonite Composite Films Incorporated with Virgin and Modified Montmorillonite

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Abstract

Chitosan (CTS) composite films were prepared by blending CTS with virgin or modified montmorillonite (vMMT or mMMT, respectively) and then spin coating. XRD analysis showed a good intercalation of CTS and the mMMT in the depolymerized 15 kDa CTS/mMMT composite. The tensile strength and rigidity of the CTS/vMMT and CTS/mMMT composite films increased, whilst the elongation at break decreased, with increasing levels of vMMT or, especially, mMMT from 0.1 to 2% (w/w). Both types of CTS/MMT composite films displayed a decreased oil and water absorption with increasing levels of incorporated vMMT or mMMT. Some aggregation of vMMT but not mMMT was observed by SEM analysis at a MMT content from 1% (w/w) upwards in the CTS/MMT composite films. The growth of spores and subsequent mycelia of the plant pathogenic fungi, *Colletotrichum gloeosporioides,* through the CTS, CTS/vMMT and CTS/mMMT composite films was inhibited.

Keywords: Chitosan, Depolymerized chitosan, Montmorillonite, Composite film

Introduction

In recent years an increasing interest in bioplastics has developed, which is mainly due to the awareness of the problems of disposal of the waste non-biodegradable petroleum-based plastics, and the non-renewable and limited resources of their fossil fuel origins. Indeed, petroleum-based plastic wastes require a long time for degradation (100’s to 1000’s of years depending upon the plastic and local environment) and so most of them end up over burdening landfill sites or polluting the sea. One approach for solving this problem is to use biomaterials instead of non-renewable polymers. Among the various natural polymers, chitosan (CTS) is considered as one of the most promising candidates for future biodegradable materials because of its attractive combination of a ready availability, non-toxicity, relatively price and good performance characteristics.CTS is chemically identical to cellulose except that the hydroxyl groups in the cellulose molecule are substituted with amino groups in CTS. Normally, CTS dissolves in dilute solutions of most organic acids($\leq$ pH 5.5), such as acetic acid, formic acid, etc, as in acid solutions the amine groups of CTS are protonated to $-NH^{3+}$ leading to its hydrophilic and cationic properties. Since most other soluble biopolymers become anionic in water, CTS cations exhibit a good affinity for other biopolymers.

Because of it’s biocompatibility, biodegradability, antimicrobial activity and non-toxicity, CTS has been extensively investigated for several decades for various uses in biomaterials, wastewater treatment, cosmetics, food packaging and textiles.(1) However, CTS films typically have poor mechanical properties compared to those of synthetic polymers, due to their hydrophilic nature and their sensitivity to the moisture content, both of which are difficult to control. In order to improve the mechanical properties and thermal stability, CTS can be modified by several methods, such as blending with synthetic(2-4) ornatural polymers.(5-6), or with inorganic fillers.

Clay is a cheap natural raw material that has been widely used for many years as an inorganic filler for plastics and rubbers to reduce the polymer consumption and cost. Montmorillonite (MMT), the main component of

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bentonite, is a layered aluminosilicate mineral that belongs to the montmorillonite/smectite group of clay minerals. The crystals of MMT consist of three layers: a silicon tetrahedron, an aluminum octahedron and another silicon tetrahedron. The unit structure is a very thin platelet (about 10 Å [1 nm] thick, but over 200 times that in width), with the stacks of clay platelets being held tightly together by electrostatic forces. Under the appropriate conditions, the gallery spaces can be filled with monomers, oligomers or polymers. Its advantages of a high surface area, large aspect ratio and a platelet thickness of 10 Å make it suitable for reinforcement purposes.(7)

The aim of this research was to evaluate the performance of CTS/MMT composite films which incorporated either virgin MMT (vMMT) or modified MMT (mMMT).Both types of CTS/MMT composite films were prepared by spin coating, and their morphological, structural and functional properties were then evaluated.

Materials and Experimental Procedures

Materials

The CTS powder, with a deacetylation degree of 95% and a molecular weight of 100 kDa, used in this investigation was purchased from Seafresh Chitosan(Lab) Co., Ltd. (Thailand). Premium grade MMT clay, under the trade name of SAC-1, with a cation exchange capacity (CEC) of 55 meq/100 g and a moisture content of 8-12% was supplied from Thai Nippon Chemical Industry Ltd. (Thailand). Hydrochloric acid and acetic acid (analytical grade) were purchased from J.T. Baker (Thailand).

Preparation of the Bulk CTS Solution

The bulk aqueous CTS solution was prepared by dissolving 0.5 g of CTS powder in 100 ml of 1% (v/v) acetic acid solution and stirring with a magnetic stirrer for 24 hours. The CTS solution was then filtered to remove the foam and undissolved impurities.

Preparation of a Depolymerized CTS Solution

An aqueous solution of CTS, having a molecular weight of 15 kDa characterized by Gel Permeation Chromatography was prepared by dissolving 0.5 g of CTS in 100 ml of 20% (v/v) conc. HCl in distilled water and stirring at with a magnetic stirrer for 24 hours until the CTS was completely dissolved.

Modification of MMT

One gram of MMT was dispersed in 10 ml of distilled water and stirred for 30 min. The depolymerized CTS solution, as mentioned above, was then added to the MMT suspension, and the mixture was stirred at 2500 rpm in a hi-speed mixer at room temperature for 1 hour to separate the MMT-CTS complex from the solution. Following harvesting by centrifugation, the precipitate was washed with distilled water and then dried at 50°C for 48 hours, prior to being ground and sieved through a 200 mesh sieve. This preparation was used as the mMMT throughout this study. In addition, mMMT was prepared with a bulk CTS having a molecular weight of 100 kDa, performed as mentioned above except for changing the depolymerized CTS solution to the bulk CTS solution. This mMMT with bulk CTS preparation was used as a test sample for X-ray diffraction (XRD) analysis.

Preparation of CTS Films

CTS films were prepared by dissolving 5 g of CTS powder in 100 ml of 30% (v/v) acetic acid solution and stirring in a hi-speed mixer at 2500 rpm for 1 hour. CTS films were then derived from this solution by spin coating and dried at room temperature for 72 hours.

Preparation of CTS/vMMT and CTS/mMMT Composite Films

CTS/vMMT composite films were prepared by mixing 5% (w/v) CTS solution in 30% (v/v) acetic acid with 0.1%, 0.25%, 0.5%, 1% or 2% (w/w) of vMMT and then stirring at 2500 rpm for 1 hour. The CTS/vMMT composite films were derived from the suspension by spin coating and dried at room temperature for 72 hours.

CTS/mMMT composite films were prepared as above, except using the mMMT derived from depolymerized CTS (see above) in place of the vMMT.

Characterization of CTS, CTS/vMMT and CTS/mMMT Composite Films

XRD measurements were taken directly from the CTS powder, vMMT, and the mMMT derived from both bulk 100 kDa CTS and the depolymerized 15 kDa CTS. The test was performed using a PW3710 Philips diffractometer with CuK$_\alpha$ radiation ($\lambda = 0.1542$ nm) in a sealed tube operated at 40 kV and 30 mA. The diffraction curves were obtained from 0 to 40° at a scanning rate of 2° min^{-1}.

For the mechanical properties, the tensile strength at maximum load, tensile modulus and the percent elongation at break of the film samples were measured with a Universal Testing Machine (Model LLOYD LR 100K). Film specimens of 150 mm x 15 mm size were conditioned for 24 hours at 25°C and 60% relative humidity before testing. The test was carried out according to the standard method of ASTM D 882, with an initial grip separation of 100 mm, a crosshead speed of 10 mm min^{-1} and a load cell of 100 N. At least five specimens of each sample were tested and the results were averaged to obtain a mean value.

The water absorption of the CTS and the different CTS/MMT composite films was determined following the standard method of ASTM D 570-95. For evaluation of the water absorption ability, film specimens of 76.2 mm x 25.4 mm size were placed in a desiccator for 24 hours, weighed, and then immersed in distilled water at ambient temperature (~28°C) for 24 hours. The test specimens were removed, patted dry with a dry lint cloth and weighed immediately. The water absorption was then expressed as the percentage increase in the weight.

The oil absorption was determined as the amount of sunflower oil absorbed by the film samples under the same testing procedure as mentioned above for the water absorption, except for changing distilled water to sunflower oil.

The water contact angles of the CTS film and the CTS/vMMT and CTS/mMMT composite film samples were measured using a CAM-PLUS MICRO (Tantec, Inc.) machine. A zero contact angle represents complete surface wetting, whilst an angle between 0° and 90° indicates that the droplet is spreading (due to molecular attraction) and contact angles of greater than 90° indicates the liquid is beading or shrinking away from the solid surface.

The oil contact angle was evaluated as outlined above for the water contact angle, except for changing the distilled water to sunflower oil.

Scanning electron microscopy (SEM) based analysis was used to study the surface morphology of the formed CTS, CTS/vMMT and CTS/mMMT composite film samples. The SEM samples were cut from composite films, mounted on an aluminum stub with double-sided adhesive tape and coated with a thin layer of gold to enhance their conductivity. Images were taken using a JEOL JSM-5410LV scanning electron microscope, and were scanned at an accelerating voltage of 15 kV.

Antifungal Activity of the CTS, CTS/vMMT and CTS/mMMT Composite Films

The asexual anamorph form of the plant pathogenic fungus, *Colletotrichum gloeosporioides* (Penz.) Penz and Succ. (Melanconiales) was directly isolated from infected chili pepper plant (*Capsicum annuum* Linn.) and maintained on potato-dextrose-agar (PDA). The culture was derived from a single spore and is available from the plant pathology laboratory upon request. The isolates were identified using morphology and colony growth characteristics. After growth, the fungus was maintained on PDA dishes at room temperature for 7 days. The isolates were transferred to a slide and then placed on the respective CTS, CTS/vMMT and CTS/mMMT composite film specimen followed by the cover slide, respectively. The dish was maintained on a PDA plate at room temperature for 7 days, whereupon the fungus germination through the film was investigated under a light microscope by covering the film specimen with a slide. The rational behind this test was to investigate the ability to use these CTS, CTS/vMMT and CTS/mMMT composite films for food packaging.

Results and Discussion

X-ray diffraction (XRD) of CTS, vMMT and the two mMMT preparations

The basal peak position, d-spacing and XRD patterns of the bulk CTS, vMMT and the bulk CTS/mMMT and depolymerized CTS/mMMT composites are summarized in figure 1.

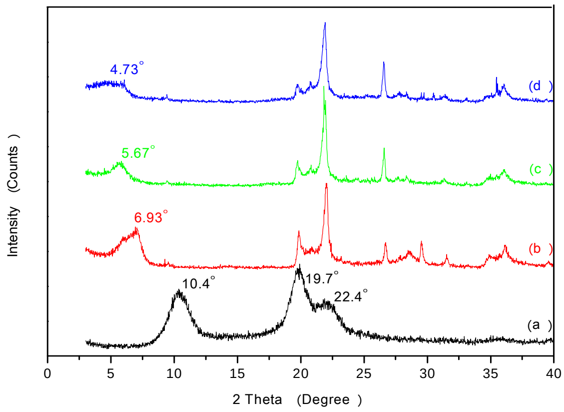


Figure 1. Representative XRD patterns of the: (a) bulkCTS,(b)vMMT,(c)bulk CTS/mMMT composite and(d) depolymerized CTS/mMMT composite.

The semicrystalline character of CTS is revealed from its respective diffractogram (Figure 1 (a)), which showed three major characteristic peaks at 2θ = 10.4°, 19.7° and 22.4° that are characteristic for CTS.(8)The peak at approximately 2θ = 10.4° was assigned to crystal form I, and the reflection peak that appeared at around 2θ = 19.7° corresponds to crystal form II. The unit cell of crystal form I, characterized by $a = 7.76$, $b = 10.91$, $c = 10.30$ A° and $\beta = 90^\circ$, was larger than that of crystal form II (characterized by $a = 4.4$, $b = 10.0$, $c = 10.30$ Å and $\beta = 90^\circ$). In this study, the intensity of the crystal form II peak at about 2θ = 19.7° was very strong, which implied that the CTS was in a crystalline state.

The XRD patterns of the vMMT, bulk CTS/mMMT and depolymerized CTS/mMMT are shown in Figure 1 (b), (c) and (d), respectively, where the vMMT showed a strong diffraction peak at 2θ = 6.93°, corresponding to the 001 lattice spacing of the silicate layer of 12.75 Å in MMT, as suggested by Changyu, *et al.*(9) Since CTS is polycationic in acidic environments, it can easily be adsorbed onto the negatively charged surface of the MMT where cationic-exchange between the cationic CTS and Na^+ and Ca^+ ions residing in the interspacing layer can take place. The XRD pattern of the bulk CTS/mMMT shows the diffraction peak at 2θ = 5.67°, corresponding to the lattice spacing of the silicate layer of 15.57 Å. The interlayer distance of the depolymerized CTS/mMMT was larger than that of the vMMT, with a diffraction peak shifted further to 2θ = 4.73°, corresponding to the lattice spacing of the silicate layer of 18.67 Å. The larger interlayer values for these two different mMMTs, compared to the vMMT, indicate the likely formation of an intercalated nanocomposite. In general, a higher degree of basal spacing expansion usually results in a higher chance of polymer intercalation and so a higher possibility of a layered-silicate delamination in the polymer matrix. That the mMMT derived from the depolymerized CTS molecule had a lower diffraction peak indicates that the depolymerized CTS chains were intercalated into the silicate layers and the coherent order of the vMMT was destroyed more.

Mechanical Properties of the CTS and CTS/MMT Composite Films.

The effect of the inclusion of different vMMT or mMMT contents on the tensile strength, Young's modulus and elongation at break of the CTS/MMT composite films were investigated, and the results are summarized in Figures 2, 3 and 4, respectively.

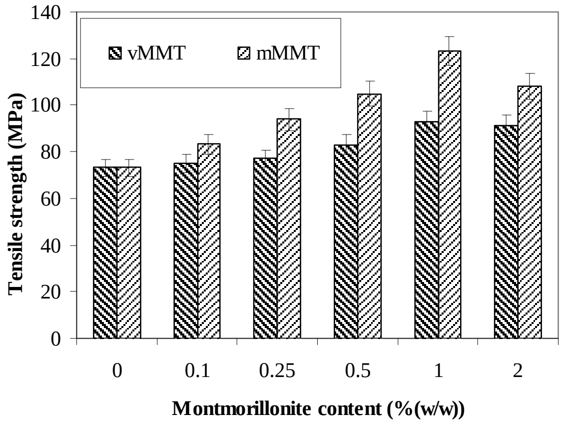


Figure 2. The effect of inclusion of different amounts of vMMT or mMMT into CTS on the tensile strength of the resultant CTS/MMT composite films.

The tensile strength of the CTS/vMMT composite films slightly increased with increasing amounts of vMMT up to a maximum (92.5 MPa) at a 1% (w/w) vMMT loading Figure 2, which represents an increase in the tensile strength compared to that for the CTS films of 27%. This then numerically, but not statistically significantly, decreased slightly to 90 MPa when the vMMT content was increased to 2% (w/w). Thus, the vMMT presented interfacial adhesion with the CTS film and could insert into the CTS matrix and reinforce the tensile strength of the CTS/vMMT composite films. However, at 2% (w/w) vMMT a heterogeneous dispersion of the vMMT in the CTS matrix results, with a resulting reduced stress distribution from CTS to the vMMT and so a reduced tensile strength.

Similar to that observed with the CTS/vMMT composite films, the tensile strength of the CTS/mMMT composite films increased with increasing levels of mMMT up to a maximum (124 MPa) at 1% (w/w) mMMT, then decreased to 108 MPa at a 2% (w/w) mMMT content. Note that the tensile strengths of the CTS/mMMT composite films were higher than those of the CTS/vMMT composite films with corresponding MMT levels. It is noteworthy that the mMMT had a more homogeneous dispersion in the CTS matrix than the vMMT.

The Young's modulus, a marker of the rigidity of these films, of the two types of CTS/MMT composite films, somewhat akin to the tensile strength, increased slightly with increasing levels of vMMT or mMMT up to 1% (w/w), at which level an approximately 14% and 98% increase, respectively, was observed compared to that seen for the pure CTS films Figure 3. Thereafter, a slight reduction compared to that seen with 1% (w/w) vMMT or mMMT, was observed in the Young's modulus at 2% (w/w) vMMT or mMMT. Furthermore, the rigidity of the CTS/mMMT composite films was significantly higher than those of CTS/vMMT composite films at the same MMT content. This may be because the mMMT derived from the depolymerized CTS provided a better compatibility and increased the interfacial adhesion between the between the mMMT and CTS, and so led to a higher rigidity of the composite film compared to either CTS or the CTS/vMMT composite films.

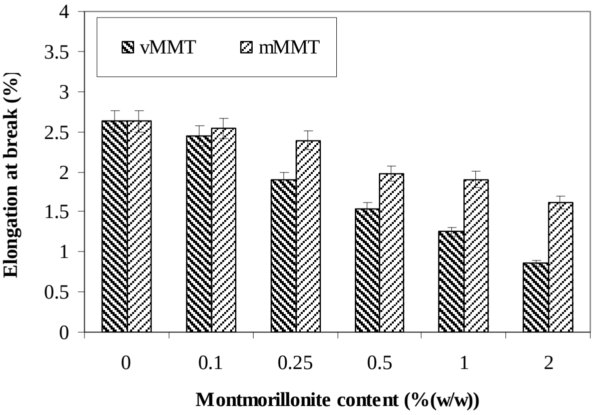


Figure 3. The effect of inclusion of different amounts of vMMT or mMMT into CTS on the Young's modulus of the resultantCTS/MMT composite films.

The elongation at break of the CTS/vMMT and CTS/mMMT composite films showed a slightly different trend to that seen for the rigidity and tensile strength Figure 4. Thus, the elongation at break decreased with increasing levels of vMMT or mMMT content in the composites, and this was significantly more marked for the mMMT than the vMMT. This may be because once incorporated with the chitosan, the vMMT and mMMT reduce the extensibility of the matrix in the film composites. The resistance created by MMT would then reduce the deformability of the CTS molecules.

Accordingly, when vMMT or mMMT were used as filler in the CTS composite films, they increased the tensile strength and Young's modulus but decreased elongation at break compared to that seen for the CTS films.

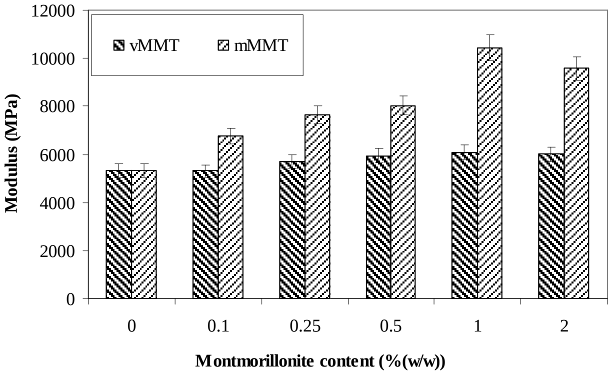


Figure 4. The effect of inclusion of different amounts of vMMT or mMMT into CTS on the elongation at break of the resultant CTS/MMT composite films.

Water and Oil Absorption

The effect of the different types and levels of MMT content on the water and oil absorption of the resulting CTS/MMT composite films obtained is summarized in Table 1. The water absorption of the CTS film was about 112% by weight, with this ability to hold the water molecules being due to the hydrophilic nature of CTS. The water absorption of the CTS/vMMT and CTS/mMMT composite films were decreased slightly as the inclusion level of either vMMT or mMMT increased, and this effect was slightly more marked for mMMT than vMMT. Thus, the addition of vMMT or mMMT into the CTS matrix slightly improved the water resistance of the CTS composite film. In addition, the larger interlayer distance between the individual silicate layers of vMMT or mMMT were not able to hold the water, but blocked the area on the CTS film to hold and interact with water molecules. Likewise, the oil absorption of the CTS/MMT composite films decreased with increasing levels of vMMT or, especially, mMMT. These results could be attributed to the particles of vMMT or mMMT inserted into the CTS film blocking the ability of CTS to adhere to the oil.

Composition of films	Water absorption	Oil absorption
CTS	112.4 ± 5.0	6.06 ± 0.80
CTS/vMMT 0.1% (w/w)	111.3 ± 5.5	6.00 ± 0.22
CTS/vMMT 0.25% (w/w)	110.0 ± 3.2	5.68 ± 0.17
CTS/vMMT 0.5% (w/w)	97.3 ± 0.6	5.62 ± 0.16
CTS/vMMT 1% (w/w)	96.3 ± 2.3	5.10 ± 0.30
CTS/vMMT 2% (w/w)	93.5 ± 1.8	5.15 ± 0.38
CTS/mMMT 0.1% (w/w)	101.0 ± 3.4	5.89 ± 0.03
CTS/mMMT 0.25% (w/w)	97.3 ± 2.0	5.66 ± 0.23
CTS/mMMT 0.5% (w/w)	89.8 ± 3.2	5.14 ± 0.66
CTS/mMMT 1% (w/w)	85.3 ± 0.5	5.17 ± 0.42
CTS/mMMT 2% (w/w)	77.3 ± 2.9	4.45 ± 0.27

Table 1. Water and oil absorption (by weight) of the CTS film and of the CTS/vMMT and CTS/mMMT composite films**.**

Water and Oil Contact Angle

The water and oil contact angle on the different CTS, CTS/vMMT and CTS/mMMT composite films (Table 2) were used as a marker for the surface wettability of these films. The water contact angle of the CTS film was about 110º, suggesting that the CTS film had a good water surface wettability, presumably due to the hydrophilic nature of CTS. The water contact angle was increased with the inclusion of increasing levels of either vMMT or mMMT. However, at the higher vMMT or mMMT inclusion levels of 1 and 2% (w/w), the addition of mMMT increased the water contact angle slightly more than that with the vMMT. Thus, the addition of mMMT increases slightly more hydrophobicity of the surface of the CTS composite films

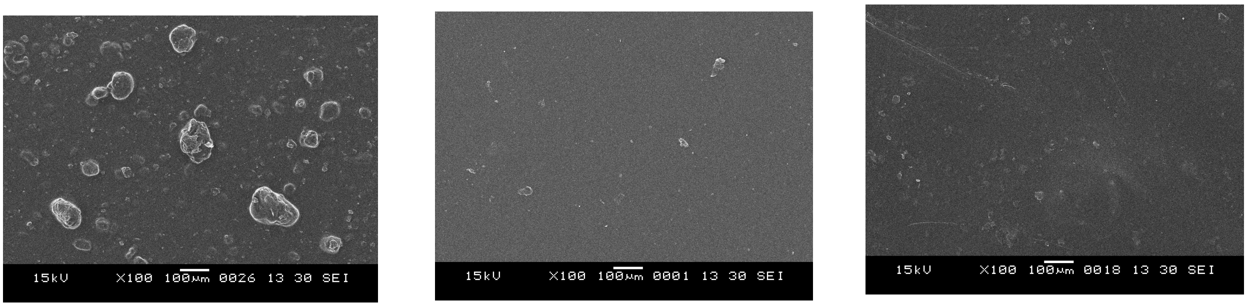
The oil contact angl of the CTS composite films also increased with in creasing vMMT or mMMT contents in the composite, and again was perhaps slightly more marked for mMMT than for vMMT at higher (1and2%(w/w)) MMT inclusion levels. These results could be attributed to the particles of vMMT or mMMT inserted into the CTS film blocking the ability of oil to adhere to the CTS. Moreover, the larger interlayer distance between the individual silicate layers of the mMMT would not be able to hold or capture as much water or oil as that compared to the CTS films.

Composition of films	Water contact angle (°)	Oil contact angle (°)
CTS	110.0 ± 0.0	36.0 ± 0.0
CTS/vMMT 0.1% (w/w)	120.3 ± 0.6	46.0 ± 0.0
CTS/vMMT 0.25% (w/w)	129.3 ± 1.2	46.7 ± 1.2
CTS/vMMT 0.5% (w/w)	133.3 ± 1.2	52.0 ± 0.0
CTS/vMMT 1% (w/w)	134.0 ± 0.0	56.0 ± 0.0
CTS/vMMT 2% (w/w)	136.0 ± 0.0	57.3 ± 1.2
CTS/mMMT 0.1% (w/w)	120.0 ± 0.0	47.3 ± 1.2
CTS/mMMT 0.25% (w/w)	130.0 ± 0.0	50.0 ± 0.0
CTS/mMMT 0.5% (w/w)	134.0 ± 0.0	54.0 ± 0.0
CTS/mMMT 1% (w/w)	136.0 ± 0.0	58.0 ± 0.0
CTS/mMMT 2% (w/w)	138.0 ± 0.0	70.0 ± 0.0

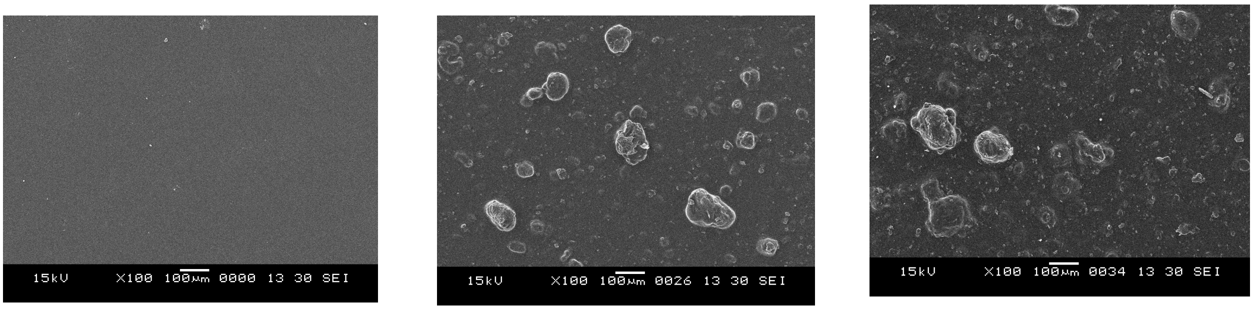
Table 2. Water and oil contact angles of the CTS film and of the CTS/vMMT and CTS/mMMT composite films.

Scanning Electron Microscopy (SEM) Based Surface Analysis of the Films

The surface morphology of the CTS film and the CTS/vMMT and CTS/mMMT composite films with different levels of MMT were evaluated by SEM in order to investigate the filler aggregation in the CTS matrix. A 100x magnification of the outer surface of the CTS film appeared relatively smooth, homogeneous and with a continuous matrix without any pores or cracks, and so with a good structural integrity Figure 5. It was flat and compact with very sparsely distributed small particles without any phase separation.



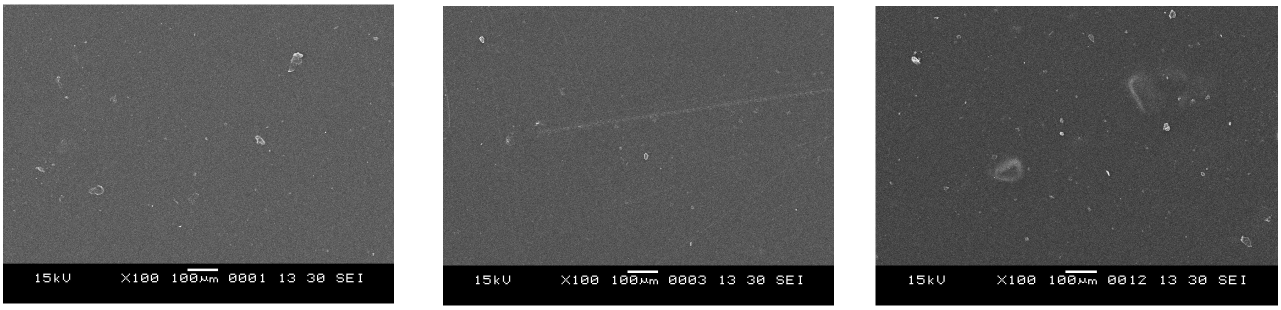
(a) CTS (b)CTS/vMMT 0.1% (w/w) (c) CTS/vMMT 0.25% (w/w)



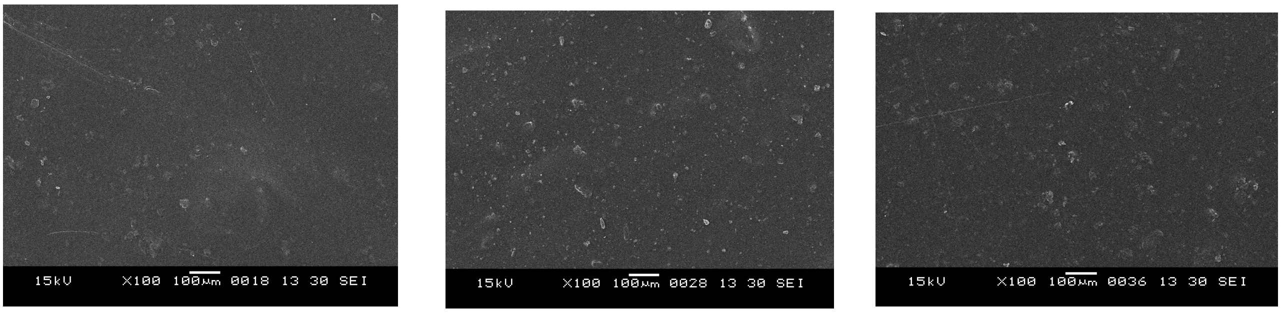
(d) CTS/vMMT 0.5% (w/w) (e) CTS/vMMT 1% (w/w) (f) CTS/vMMT 2% (w/w)

Figure 5. SEM micrographs (x100 magnification) of the CTS/vMMT composite films with vMMT contents of (a) 0% (pure CTS), (b) 0.1%, (c) 0.25%, (d) 0.5%, (e) 1% and (f) 2% (w/w).

A good dispersion of vMMT in the CTS matrix at lower vMMT contents (0.1-0.5% (w/w)) was also evident Figure 5, and likely reflects the hydrogen bonding attractions between CTS and vMMT, resulting in good distribution of the vMMT within the CTS matrix. However, the CTS/vMMT composite films containing 1 and 2% (w/w) vMMT showed a higher level of aggregation of the vMMT. The poorer distribution of vMMT particles in the CTS matrix of the composite at high vMMT contents could be attributed to the formation of a flocculated structure in the composite, due to the hydroxylated edge-edge interactions of the silicate layers formed from the hydrogen bonding interactions between the silicate hydroxylated edge groups and the amino or hydroxyl functional groups in the long chains of CTS (10) . In contrast, the CTS/mMMT composite films showed a better homogenous dispersion of the mMMT within the CTS matrix, even at 1 and 2% (w/w) mMMT levels Figure 6, suggesting a better compatibility of the mMMT in the CTS matrix than that of the vMMT.



(a) CTS (b) CTS/mMMT 0.1% (w/w) (c) CTS/mMMT 0.25% (w/w)

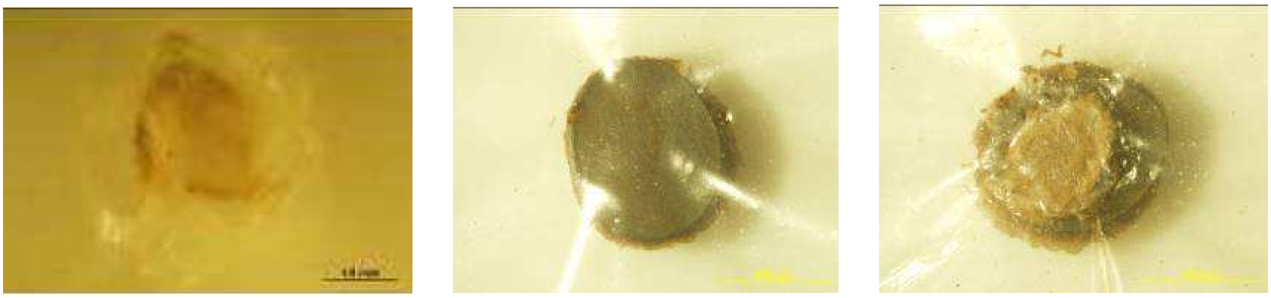


(d) CTS/mMMT 0.5% (w/w) (e) CTS/mMMT 1% (w/w) (f) CTS/mMMT 2% (w/w)

Figure 6. SEM micrographs (x100 magnification) of the CTS/mMMT composite films with mMMT contents of (a) 0.1%, (b) 0.25%, (c) 0.5%, (d) 1% and (e) 2% (w/w).

Antifungal Activity of the CTS and the CTS/vMMT and CTS/mMMT Composite Films Towards Colletotrichum Gloeosporioides

The inhibitory effect of the CTS and of the CTS/vMMT and CTS/mMMT composite films on the spore germination and subsequent mycelium growth of the anamorph (asexual) form of the plant pathogen, *C. gloesporioides* was studied.The images of fungus germination and mycelium growth of *C. gloeosporiodes* on the CTS and the CTS/vMMT and CTS/mMMT composite film at all inclusion levels (0-2% (w/w)) are shown in Figures 7 and 8. The examination results revealed that the underneath of the CTS and the CTS/vMMT and CTS/mMMT composite films were free of germinated spores of *C. gloeosporiodes*. This implied that all three types of film prevented the germination of spores and subsequent growth of *C. gloeosporiodes* mycelia pass through them, and so the incorporation of the vMMT or mMMT into the CTS matrix did not deteriorate the antifungal activity of the virgin chitosan film. This is in accord with the results of Agullo, *et al.*(11-12), who observed that the use of a CTS-based coating could delay the growth of *Alternaria sp.*, *Penicillium sp.* and *Cladosporium sp.* The polycationic property of CTS allows it to interact with negatively charged substances, and so exhibits an antifungal activity on molds.



(a) CTS (b) CTS/vMMT 0.1 % (w/w) (c) CTS/vMMT 0.25% (w/w)

(d) CTS/vMMT 0.5% (w/w) (e) CTS/vMMT 1% (w/w) (f) CTS/vMMT 2% (w/w)

Figure 7. Images of fungus germination on CTS film and on the CTS/vMMT composite films with vMMT contents of (a) 0% (pure CTS), (b) 0.1%, (c) 0.25%, (d) 0.5%, (e) 1% and (f) 2% (w/w).

(a) CTS (b) CTS/mMMT 0.1 % (w/w) (c) CTS/mMMT 0.25% (w/w)

(d) CTS/mMMT 0.5% (w/w) (e) CTS/mMMT 1% (w/w) (f) CTS/mMMT 2% (w/w)

Figure 8. Images of fungus germination on CTS film and on the CTS/mMMT composite films with mMMT contents of (a) 0% (pure CTS), (b) 0.1%, (c) 0.25%, (d) 0.5%, (e) 1% and (f) 2% (w/w).

Conclusions

CTS composite films were made by adding either vMMT or mMMT to CTS in solution and forming the composite film by spin coating. XRD analysis showed a good intercalation of CTS and the mMMT in the depolymerized 15 kDa CTS/mMMT composite. The tensile strength and rigidity (as Young's modulus) were both found to increase, whilst the elongation at break decreased, with increasing levels of vMMT or mMMT in the CTS/MMT composite films, whilst the water and oil absorption were both decreased. These effects are attributed to the MMT particles being embedded in the CTS matrix and so obstructing the ability of CTS to adhere to the water and oil. Inclusion of either vMMT or mMMT into the CTS matrix (as composite films) also increased the water and oil contact angles of the composite films, consistent with the observed lower ability of the composite films to absorb water or oil. Some aggregation of vMMT but not mMMT was observed by SEM analysis at a MMT content from 1% (w/w) upwards in the CTS/MMT composite films. Finally, the CTS and CTS/MMT composite films had some antifungal activity.

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