

Improving the Physical and Chemical Functionality of Starch-Derived Films with Biopolymers

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ABSTRACT: The physical and chemical properties of composite starch-based films containing cellulosic fiber, chitosan, and gelatin were investigated. Films containing both cellulosic fibers and chitosan demonstrated tremendous enhancements in film strength and gas permeation. The water absorbency of composite films could be greatly reduced in film composites containing cellulosic fibers and gelatin, but the inclusion of chitosan into these films provided a higher hydrophilicity, increasing water absorbency. Film transpar-

ency was not noticeably affected in the composite films that were made. These films may have wide application in the food packaging, agricultural mulching, and the medical industries. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2542–2548, 2006

Key words: adsorption; biopolymers; composites; mechanical properties; membranes

INTRODUCTION

The importance of the role of plastic films in the daily needs of modern society cannot be overemphasized. They have been widely applied in food and merchandise packaging, agricultural mulching, gas and liquor separation, and medical technologies. In 2000, more than 40 million tonnes of petroleum-based plastic material was used worldwide in the packaging industry alone. However, the bulk of this material was for single-use applications and was thus discarded, contributing to growing landfills. Given real and pressing environmental concerns, the rising cost of petroleum, and the eventual depletion of our oil reservoirs, many research efforts have focused on developing renewable and biodegradable films. Such films would overcome the intrinsic deficiencies of petroleum-based films given their advantages in renewability, biodegradability, and biocompatibility. There are two realistic ways to develop biodegradable films. One is to incorporate biodegradable synthetic materials, such as polylactide, polyesters, and polycaprolactone into the films. However, given the high cost of these materials, their use is limited. Thus, the alternative way is to use abundant, natural materials, (which is becoming more and more attractive) since, unlike the latter polymers, they are renewable.

Starch is one of the naturally occurring biomaterials that are abundant and have a low cost for commercial applications. It has been widely used in fermenting as well as in other chemical manufacturing industries. In packaging and agricultural mulching industries, starch-based films have significant potential to replace synthetic films such as polyethylene (PE). In the last several decades, great efforts have been made to develop starch-based films that display improved film properties. However, two disadvantages of starch-based films that have limited their use are inherently low moduli of elasticity (strength) and high hydrophilicity (leads to enhanced biodegradability). To overcome these properties, two approaches have been typically adopted: the copolymerization of starch with synthetic polymers or the admixture of starch with polymers.^{1–5} However, synthetic polymers such as PE are nonbiodegradable even after the starch has degraded. Therefore, such a film would impact the environment unfavorably.

Recently, there has been a research effort that has reported that cellulosic fibers may be added to modified starches such as hydroxypropylated starch to enhance film mechanical properties.⁶ Cellulose fibers were found to improve starch film performance by decreasing water uptake.⁷ Blending starch with polyester polymers demonstrated good biodegradability for agricultural mulch applications,⁸ while gelatin (another biopolymer) was reported to function as a strength reinforcement agent for improved mechanical performance.⁹

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Hence, the objective of the present investigation was to provide a simple study on the effect of several natural biopolymers on the physical and chemical properties of starch-based films. The influence of these polymers on film strength, water absorbency, transparency, and gas permeation were investigated.

EXPERIMENTAL

Materials

Starch: commercial corn starch was used without modification.

Fiber: bleached mechanical pulp and kraft Southern pine pulp from laboratory manufacture were dispersed in a blender with sufficient water to make a pulp slurry of 10% solids content.

Chitosan: commercial chitosan was dissolved in 1% acetic acid to make a 2% (m/v) solution.

Gelatin: analytical chemistry purity (purissimo) class gelatin was dissolved in water to make up a 20% solution.

Film preparation

The materials were mixed in a quantitative manner with starch while the mixture of starch was gelatinized at 80°C for 25 min. Glycerol as a plasticizer was added at a 25% ratio based on total dry weight of composite materials. The total mixture of starch and other materials was 20 g and kept at a concentration of 4 g/100 mL. Composite material design was varied according to the described experiment plan. After cooling and observing the dispersion was homogeneous, 50 mL of the sample (2 g dry material) was poured into a Petri dish and then dried at 60°C in an oven to cast the films.

Strength measurement

Tensile tests were performed with an ALWETRON TH1 horizontal tensile tester in accordance with TAPPI Method T-404 cm-94.

Water uptake

Film samples (80 × 15 mm²) were conditioned at 25°C in a desiccator containing sodium sulfate to ensure a relative humidity (RH) ratio of 95% for a designated time. The excess water was then dried with tissue paper applied onto the film surface. Water uptake was calculated as follows:

$$\text{Water uptake \%} = \frac{W - W_0}{W_0} \times 100$$

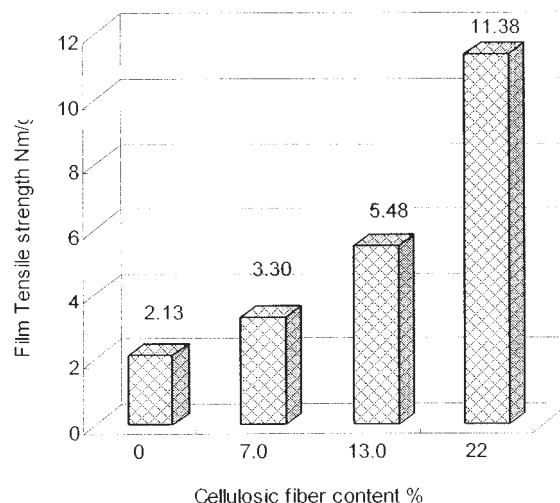


Figure 1 Influence of cellulosic fiber on film strength (Short fiber). Bleached mechanical pulp was used as short fiber.

where W_0 is dried film sample weight, and W is the weight of the film sample after exposure to 95% RH, respectively.

Opacity measurements

Film opacity was measured with a BNL-3 Opacimeter. The measurements were carried out on a black and white background.

Gas permeation

A 20 mL headspace vial was sealed with a crimp cap and septa, and its bottom was cut off and polished. The film sample was covered and sealed on the exposed bottom of the vial. A 1.0 mL slug of carbon dioxide was injected into the sealed vial and the vial was allowed to remain in a bulk air environment to allow a free gas exchange through the film. After 10 min, the content of carbon dioxide in the vial was determined by gas chromatography. A control sample without the film was also tested to establish a baseline for the changes in the content of carbon dioxide.

RESULTS AND DISCUSSION

Film strength properties

As already cited, poor strength properties (elastic moduli, tensile, compression) of neat starch films are major drawbacks for their use in diverse commercial applications. Improvements in the mechanical properties of film are therefore mandatory; Figure 1 provides an illustration of how the addition of cellulosic fiber impacts film strength. An appreciable enhancement by increasing the cellulosic fiber content was immediately observed, in which as much as five-fold increases

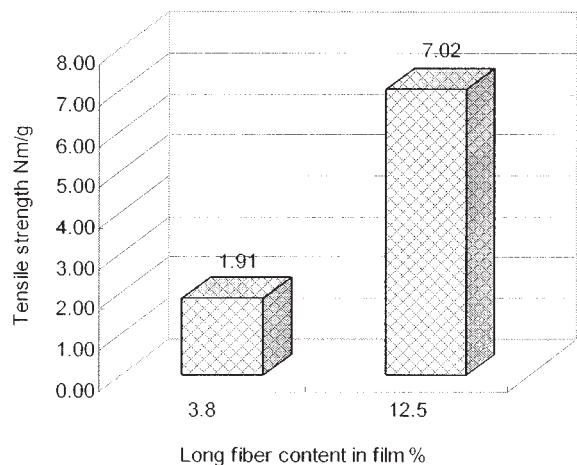


Figure 2 Influence of cellulosic fiber on film strength (Long fiber).

in film tensile strength were achieved by incorporating up to 22% fiber content to these films.

To investigate how different fiber lengths influence film strength, long fibers (up to 10 mm) from softwood kraft pulps were applied to starch films. Figure 2 shows the film strength development using Southern softwood long fibers. Although no obvious differences in the tensile properties of film were observed relative to the short fiber, applying long fibers in starch had a negative effect on film uniformity. Because of the entanglement induced from long fiber–fiber interactions, it was difficult to uniformly disperse such fibers in a starch mixture to result in a homogeneous film.

Chitosan, another biopolymer that has a cellulose-like structure, was mixed in starch with the purpose of enhancing the film strength since its tertiary structure (having a glucose-based monomer unit) is similar to that of starch and cellulose and thus should undergo hydrogen bonding. The chitosan compound dissolved in weak acidic acid solution was easily incorporated into the starch dispersion to form a homogeneous film. The influence of chitosan on the strength of these starch-based films is plotted in Figure 3.

In a similar vein to cellulosic fiber, chitosan significantly enhanced starch film strength. A tremendous tensile increase was achieved when the chitosan content comprised 12.5% of the starch film. Compared to the original starch film, an almost 10-fold increase in tensile strength was reached with 28% content of chitosan in the film. The results clearly indicate that both cellulosic fiber and chitosan can easily be incorporated into the films while significantly enhancing their strength. Figure 4 shows the impact of gelatin on starch film strength. Gelatin has been previously reported to improve starch film strength.⁹ However, in our experiments, gelatin did not show any obvious enhancements in starch-based film strength.

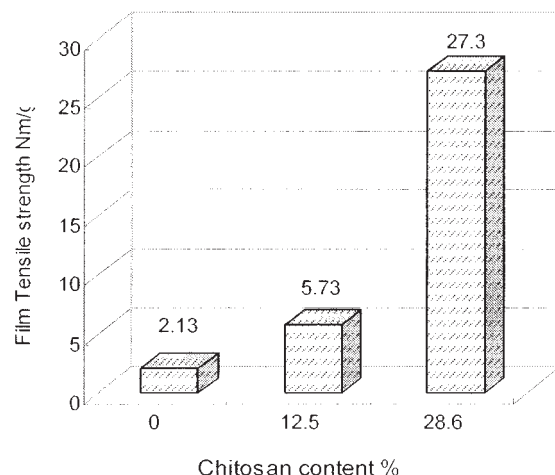


Figure 3 Influence of chitosan on film strength.

Water absorbency

Owing to the strong hydrophilicity of starch molecules, a neat starch film displays high water absorbency (54.7% is saturation limit). This factor impedes the application of pure starch films for most nonabsorbency applications. However, incorporation of various amounts of cellulosic fibers into the starch matrix was able to reduce the water absorbency of these films as shown in Figure 5. Although cellulose is typically a hydrophilic polymer, the high crystallinity of the cellulose polymer and tight microfibrils structure within the fiber tend to discourage water absorbency when compared with that of amorphous starch. Approximately 40% reduction in total water absorbency was achieved by a 6.7% fiber addition in the film, while the film water absorbency was further reduced to more than 50% when the cellulosic fiber content reached to 12.5%. However, continuing to increase fiber percentage within the film did not achieve any further im-

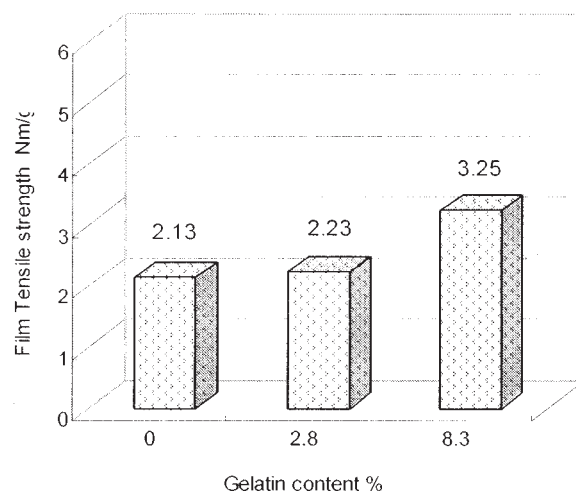


Figure 4 Influence of gelatin on film strength.

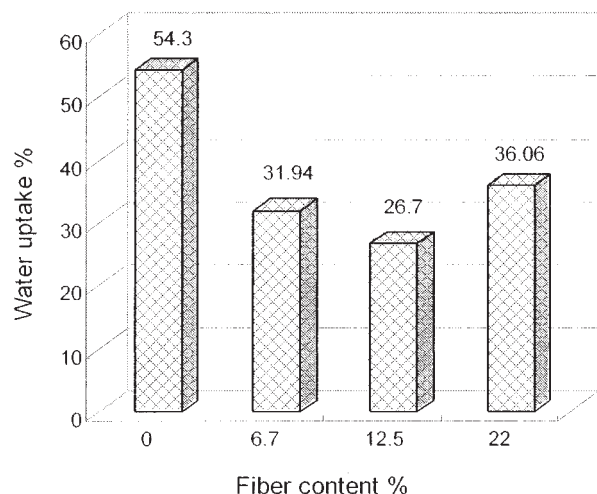


Figure 5 Influence of fiber (mechanical pulp fiber used) on film water absorbency (24 h).

provement in water absorbency. When the fiber content of the films reached 22%, the water uptake increased to 36.1% when compared with 26.7% of water uptake in the case of 12.5% fiber content. This result indicates that the combination of cellulosic fiber with starch improves water resistance to a certain degree since, as already known, cellulosic fibers are hydrophilic materials, although their hydrophilicity is weaker than that of starch.

Contrary to cellulosic fibers, chitosan had a reverse role on film water absorbency. Figure 6 illustrates the influence of chitosan on film water uptake. With increasing chitosan content to 28%, the water uptake of the film linearly increased. When the chitosan content reached one third of the total film by mass, as much as a two-fold increase in water uptake was observed when compared with that of a pure starch film. A

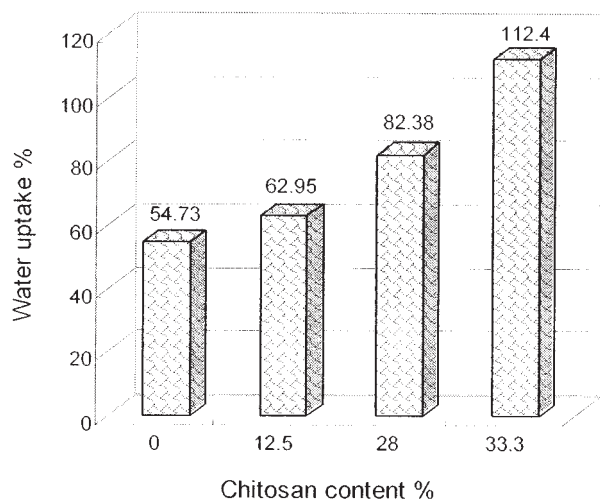


Figure 6 Influence of chitosan on film water absorbency. (24 h).

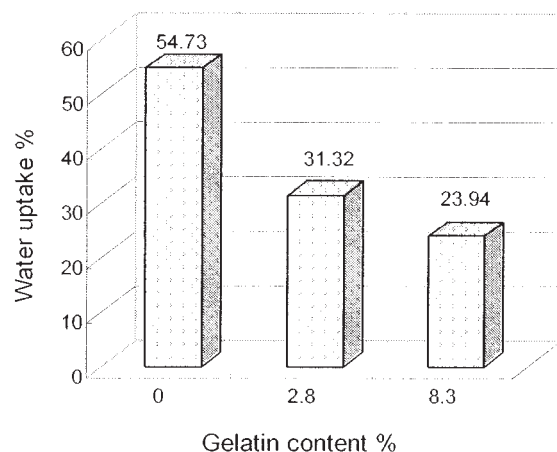


Figure 7 Influence of gelatin on film water absorbency. (24 h).

higher water absorbency of chitosan is ascribed to its chemical features since besides the hydrophilic hydroxyl groups on the chitosan molecule, it possesses strong hydrophilic amine groups on the chitosan molecule, which encourage higher water absorbency. Furthermore, unlike the cellulosic fibers, chitosan is freely soluble, which allow these molecules more degrees of freedom with respect to water absorption.

Gelatin functioned as an efficient water resistant agent: its influence on film water uptake is plotted in Figure 7. A 2.8% total incorporation of gelatin to the film resulted in a 40% reduction in water uptake, while almost 60% lower water uptake was achieved by 8.3% gelatin levels in the film.

To further investigate the influence of various non-starch components on film water absorbency, the changes in water uptake over a discrete time window were plotted in Figure 8. Although different fiber content resulted in differences in water absorbency levels, the water uptake over extended time at all fiber levels did not exhibit much change. The latter result certainly demonstrates how the cellulosic fiber component influences water uptake. Even though cellulosic fibers were not expected to impart very high water resistance to the film, it was able to obviously improve water resiliency of starch-based films despite changes in water conditions. Because starch films are very sensitive to changes in moisture that results in changes in their mechanical properties, controlling film moisture content is highly important. Hence, the moisture stabilization provided by cellulosic fibers is significant for new applications that are moisture sensitive such as gas selective membranes, ion channels, etc.

A film containing chitosan also demonstrated a high sensitivity to water absorbency. Water uptake not only increased with an increase in the chitosan content, but kept increasing over a long time period. High water sensitivity would tend to impair film strength. To

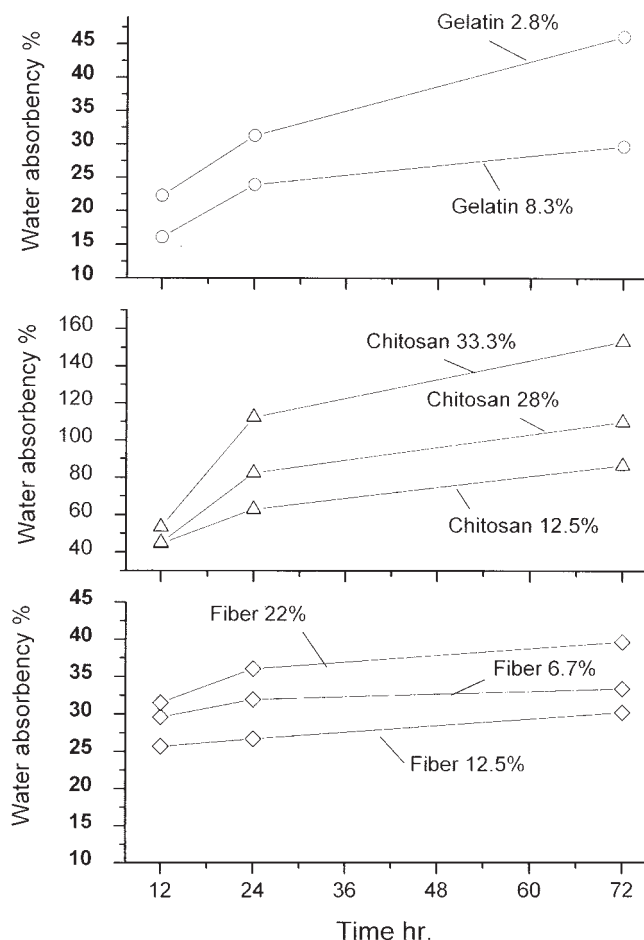


Figure 8 Influence of various nonstarch components on the water uptake rate of film.

avoid adverse impacts on film strength, high chitosan content was avoided. Gelatin may be used to enhance water resistance of the films to establish a water threshold to uptake (Fig. 7). However, at a low gelatin content (2.8%), water absorbency displayed an obvious change over time. The data indicated that a low gelatin level would not be enough to provide high moisture stabilization though it did impart lower water uptake. When a higher gelatin level was added to the starch-based films (8.3% in the current experiments), the films were more resistant to water uptake.

Transparency of films

Figure 9 illustrates the influence of cellulosic fibers on the transparency of starch-based films. The transparency of the film can be decreased with an increase in the fiber content of the film. As opposed to cellulosic fibers, as shown in Figure 10, chitosan did not impair film transparency.

When light strikes a film surface, it is reflected, absorbed, or transmitted and as a result of the light-product interaction a color, gloss, and transparency is

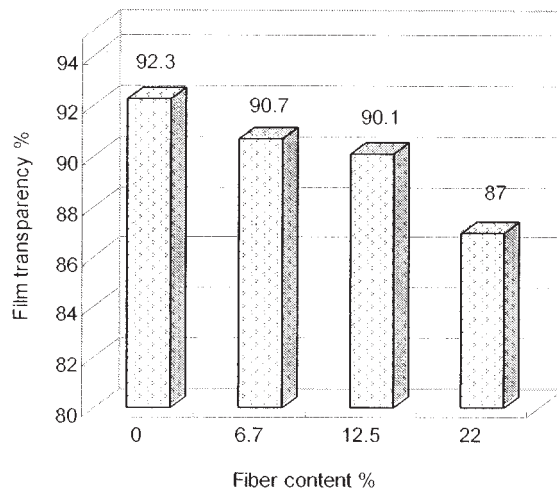


Figure 9 Influence of fiber on film transparency.

exhibited by the film. Kubelka–Munk theory¹⁰ proposed a model for the explanation of optical properties of multicomponent materials. The light diffusion occurs at the interface of these different components and greatly impairs the light transmission. Scallan^{11–13} investigated the influence of the fundamental properties of paper as well as fillers on paper optical property. Adding filler into cellulose fiber paper increases the interface area and leads to an increase in the light diffusion within the internal structure of paper, and as a result, paper opacity is increased. In the case of multicomponent films, a chitosan solution mixed with a starch matrix formed a homogeneous matrix. After drying, this homogeneous matrix formed a continuous phase in the film state. On the other hand, cellulosic fibers are not water soluble and randomly disperse in the starch matrix, and as such, exist in film as a discontinuous phase after drying. Therefore, cellulosic fibers provide more interfacial area within a film

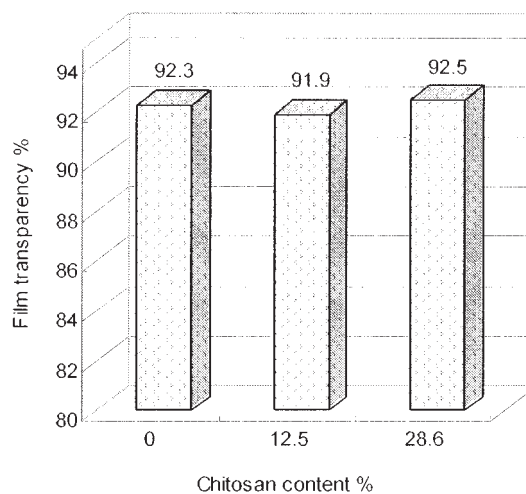


Figure 10 Influence of chitosan on film transparency.

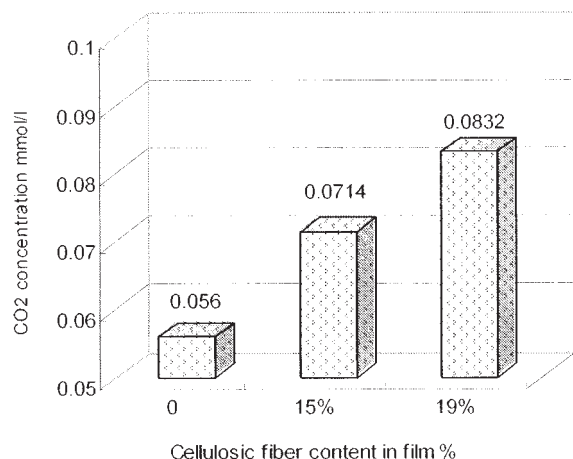


Figure 11 Influence of cellulosic fiber content on film gaseous permeability (10 min, 1.0 mL CO₂ in 20 mL vial).

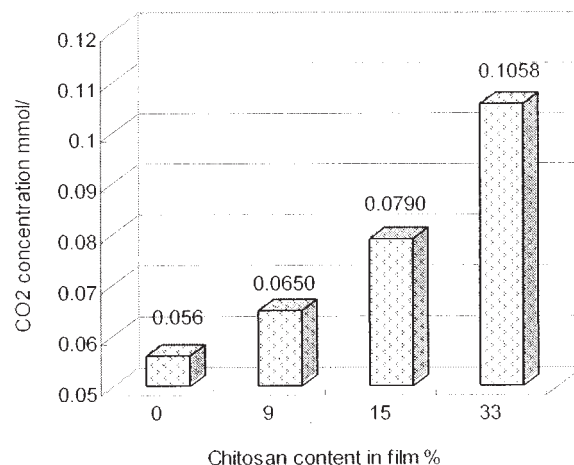


Figure 12 Influence of chitosan content on film gaseous permeability (10 min, 1.0 mL CO₂ in 20 mL vial).

structure. The light diffusion is increased and results in a reduction in film transparency.

Overall, starch-based films maintain relatively high transparency while additions of various biopolymers did not have significant effects on its transparency.

Influence of fiber and chitosan on film gas permeation

Many different films have been widely applied in separation processes, including gas and liquor separation. In the packaging and agricultural industries, the gas permeability of films are also important for specific functions. In the current work, preliminary results for the gas permeation of starch-based films are provided. In Figure 11, the changes of carbon dioxide gas permeation through different cellulosic fiber contents of the composite films are illustrated. Interestingly, the permeation rate of carbon dioxide was influenced by varying the cellulosic fiber ratios in the starch film. Over a certain time period, the concentration of carbon dioxide in a film-sealed vial increased with the increase in fiber content. For a pure starch film, the carbon dioxide concentration in the vial reached almost the same level as that in air after 10 min. However, When compared with a starch film, a 50% increase in the carbon dioxide concentration was achieved by using a film having 19% cellulosic fiber content. Similar features for chitosan composite films were also observed (Fig. 12). When the chitosan content in these films reached 33% of the total film composition, almost a two-fold increase in the remaining carbon dioxide concentration could be achieved in the vial when compared with that of a pure starch film. This phenomenon could not be explained by a simple variation in the film densities by changing the film components. In the fiber and chitosan films, film densities decreased with an increase in the concentration

of the biopolymers as shown in Figure 13. Both cellulosic fiber and chitosan lower film density. Certainly, a lower film density could result in larger film pore size and faster gas permeation rate. Therefore, biopolymer incorporation in these films has a function that is currently not understood for gas permeation and will serve as the subject of future investigations.

CONCLUSIONS

The incorporation of biopolymers with starch can modify the physical and chemical properties of starch-based films. Some important improvements for starch-based films could be achieved while maintaining the natural advantages of starch films. The inclusion of cellulosic fibers into starch film greatly enhance film strength—as much as five-fold increase in the tensile strength of these films could be achieved by adding 22% of cellulosic fiber in film when compared with

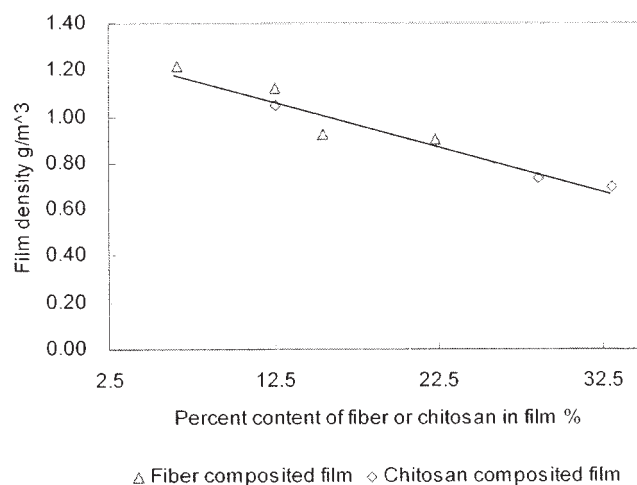


Figure 13 Film density as function of component content.

that of neat starch films. Furthermore, cellulosic fibers also demonstrated an important influence on film water absorbency. A 12.5% of fiber content could decrease film water uptake by more than 50% than that of the neat starch film. Another significant effect of fiber on water absorbency is its stabilization of film water sensitivity although there is a slight decrease in film transparency.

Similar to the cellulosic fibers, chitosan contributed a tremendous improvement to film strength. A 10-fold increase in film strength was observed with 33% chitosan content. However, chitosan demonstrated a negative impact on film water absorbency. The increase in film water uptake was observed with an increase in the chitosan content, especially in the high chitosan content.

Gelatin imparted good water resistance to the starch-based films. A small amount of gelatin effectively reduced film water uptake and did not show any obvious impact on other film properties.

Both cellulosic fiber and chitosan demonstrated a profound influence on film gas permeation. The gas

permeation rate decreased with an increase in both fiber and chitosan content although the mechanism remains unknown and needs further investigation.

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