

# VISCOSITY OF CHITOSAN/MONTMORILLONITE MIXTURES FOR COATINGS FOR PAPERBOARD PACKAGES

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## ABSTRACT

The increasing demand for fresh food has created a need for better packages that improves the food preservation, prevents microbial growth and prolongs the shelf life. A solution to this problem might be to replace the traditional packaging plastics with a biopolymer such as chitosan. Chitosan is a promising biopolymer to use as films or coatings due to its excellent oxygen barrier and film forming abilities. The polycationic property of chitosan makes it antimicrobial at moist conditions. Unfortunately, the oxygen barrier impairs in presence of water vapour. However, added and semi-exfoliated montmorillonite (MMT) may partly compensate the loss of barrier properties. On the other hand, it has previously been shown to reduced film forming ability. The purpose of this study is to investigate how the film forming properties, in terms of e.g. viscosity, is affected by the MMT and chitosan concentrations in coating solution mixtures. The viscosity of chitosan was shown to increase dramatically with the concentration and the solutions were apparently only possible to apply as coatings on paperboards up to 3 wt%. Solutions with higher chitosan concentrations had too high viscosity for application and were also impossible to degas for removal of air bubbles. However, for the solutions with too low concentration, it may absorb into the paperboard. The solution with 3 wt% chitosan appeared to be most appropriate as paperboard coating, and still possible to degas in the vacuum treatment.

## 1. INTRODUCTION

The market of minimally processed food is increasing and as a result also the occurrence of food borne diseases, such as *Listeria monocytogenes* in e.g. meat [1]. The increasing demand for fresh food has created a need for better packages that improves the food preservation, prevents microbial growth and prolongs the shelf life. However, packaging plastics made from petroleum sources have been found to disturb the ecosystem of nature [2]. A solution to this problem might be to replace the traditional packaging plastics with biopolymers.

Chitosan is an interesting biopolymer for production of renewable and biodegradable plastics for packaging applications [3,4]. Chitosan is the deacetylated product of chitin, mainly found in the exoskeleton of e.g. shellfishes [5]. Chitin is the second most abundant polysaccharide in the world after cellulose [6]. The major source for chitin extraction is the exoskeleton of shellfishes and some insects [7]. Chitin can also be found in the cell walls of different fungi such as Mucorales [5].

Chitosan, mainly composed of  $\beta$ -(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units, has a  $\text{NH}_2$ -group in a C-2 position. The high content of OH-groups makes it hydrophilic. Chitosan is soluble in acidic conditions (pH below 6.5), through protonation of the  $\text{NH}_2$ -groups to  $\text{NH}_3^+$  [8]. These make chitosan easy to modify as the  $\text{NH}_3^+$  serve as sites for attachment of anionic groups. This polycationic property also makes chitosan antimicrobial, because it can interact with the negatively charged groups present in bacteria, mold and yeasts [9]. There have been several applications for chitosan developed: For example, as a component in weight reducing drugs because of its ability to bind to fatty acids and fat soluble vitamins [10], and in textiles

since it has an anti-electrostatic effect [11]. It has also been used in e.g. contact lenses, glues, medicines and hair care products [12].

Because of chitosan's excellent film forming abilities, antimicrobial activities and barrier properties, it is interesting as coating for food packages. Chitosan is also a good barrier for oxygen ( $0.6 \text{ mol} \cdot \text{mil} / \text{m}^2 \cdot \text{day} \cdot \text{atm}$ ) [13] because of the high content of hydrogen bonds and its crystallinity.

### **Montmorillonite as an additive**

In this study has also a nanometer-thick mineral flakes been used in order to foremost enhance the oxygen barrier properties, of the chitosan coating material, in moist condition. However, this study focuses on the coating solution itself and its viscosity; the performances of the resulting barrier coated board will be presented in a later report.

The most commonly used clay is montmorillonite (MMT), which is a natural smectic clay composed of 2:1 layered phyllosilicates [15-20]. The layers are about 1 nm thick with a high aspect ratio and consist of two silica tetrahedral sheets and one central octahedral sheet of alumina or magnesia [18-22], linked by shared oxygen atoms [16]. The layers organize themselves into stacks with regular van der Waals gaps between them, called interlayers which normally are 0.3-0.5 nm [16,18,20,21]. Isomorphic substitution within the layers generates a negative charge in the interlayer. The net charge is counterbalanced by cations commonly  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Na}^+$  [22], resulting in hydrophilic properties of the clay [15-21]. To make the silicates useful in nanocomposites, the layers must be separated to attain the highest surface area possible [20,23]. Since MMT belongs to the swelling clays [22] the delamination is normally done by absorbing water or organic species [16,19]. In order to enable intercalation of a polymer into the silicate interlayers coupling agents can be used [24-26], or the inorganic cation can be exchanged by an onium cation [16,20,21,27] to enhance the compatibility between the silicate and the polymer [23]. Ion exchanging makes the clay organophilic and facilitates polymer intercalation within the galleries [16-18,20,21] due to the decreased surface energy [19-21,28,29]. There are generally three routes of intercalate the clay with a polymer; direct mixing (melt intercalation), solution mixing and in-situ polymerization [20,29]. The aim is to achieve an exfoliated morphology, in which the sheets are totally delaminated and uniformly dispersed throughout the polymer matrix, instead of an intercalated structure, where the layers still are ordered but contain extended polymer chains in the interlayer [15,18,20,21,25,30-33]. In an exfoliated nanocomposite the entire surface area of the silicate layer is available to interact with the polymer [25], resulting in that less content of clay is needed to enhance the properties compared to conventional fillers [34,35]. This is generally attained when a great interaction between the silicate and the polymer matrix occurs [23,27], and when the clay content is low [20,25,36]. The intercalation is diffusion controlled [37] and may be influenced by the size of the organic modifier. The longer the chain length of the organic cation is, the larger becomes the interlayer spacing which may ease intercalation and exfoliation if the compatibility is adequate [21,38-40].

Many studies have reported that incorporation of a small amount ( $\leq 5 \text{ wt}\%$ ) inorganic clay minerals into polymer matrices improves e.g. mechanical properties [15,24,25,28,30,36-38,41-57], water and gas barrier properties [36,47,53,58-60], thermal stability [15,25,26,28,31,38,44-46,53-55,61-63], resistance to swelling [28,54] and ion conductivity [44,64]. The reduction in permeability is due to the presence of dispersed silicate layers in the polymer matrix. These particles are



The solutions of 1-5 wt% chitosan were, respectively, mixed in a Waring commercial blender on highest speed for 5 minutes. All solutions were subsequently degassed over night in a vacuum oven (Nuve FN 400, LabRum Klimat AB, Sweden) at room temperature for removal of air bubbles.

*Chitosan solutions with montmorillonite.* 0.09 wt % (i.e. 3 wt% per chitosan dry weight) give exfoliated structure as previously shown [75] and thus used as one three different mixtures: Each of three acetic acid solutions (1 wt%) were stirred with 0.09 wt% MMT for 24 h at ambient temperature. Chitosan was then added to a concentration of 3 wt% for two of the solutions, and to 2 wt% for the other. One of the solutions with 3 wt% chitosan, and the solution with 2 wt% chitosan, were thereafter stirred for 9 h at ambient temperature. The other solution with 3 wt% chitosan was stirred for 9 h at an elevated temperature of 60°C.

*Chitosan films with montmorillonite.* Acidic water solutions of chitosan were prepared by adding 3 g of chitosan and 3 g of acetic in 250 ml of deionized water. The solutions were placed on magnetic stirrer and stirred vigorously for about four hours until the chitosan got dissolved. Each of the natural and modified MMT was solved in a solution of 20 ml deionized water and at least 3.5 ml of ethanol. These solutions were ultrasonicated for 15 minutes, in an Elma Transsonic T420 apparatus, and then poured into the chitosan solution. Subsequently the final solutions were stirred for another 30 minutes and then vacuum degassed to remove any air bubbles. Finally 40 g of the solutions was spread onto level, circular 14 cm diameter petri dishes, getting a dry film thickness of approximately 450  $\mu\text{m}$ . The petri dishes were coated with Teflon™ on aluminum foil, Bytac Type AF-21, received from Saint-Gobain Performance Plastics (USA). The film-forming solutions were dried overnight at room conditions and then conditioned at approximately 23 °C in 50 % relative humidity for 5 days before testing. Blends were prepared with 0, 0.75, 4.5, 10 and 25 wt% of the MMT, based on the dry weight of chitosan.

*Viscosity measurements.* The dynamic viscosity of the chitosan solutions, with or without the montmorillonite, was measured after vacuum degassing by using a Brookfield model DV-1+ viscometer supplied by Chemical Instrument AB (Sweden). The viscosity was determined when the value had become stable. Solutions with chitosan concentrations between 1 wt% and 5 wt% were studied and different spindles from 1 (used for solutions with lower viscosity) to 7 were utilized. 5 solutions of each composition were tested. The viscosity was measured when the spindle rotation was 2.5 rpm, except for the solution with 5 wt% chitosan which was measured at 0.5 rpm. The viscosities of chitosan/MMT solutions were also measured for the three different sample preparation methods.

*Light transmission microscopy.* The morphology of the films was examined by using optical microscopy (OM). Small pieces of each film were cut and placed on microscope slides. Representative sections of each film were analyzed with a Leitz Ortholux POL BK II optical microscope equipped with a Leica CD300 camera. Photos were taken using the computer program Leica IM50 v1.20. The equipments were from Leica Microsystems AB (Sweden).

*X-ray Diffraction (XRD).* X-ray diffractograms of films were obtained in a Siemens D5000 diffractometer with Cu radiation (50 kV, 40 mA). The scanning speed and the step size were 0.15°/min and 0.02°, respectively. The specimen rotation speed was 15 rpm.

*Scanning electron microscopy.* Scanning electron microscopy (SEM) was used in order to study the morphology of the film samples. Small pieces were cut out from each sample and were attached to aluminium carriers with carbon tape. The structures

were depicted directly with an Environmental Scanning Electron Microscope-Field Emission Gun (XL-30ESEM-FEG) obtained from Philips. The working conditions were low vacuum mode with a sample chamber pressure of 0.7 torr. The acceleration voltage was 15 kV, the working distance (WD) was 10 mm and a BSE detector (Backscattered Electrons) was used.

### 3. RESULTS AND DISCUSSION

The optical micrographs of the films in Figure 1 show substantial differences between the different chitosan/MMT (chitosan/montmorillonite) composite films. The neat chitosan film and those with low MMT concentrations ( $\leq 4.5$  wt%) have similar appearance; small or no agglomerates. Formations of agglomerates become more significant at higher MMT concentrations ( $\geq 10$  wt%). The stripes is a pattern from scratches in the petri dish and the clear particles in figure 1 e is dust.

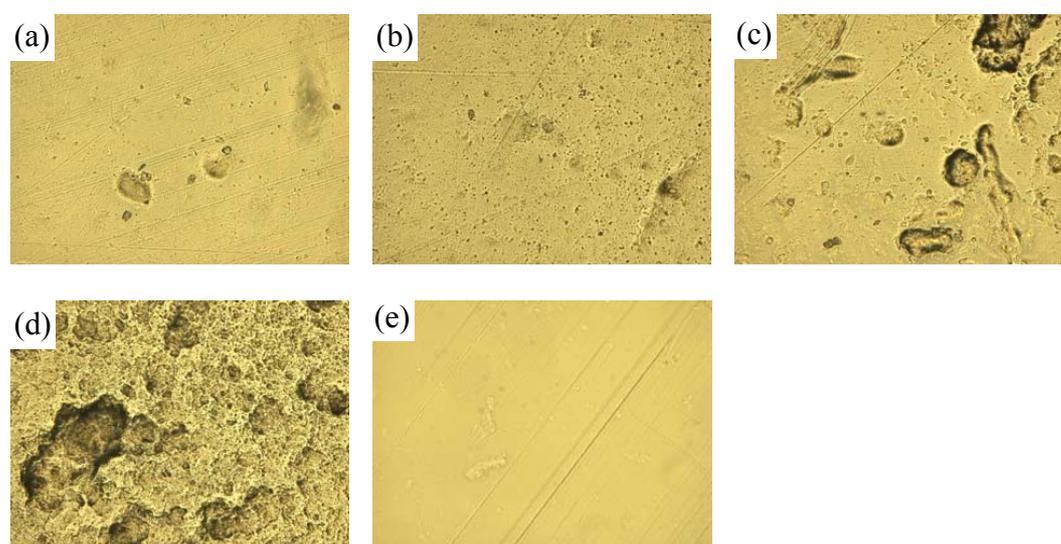
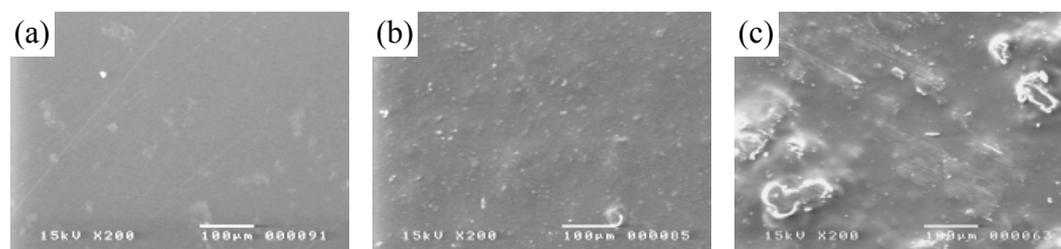


Figure 1: Optical micrograph (x6.3) of a chitosan film containing: (a) 0.75 wt% MMT, (b) 4.5 wt% MMT, (c) 10 wt% MMT, (d) 25 wt% MMT, (e) neat chitosan film.

Decreasing dispersivity and increasing aggregates, with increasing MMT concentration was also observed in SEM (Figure 2). The surfaces turned rougher and with more particles of undispersed and non-exfoliated MMT. The smaller white particles, most clearly observed in Figure 2 e, are most likely contaminations of Au/Pt from the sputter treatment and possible also dust particles.



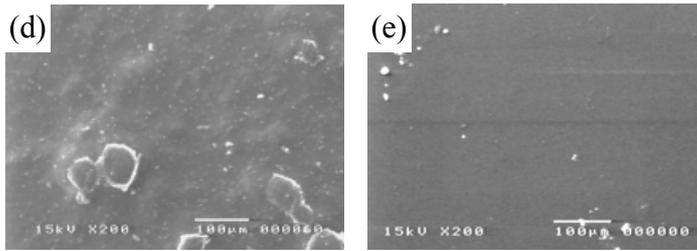


Figure 2. Scanning electron micrograph (x200) of a chitosan film containing: (a) 0.75 wt% MMT, (b) 4.5 wt% MMT, (c) 10 wt% MMT, (d) 25 wt% MMT, (e) neat chitosan film.

The XRD analysis show d-spacing for MMT- $\text{Na}^+$  at  $2\theta = 7.22^\circ$  [6]. That peak do gradually decrease as the MMT exfoliates. The tests show that the peak is still present in all of the samples, indicating that full exfoliation has not occurred (the graph is published elsewhere). The peaks are however shifted towards lower  $2\theta$ , indicating that intercalation has occurred. The peak intensity is approximately the same for all of the preparation approaches so the heating of chitosan does not increase the exfoliation rate noticeably. Full exfoliation is not achieved probably due to the higher viscosity of the solutions. Chitosan solutions with lower viscosities, achieved by a lower chitosan concentration in the solutions, have been used in previous studies showing almost full exfoliations. However, a higher viscosity is required to get a more homogenous coating for application on e.g. paper or paperboards.

The XRD-study showed characteristic crystalline peaks around  $2\theta = 10^\circ$  and  $20^\circ$  which correspond to crystal 1 and crystal 2 in chitosan. A well known factor that affects the exfoliation rate is the MMT concentration. The XRD study did also show that the degree of exfoliation increases with decreasing MMT concentration. The solution with 1.5 wt% showed an almost full exfoliation and intercalation compared with the solutions with 3 and 4.5 wt%. However, the d-space of the clay galleries has increased and intercalation has occurred also for the solutions with 3 and 4.5 wt% MMT.

The viscosity of the solutions without MMT increases with the chitosan concentration as expected. Solutions with more than 3 wt% chitosan had too high viscosities to be degassed in the vacuum oven, an operation needed to remove air bubbles induced during the previous mixing. On the other hand, solutions with too low viscosity, e.g. that for a chitosan concentration of at 2 wt%, would probably be absorbed into most non-precoated papers or paperboards.

Table 2: The viscosity of chitosan solutions with montmorillonite, prepared with different methods.

Sample	Spindle No	Speed [rpm]	Viscosity [cPa s]
3 wt% chitosan, 0 wt% MMT (Room temperature)	3	5	18200
2 wt% chitosan, 0.09 wt% MMT (Room temperature)	3	5	3700
3 wt% chitosan, 0.09 wt% MMT (Room temperature)	6	5	69600
3 wt% chitosan, 0.09 wt% MMT (60°C)	6	5	56000

As shown in Table 2, the viscosity of the chitosan/MMT solutions prepared at 60 were lower than for that prepared at 30°C. That could potentially be due slip between non-exfoliated, but intercalated, clay particles [41]. The intercalation is higher for the solution prepared at 60 than 30°C. However, that difference would then be too small to be observed in the XRD study.

Generally, addition of filler or a reinforcing additive to a polymer solution/melt results in increased viscosity due to decreased free volume and immobilization of the polymer caused by the generated interparticle interactions [76,77]. The results in Table 2 is well in agreement with studies showing an increasing viscosity with increasing clay concentration in polymer melts [21,44,51,55].

#### 4. CONCLUSIONS

The chitosan/MMT sample containing 1.5 wt% MMT seems to have a more exfoliated structure than the other samples. The viscosity of chitosan was shown to increase dramatically with the concentration and the solutions were apparently only possible to apply as coatings on paperboards up to 3 wt%. Solutions with higher chitosan concentrations had too high viscosity for application and were also impossible to degas for removal of air bubbles. However, for the solutions with low chitosan concentration the viscosity may instead be too low, resulting in absorption into the paperboard and high amounts of pinholes. The solution with 3 wt% chitosan appeared to be most appropriate as paperboard coating, and still possible to degas in the vacuum treatment.

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