

Influence of Natural Biomaterials on the Elastic Properties of Starch-Derived Films: An Optimization Study

Weiping Ban,[†] Jianguo Song,[‡] Dimitris S. Argyropoulos,[§] and Lucian A. Lucia^{*§}

Institute of Paper Science and Technology, Georgia Institute of Technology, 500 Tenth Street, Atlanta, Georgia 30332-0620, Dalian Institute of Light Industry, Dalian, China 116034, and Forest Biomaterials Laboratory, College of Natural Resources, North Carolina State University, Campus Box 8005, Raleigh, North Carolina 26795-8005

A D-optimization design was applied to investigate the strength properties of biomaterial-doped starch films. The individual effect of each additive and associated interactive effects were investigated. Cellulosic fibers and chitosan were able to substantially enhance film strength. Lignin and gelatin also demonstrated significant interactive effects on strength, while different interactive effects were evident between the major biopolymers (fiber and chitosan) and minor biopolymers (lignin and gelatin). The film stretch depended on the material composition where diminishing returns were observed for stretch, while strength increased for increasing levels of each of the biopolymers. An increase in fiber and chitosan contents led to increases in film density that correlated well with strength. The latter data indicate that fiber and chitosan biopolymers act synergistically by providing increased film bonding that eventually generates a stronger film.

Introduction

Synthetic plastic films have been widely applied in the packaging industry and agricultural mulching. Approximately 40 million metric tons of such films are consumed annually on a global basis. Currently, virtually all of these packaging film products are derived from petroleum-based materials that are non-biodegradable. Since the depletion of oil, current economic impact, and the environmental impact of non-biodegradables are genuine concerns, societal and environmental pressures continue to prompt efforts to develop renewable, cost-effective, and environmentally friendly materials for the manufacture of a number of products, including these films. One material to pursue to address these concerns is starch, which is one of the most abundant and versatile natural polymers or biomaterials on the planet having a cost and biodegradability that are very favorable.

Starch-based films have therefore attracted much research in the past several decades. However, owing to its drawbacks in unacceptable two-dimensional strength and diminished water resistance compared to a number of equivalent market film products, the application of pure starch films is extremely limited. To overcome these deficiencies, two approaches have been pursued: either copolymerization of starch with synthetic polymers or blending starch with other polymer components.^{1–5} Yet, the synthetic copolymers in general are non-biodegradable, despite the biodegradation of the starch. Therefore, such materials would still exert a harmful impact on the environment given their non-biodegradability while the intrinsic advantages of starch-based films would be negated.

With respect to the second approach to overcome the intrinsic deficiencies of starch, several research reports have indicated that cellulosic fibers may be added to modified starch such as hydroxypropylated starch to enhance film mechanical properties.⁶ Cellulose microfibrils have been found to improve starch

film performance by a decrease in water uptake.⁷ Blending starch with polyester polymers also showed good biodegradability for mulch preparations.⁸ Gelatin, another biopolymer, was also reported to function as a strength reinforcement agent and also improved film performance.⁹

Our previous research investigated composite films that blended cellulosic fibers, chitosan, and gelatin with starch.¹⁰ The objective of the present effort, therefore, was focused on the engineered optimization of these biopolymer films. A D-Optimum Design was applied to investigate the effect of each biopolymer on film strength properties and their interactive effects were discovered. Optimization designs are used to develop empirical models that describe the relationship between each response and all factors investigated. Each quantitative factor appears in at least three (usually five) levels and individual, interaction, and curvature effects are estimated. The D-optimization approach,^{10–12} based on the maximization of the determinant of Fisher's information matrix, is used for the experiment design, together with the analysis of the sensitivity coefficients.

Experimental Section

Materials. *Starch:* Commercial corn starch without modification. *Fiber:* Bleached mechanical pulp and kraft Southern pine pulp from the laboratory were dispersed in a blender and made into a pulp slurry of 10% solids concentration diluted with water. *Chitosan:* Commercial chitosan was ordered from Sigma-Aldrich, practical grade, >85% deacetylated, viscosity >200cP and dissolved in 1% acetic acid to make up a 2% solution. *Gelatin:* ACS chemistry grade gelatin was dissolved in water to make up a 20% solution. *Lignin:* Lignin used in experiments was kraft lignin from Sigma-Aldrich, average $M_w \sim 28000$.

Film Preparation. The biomaterials were mixed with starch and a mixture of starch was gelatinized at 80 °C for 25 min. Glycerol was added as a plasticizer with a content of 25% based on total dry weight of the combined biomaterials. The total mass of starch and other biomaterials was 20 g and maintained at a concentration of 4 g/100 mL. The composition of the biomaterials was varied according to the described experimental plan.

* To whom correspondence should be addressed.

[†] Georgia Institute of Technology.

[‡] Dalian Institute of Light Industry.

[§] North Carolina State University.

Table 1. D-Optimum Design

test no.	X1(fiber)		X2(chitosan)		X3(lignin)		X4(gelatin)		starch
	coding	value	coding	value	coding	value	coding	value	
1	0	15.00	0	15.00	0	2.50	1.8	10.00	57.50
2	0	15.00	0	15.00	0	2.50	-1.5	0.83	66.67
3	-1	6.18	-1	6.18	-1	1.03	0.6	6.67	79.95
4	1	23.82	-1	6.18	-1	1.03	0.6	6.67	62.30
5	-1	6.18	1	23.82	-1	1.03	0.6	6.67	62.30
6	1	23.82	1	23.82	-1	1.03	0.6	6.67	44.66
7	-1	6.18	-1	6.18	1	3.97	0.6	6.67	77.01
8	1	23.82	-1	6.18	1	3.97	0.6	6.67	59.36
9	-1	6.18	1	23.82	1	3.97	0.6	6.67	59.36
10	1	23.82	1	23.82	1	3.97	0.6	6.67	41.72
11	1.7	30.00	0	15.00	0	2.50	-0.9	2.50	50.00
12	-1.7	0.00	0	15.00	0	2.50	-0.9	2.50	80.00
13	0	15.00	1.7	30.00	0	2.50	-0.9	2.50	50.00
14	0	15.00	-1.7	0.00	0	2.50	-0.9	2.50	80.00
15	0	15.00	0	15.00	1.7	5.00	-0.9	2.50	62.50
16	0	15.00	0	15.00	-1.7	0.00	-0.9	2.50	67.50

After cooling and allowing the dispersion to become homogeneous, 50 mL of this dispersion (2 g of dry material) was acquired and poured into a Petri dish, followed by drying at 60 °C to cast the film.

Strength Measurements. Before physical strength measurements, all film samples were conditioned at constant temperature and humidity (25 °C, 50%) in a conditioning laboratory for 24 h. Tensile tests were performed with ALWETRON TH1 horizontal tensile tester. Stretch was read at the break point.

Experimental Design. Quadratic D-Optimum Design was applied in the current research. The experimental program used four independent variables:

X_1 , fiber (0–30%); X_2 , chitosan (0–30%); X_3 , lignin (0–5%); X_4 , gelatin (0–10%).

The following functions were considered as dependent variables:

Y_1 , film tensile strength, Mpa;

Y_2 , film stretch at the maximum tensile, %.

The experiment design is summarized in Table 1. All experiments were at least duplicated if not triplicated to ensure a higher than 95% confidence level.

Results and Discussion

Strength Properties of Starch-Based Films. Through a Quadratic D-Optimum experimental design, a data regression equation for film tensile strength was determined and is shown as follows:

$$Y_1 = 13.9876 + 5.6105X_1 + 5.4783X_2 - 0.8809X_3 - 1.4341X_4 - 0.5008X_1^2 - 0.7191X_2^2 + 1.6452X_3^2 + 1.9176X_4^2 + 1.1050X_1 \times X_2 - 0.2176X_1 \times X_3 - 1.0869X_1 \times X_4 - 1.1275X_2 \times X_3 + 2.8327X_2 \times X_4 - 1.8309X_3 \times X_4 \quad (1-1)$$

where each variable represents a composite component that was applied to develop the starch film as shown in Table 1.

The contribution of each of the variables and their effect on strength may be divided into three levels based on their coefficients: a top level represented by the cellulosic fiber (X_1), chitosan (X_2), and the interaction of chitosan and gelatin that signifies a major effect on film strength; a secondary level represented by lignin (X_3), gelatin (X_4), the interactions of the fiber and chitosan, fiber and gelatin, chitosan and lignin, and lignin and gelatin with a minor effect on strength; and the final level is one where the rest of the components show an

insignificant effect on strength. After deconvoluting the insignificant terms, the equation was simplified as follows:

$$Y_1 = 13.9876 + 5.6105X_1 + 5.4783X_2 - 1.4341X_4 + 1.6452X_3^2 + 1.9176X_4^2 + 1.1050X_1 \times X_2 - 1.0869X_1 \times X_4 - 1.1275X_2 \times X_3 + 2.8327X_2 \times X_4 - 1.8309X_3 \times X_4 \quad (1-2)$$

Based on regression equation (1-2), the effect of the various factors on film strength with associated interactions are plotted in Figures 1–10.

It is obvious that cellulosic fibers greatly enhance the strength of starch-based films. Figure 1 displays a linear increase in film strength with a concomitant increase in cellulosic fiber content. More than a 3-fold increase in film strength can be expected by increasing the fiber content up to 30%. Similar to the addition of cellulosic fibers, chitosan can also play an important role in the enhancement of starch-based film strength as shown in Figure 2. In comparing three levels of different film components as shown in Figure 2, sample number 3 demonstrates the most

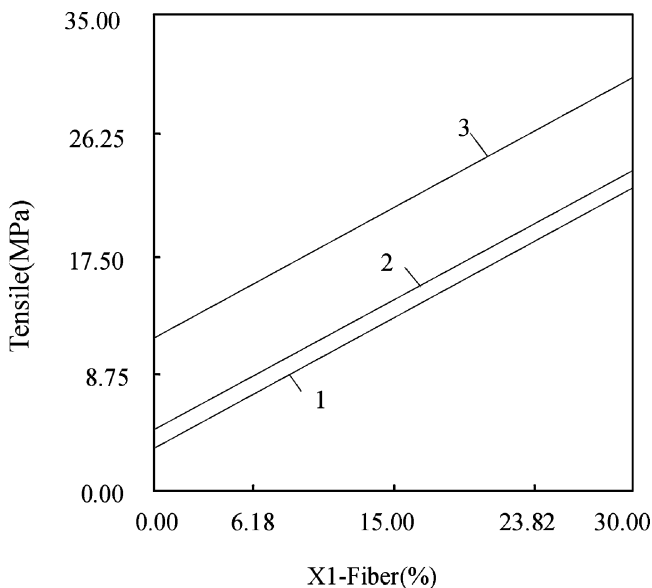
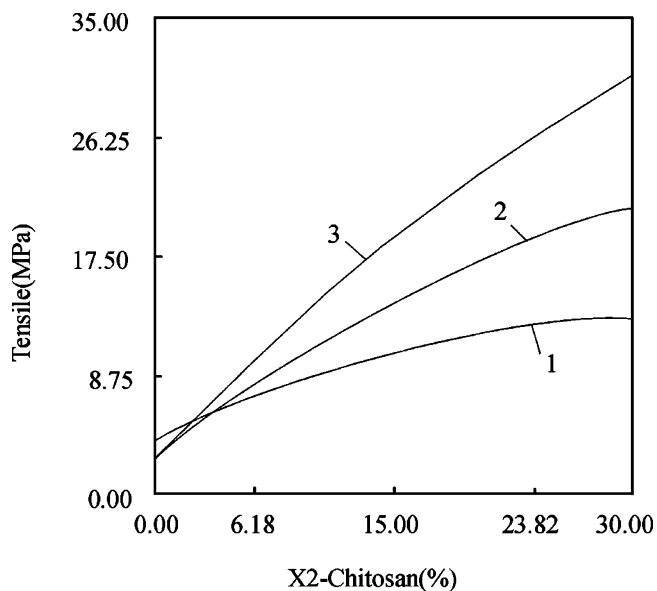
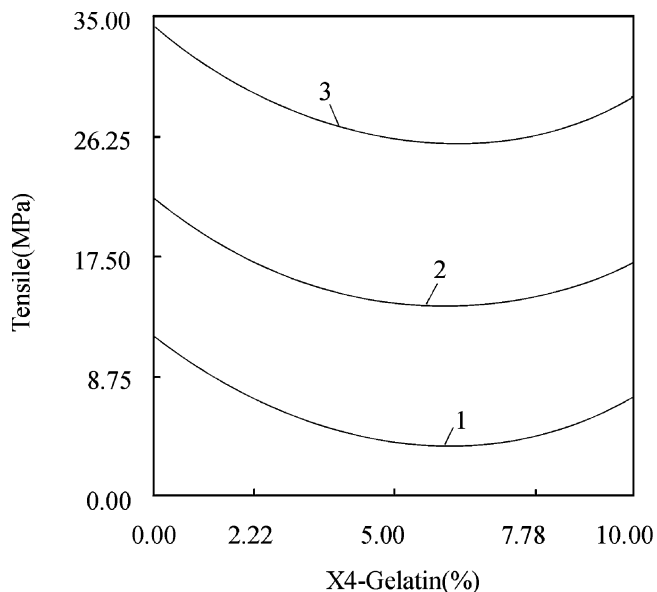


Figure 1. Individual effect of cellulose fiber on film tensile strength.



No	X1-Fiber%	X3-Lignin%	X4-Gelitin%
1	6.67	1.03	2.22
2	15.00	2.50	5.00
3	23.82	3.97	7.78

Figure 2. Individual effect of chitosan on film tensile strength.



No	X1-Fiber%	X2-Chitosan%	X3-Lignin%
1	6.67	6.67	1.03
2	15.00	15.00	2.50
3	23.82	23.82	3.97

Figure 3. Individual effect of gelatin on film tensile strength.

obvious strength increase relative to chitosan content. The result indicates that other components may have important interactions with chitosan for strength improvement. As opposed to both cellulosic fibers and chitosan, gelatin did not show any significant influence on film strength. Overall, its minor negative effect on strength is shown in Figure 3. However, the difference of strength in the controlled film composition levels indicates a strong interactive component exists between gelatin and other variables.

The interactive effect of fiber and chitosan on strength is plotted in Figure 4. Consistent with the strength contributions

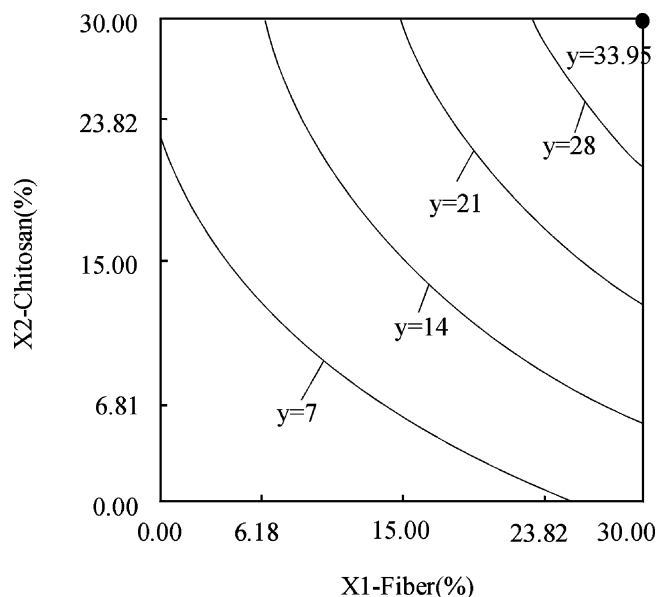


Figure 4. Interactive effect of fiber and chitosan on film strength.

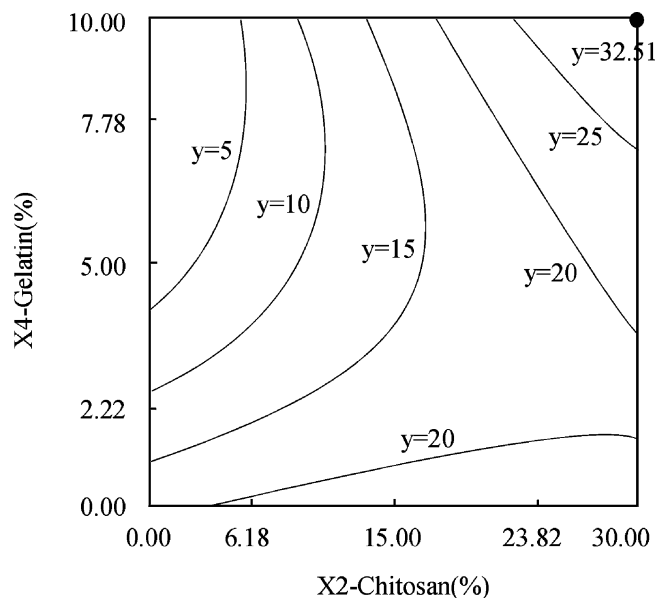


Figure 5. Interactive impact of chitosan and gelatin content on film tensile strength.

of the fibers or chitosan to starch, the combination of both variables provides an even enhanced film strength. A maximum strength is achievable with increasing levels of fiber and chitosan. Furthermore, the group of linear curves suggests that continual substitution of the fibers with chitosan (or chitosan with the fibers) is possible to achieve very high film strengths. The additions of either fiber or chitosan to starch for strength improvements tend to reinforce one another. The results thus demonstrate an alternative means for the enhancement of starch-based film strength that is in keeping with the second approach for improving starch film strength stated earlier (vide infra).

Although gelatin by itself appears to have no significant influence on film strength, its interaction with other components is significant. Figures 5 and 6 illustrate the interactions of gelatin with chitosan and cellulosic fibers on film strength. Interestingly, different effects on film strength in applying gelatin with chitosan versus gelatin with cellulosic fibers were observed. When a lower chitosan content was used (<15%), increasing the gelatin content did not show an enhanced effect on film strength. However, when the chitosan content in film reached

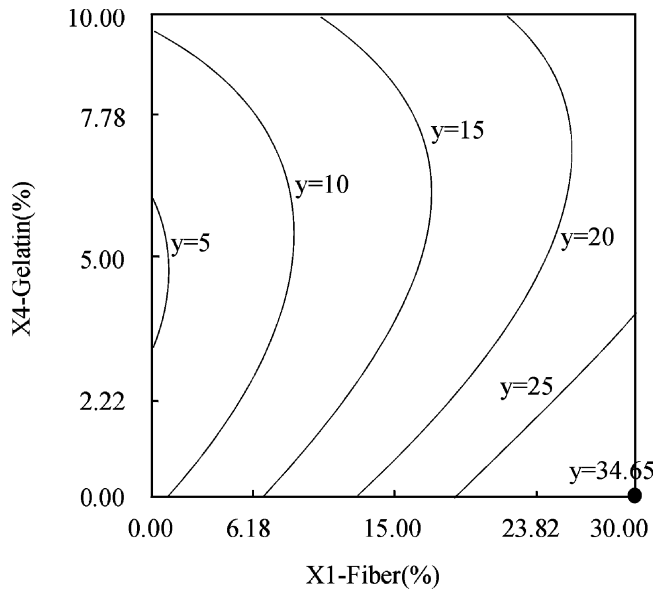


Figure 6. Interactive impact of cellulosic fiber and gelatin content on film tensile strength.

a particular level (>15%), gelatin played a more pronounced role in conjunction with chitosan for increasing film strength. The strength is increased by increasing the gelatin content. The maximum film strength was achieved by using both a maximum chitosan and gelatin content (Figure 5). The data indicates gelatin has a positive impact on film strength in conjunction with chitosan. Conversely, an increase in the level of gelatin did not provide a positive interaction with cellulosic fiber toward strength development. The highest film strength that could be reached by the maximum fiber content without gelatin was therefore determined. The results indicated that gelatin demonstrated a negative interaction with cellulosic fibers, especially at high fiber contents.

For lignin, a minor component, no significant influence on film strength was observed. However, it exhibited interactive effects. Interestingly, like gelatin, interactions of lignin with fiber and chitosan were quite different. To acquire the highest tensile, the inclusion of lignin with cellulosic fiber demonstrated a positive effect. The highest feasible fiber content coupled with the highest level of lignin could achieve high strength, as shown in Figure 7. On the other hand, interaction between chitosan and lignin demonstrates that optimal strength could be achieved by the highest chitosan content with the lowest level of lignin (Figure 8). The results indicate that not only does each component affect film properties but also their interactive effects should be taken into account for total film strength properties. The different interactive effects among lignin, fiber, and chitosan are partly attributable to affinity influences. The affinity between each pair of components is different, and therefore their combinatorial effect on a specific property would either be enhanced or be impaired. Lignin derived from natural plants should in theory have a good affinity to cellulosic fibers, but it appears to lack affinity to chitosan.

Overall, both cellulosic fiber and chitosan tremendously contribute to the enhanced strength of starch-based film. Both components show the same function for strength enhancement and can replace each other, which suggests a similar mechanism is operative for strength enhancement based on their similar structures. Therefore, an important consideration affecting the physical strength of films is affinity differences among components.

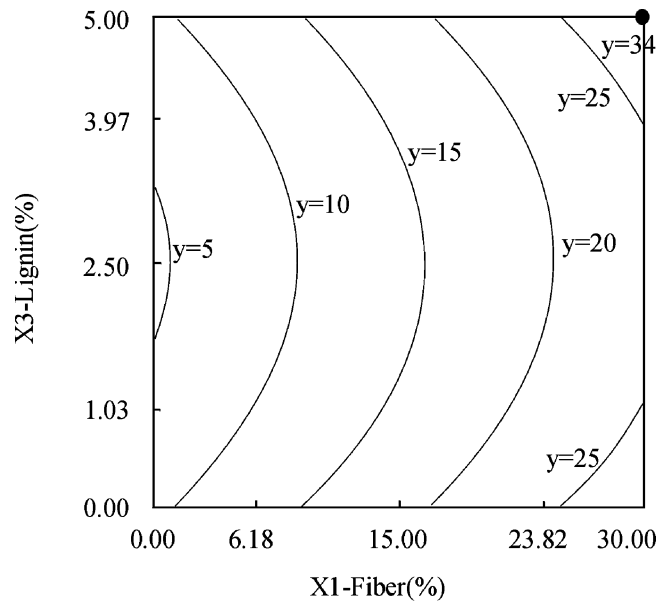


Figure 7. Interactive effect of fiber and lignin on film strength.

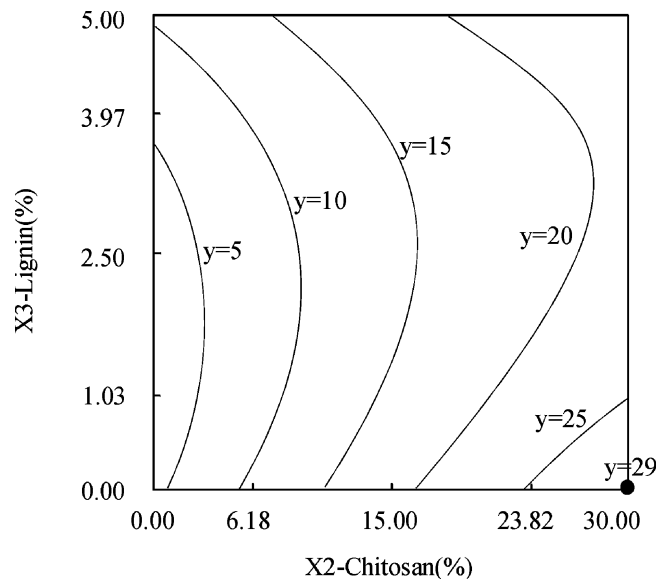


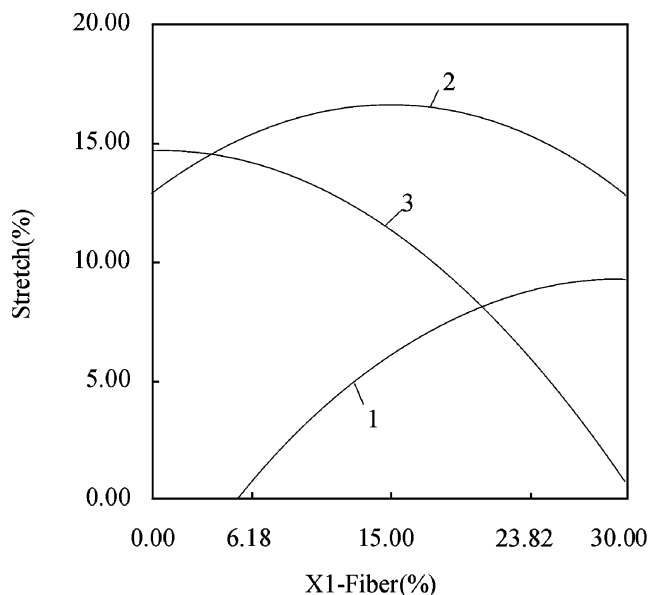
Figure 8. Interactive effect of chitosan and lignin on film strength.

Elastic Properties of Films. Film stretch reflects the flexibility of the film. In most cases, a higher stretch is always expected with a high tensile strength. The regression equation that film stretch is expressed as a function of each composite component and their interactions is shown as follows:

$$Y_2 = 16.6100 - 0.5920X_1 + 0.5659X_2 + 1.2414X_3 + 1.4577X_4 - 1.2920X_1^2 - 2.1036X_2^2 - 2.7832X_3^2 - 4.0289X_4^2 - 1.6521X_1 \times X_2 - 2.4654X_1 \times X_3 + 0.0417X_1 \times X_4 - 0.3396X_2 \times X_3 - 1.1553X_2 \times X_4 + 2.0948X_3 \times X_4 \quad (2-1)$$

After ignoring the insignificant terms in the equation, it can be simplified to

$$Y_2 = 16.6100 + 1.2414X_3 + 1.4577X_4 - 1.2920X_1^2 - 2.1036X_2^2 - 2.7832X_3^2 - 4.0289X_4^2 - 1.6521X_1 \times X_2 - 2.4654X_1 \times X_3 - 1.1553X_2 \times X_4 + 2.0948X_3 \times X_4 \quad (2-2)$$



No	X2-Chitosan%	X3-Lignin%	X4-Gelatin%
1	6.67	1.03	2.22
2	15.00	2.50	5.00
3	23.82	3.97	7.78

Figure 9. Individual effect of fiber on film stretch.

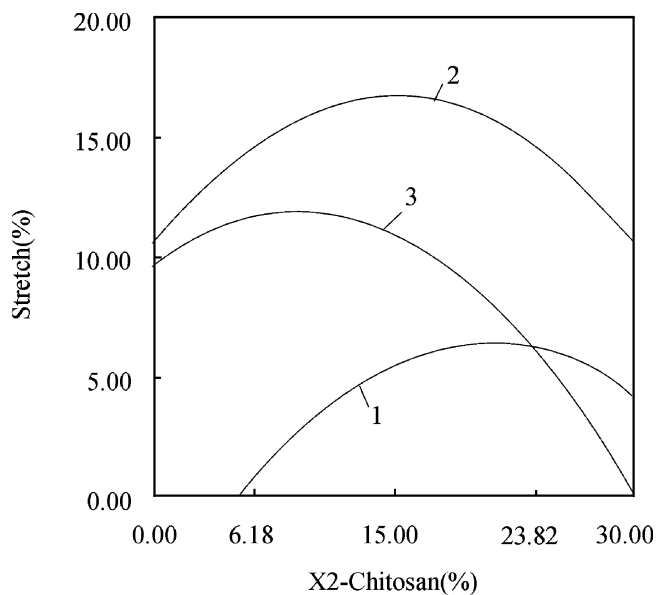
The independent effect of each individual factor on film stretch is represented in Figures 9–12. There is a common theme among these figures. With use of three different levels of contents, a much higher stretch could be acquired at a middle level of content. Both high and low levels showed lower stretch properties.

The effect of fiber on stretch showed an interesting effect. When the contents of other components were kept at a low level, an increase in the fiber ratio contributed to an increase in film stretch as shown in Figure 9. However, when the contribution of each of the total components reached a high level, the stretch was dramatically decreased with increasing fiber content. The data affirm the contribution of cellulosic fiber on the improvement of starch film elasticity, but its effect appears limited.

The influence of the other composites, chitosan, lignin, and gelatin, on stretch show similar features, as shown in Figures 10–12. The film stretch increased with an increase of component content until an appropriate level. After that, continuing to increase their content would result in a decrease in stretch. Each component showed an optimal content for maximum stretch in all three composites levels.

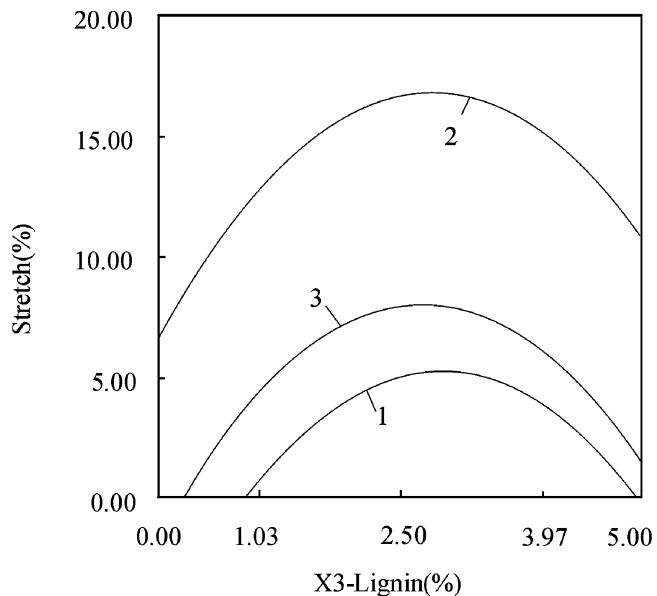
The interactions of each of the components on stretch also demonstrate that an optimal composition exists to achieve maximum stretch. Figure 13 plots the interactive influences of fiber and chitosan. In the experimental range, the middle level of each component could provide better stretch properties. The rest of the interactions for stretch are similar and omitted here for brevity.

From our experimental results, it can be deduced that film stretch is dictated not only by the addition levels of each component but also by the total component content in the film. The high levels of ancillary materials in these films indicate by necessity a lower starch content. Figure 14 shows the influence of starch on film stretch. For two levels of fiber and chitosan, the film stretch increased with increasing starch content. This result explains why a lower film stretch is observed at a higher level of components. Starch has a good plasticity contribution



No	X1-Fiber%	X3-Lignin%	X4-Gelatin%
1	6.67	1.03	2.22
2	15.00	2.50	5.00
3	23.82	3.97	7.78

Figure 10. Individual effect of chitosan on film stretch.

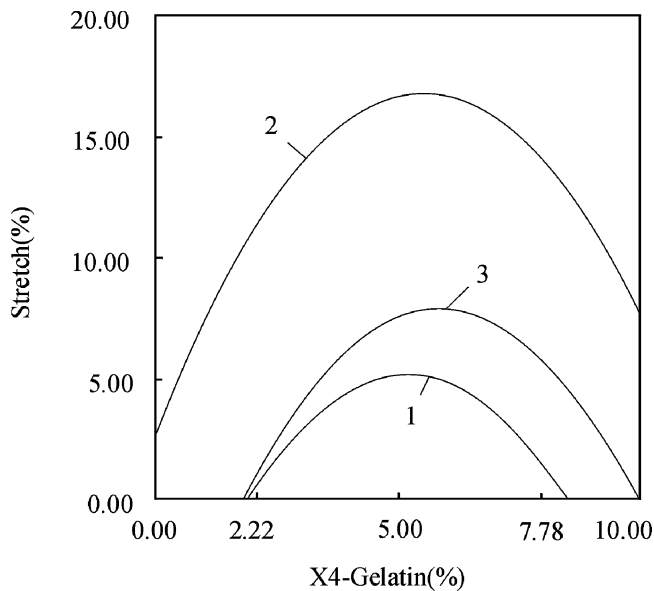


No	X1-Fiber%	X2-Chitosan%	X4-Gelatin%
1	6.67	6.67	2.22
2	15.00	15.00	5.00
3	23.82	23.82	7.78

Figure 11. Individual effect of lignin on film stretch.

to film flexibility. Obtaining the highest strength by diminishing the starch content therefore sacrifices film flexibility. Therefore, a balance must be struck for strength and flexibility enhancements in these films.

In summary, a balance for film strength and stretch exists that is a function of total composition and component levels. Below the middle level of each component, a strength increase accompanies an increase in stretch; after that, increasing the components contributes to an increase in strength, but with an accompanying decrease in film stretch.



No	X1-Fiber%	X2-Chitosan%	X3-Lignin%
1	6.67	6.67	1.03
2	15.00	15.00	2.50
3	23.82	23.82	3.97

Figure 12. Individual effect of gelatin on film stretch.

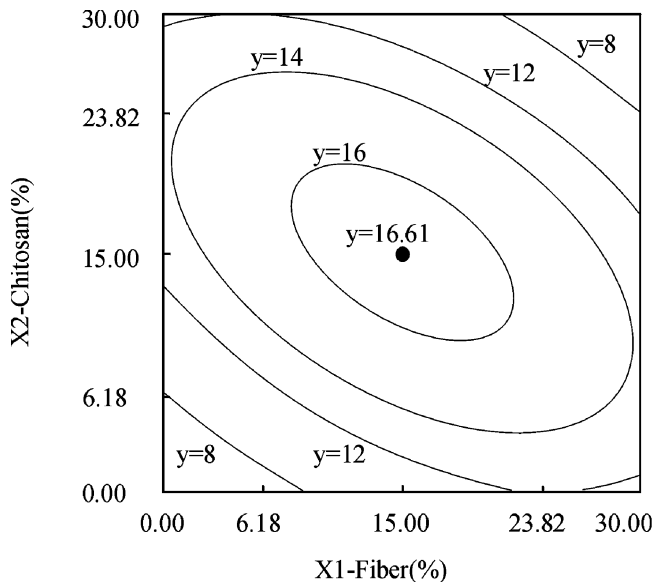


Figure 13. Interactive effect of fiber and chitosan on film stretch.

Film Density and Correlation with Strength. The film density not only depends on the density of the materials in the film but also, more importantly, depends to a great extent on the combination of materials which influences strength, gas, or liquor permeation as well as optical properties. To investigate the influence of each component on film density, changes in film density as a function of the average density of each component at different levels are illustrated in Figure 15. For the two minor components, increasing gelatin levels decreased the film density; lignin appeared to have a similar effect on film density with its content change, but it is not significant due to a lower addition level. However, due to their lower ratios in films, the influence of these minor components is quite limited. The main components, cellulosic fibers and chitosan, showed a significant effect on film density. Film density increased with increasing levels of fiber and chitosan. For certain

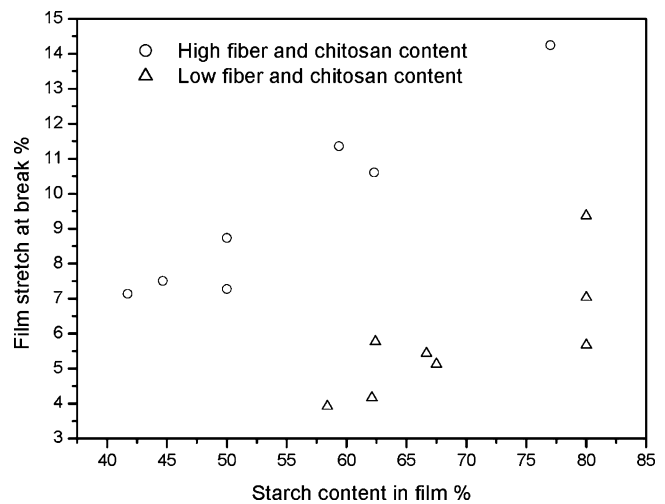


Figure 14. Film stretch as a function of starch content.

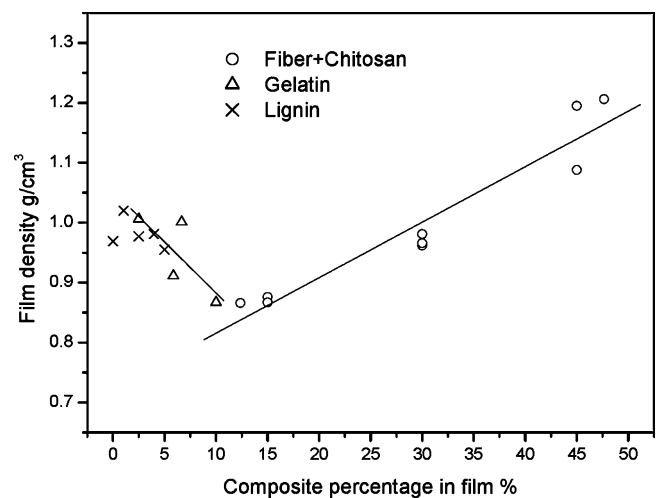


Figure 15. Influence of components on film density.

materials, there are only two ways that lead to an increase in film density: either by increasing the bonds between the molecules of the materials or by adding a high-density component. The former method results in a tighter film structure and strength increase; the latter one results in an increase in film density, but does not increase molecular bonding. For example, filler increases film density but it does not contribute to film strength.

To verify the function of the components on the increase of film density, a correlation of film density with strength was plotted in Figure 16. Very clearly, the changes in film density correlated well with strength change: a higher density led to a higher film strength. Although different levels of fiber and chitosan contribute to different strength levels, an increase in density certainly results in an increase in strength. The results indicate that the density increase from an increase in fiber and chitosan contents can be ascribed to an enhancement in film bonding, which results in a tighter and stronger film structure. The literature reported that the crystallinity of starch films could be increased with an increase in the cellulosic fiber content.⁶ Therefore, fiber and chitosan likely introduce more bonding points and provide a more rigid structure as evidenced by our strength data.

Furthermore, with correlation of density with strength, films can be divided into three groups differing in film strength levels. It is no surprise that high or low fiber and chitosan contents lead to either high or low strength levels. However, the highest

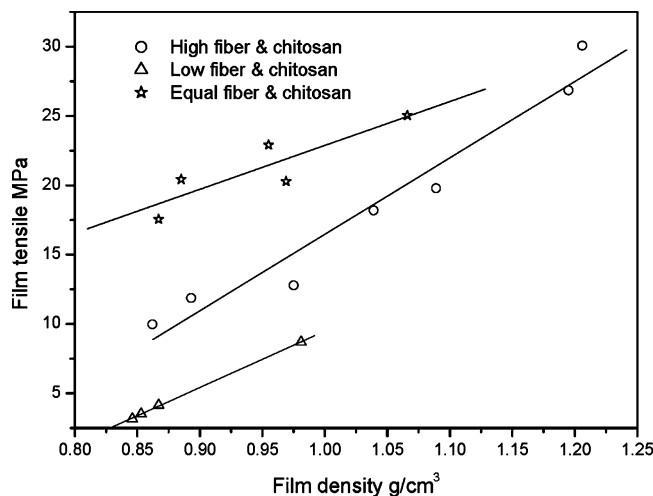


Figure 16. Correlation of film density with tensile strength.

strength levels were observed when fiber and chitosan content were at an equal level. This result indicates that not only do the contents of fiber and chitosan influence film strength but also that their ratio affects it as well.

Conclusions

The strength of starch-based films can be tremendously enhanced by the incorporation of either cellulosic fibers or chitosan or both. Film tensile showed a linear increase with an increase in fiber and chitosan content. The two minor components (gelatin and lignin) showed significant interactive effects on film strength which depended on the affinity with fiber or chitosan.

A higher fiber and chitosan content resulted in a decrease in film stretch. In the current experimental range studied, middle levels of all components as defined in this study resulted in a better stretch.

Finally, fiber and chitosan contents showed a significant influence on film density. Higher levels of fiber and chitosan result in a higher film density, and an increase in film density

correlates well with an increase in film strength, which suggests that fiber and chitosan primarily function to provide stronger bonding in these films.

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