

FABRICATION AND CHARACTERIZATION OF CHITOSAN-COATED STARCH-POLYVINYL ALCOHOL COMPOSITE FILM

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ABSTRACT

Innovations in engineering ought to address current environmental issues brought by several industries. Among the leading fields producing much plastic wastes is the food-packaging industry. This study used starch-based polymers to try and solve the problem. To produce films, the researchers mixed starch and polyvinyl alcohol, two natural biodegradable polymers, using solution casting. Chitosan was added to form laminates on the film and improve its antimicrobial properties.

*UTM results showed 284% increase in the tensile properties of the film. In addition, antimicrobial tests showed that increasing Chitosan concentration decreases the growth of both *E. coli* and *S. typhimurium* bacteria.*

The study also addressed the brittleness issues of starch by adding both PVA and Chitosan layers. Results showed that the Starch-PVA system has a vast potential especially since starch is cheap and abundant. Future academic research may also be devoted to improve the microbial inhibition capability of these films.

1. RATIONALE AND SIGNIFICANCE

There is a growing interest in developing biodegradable polymers and products from renewable natural resources to reduce the environmental impact of plastic wastes. Materials specialists are challenged to come up with alternatives that will liberate industries from dependence on conventional, non-biodegradable, petroleum-derived plastics.

Starch is among the favored materials because of its low cost, availability and high production from annually renewable resources. However, the low water resistance, high brittleness and poor mechanical properties of starch-based plastics hindered their extensive application.

Polyvinyl alcohol (PVA) is another potential biodegradable polymer. It is water-soluble with good optical and film forming properties as well as enhanced mechanical properties. Adding PVA into starch-based plastics may improve the former's properties. Starch or PVA-based films are eyed by the food and medical industries as potential packaging materials, edible coating, drug delivery systems and membranes.

Chitosan, a natural polysaccharide biopolymer from crustaceans, has been found to have good film-forming and mechanical properties. It also showed anti-microbial properties beneficial for both food and medical applications. Chitosan is often blended with starch or PVA. Furthermore, the researchers discovered that the areas with exposed Chitosan exhibited antimicrobial properties.

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Thus, creating a laminate or coating from this material may be a more practical method of harnessing these properties. In addition, this will cut down on the amount of Chitosan needed to form the final films.

2. OBJECTIVES

The general objectives of this study include fabrication of Chitosan-coated starch-polyvinyl alcohol composite films and the characterization of their properties. The study aims to determine the effects of the amount of PVA and Chitosan to the mechanical and water-resistance properties of the composite film, as well as the antimicrobial properties of Chitosan coatings. It also seeks to identify the surface, thermal and chemical properties of the fabricated films.

3. PROBLEM STATEMENT AND DESCRIPTION

Environmental issues like global warming and plastic waste build up in landfills pose great challenges to the country. Among the potential solutions includes the development of biodegradable plastics from natural and annually renewable materials like starch. Using this alternative material will decrease the demand for less sustainable, non-biodegradable conventional plastics that cause environmental harm. This study may provide solution to the problem as well as a foundation for future studies to develop starch-based plastics. Through this study, the researchers hope to improve starch plastic by resolving several of its issues, including mechanical and moisture properties, brittleness and processability. Several solutions have been proposed, including chemical modification of starch, the production of starch composite systems, crosslinking and copolymerization, and surface treatments. Of these, the most basic involves combining starch with other superior materials like polyvinyl alcohol which is a synthetic biodegradable polymer with better mechanical and film-forming properties. Researchers propose blending starch and PVA at certain ratios while determining which combination produces the most outstanding properties.

The films that can be produced from the study may be used for food packaging. Other than resolving these issues, however, antimicrobial properties need to be optimized. The addition of Chitosan, which is proven to improve resistance to bacterial growth, will be maximized through a coating on the Starch-PVA films.

The Starch-PVA Chitosan-coated films are seen as forerunners of polymer films with life spans corresponding to their applications. This is believed to dramatically decrease plastic wastes in landfills. Furthermore, the process of producing such films can be improved for mass production.

4. METHODOLOGY

The starch-based plastics were fabricated using a method known as solution casting. This is used to create thin films by casting the solution onto a substrate or mold, then evaporating the solvent until the solution hardens and dries into a thin film. The researchers used experimental design to investigate the effects of the added components to the properties of the fabricated films.

For this study, the researchers made and characterized films with varying amounts of PVA. Glycerol was added as plasticizer. These films were coated using solution casting with varying concentrations of Chitosan.

The study wants to determine if such films can be produced using solution casting. It also aims to increase the mechanical strength of the film compared with the plain starch films. In addition, it seeks to increase its antimicrobial properties with the formation of Chitosan coating.

Standard test methods were used to confirm the hypothetical effects of the PVA and Chitosan on the starch-based films. These tests also determined the properties of the products which is helpful in determining their potential applications. The tensile properties (tensile strength and elongation at break) of the films were determined using the UTM according to the ASTM D882. The researchers also used ANOVA to study the effect of PVA and Chitosan on the mechanical property of the film. The test results determined the samples with optimal tensile properties for the antimicrobial test.

The researchers used the agar plate assay method in investigating the antimicrobial properties of the product. They determined the inhibitory effect and degree bacterial growth on the films to analyze and confirm the antimicrobial property of Chitosan. Swelling degree and contact angle were determined using improvised set-ups to observe the water responses of the fabricated samples. DSC and FTIR were also used to determine the thermal and chemical transformation of the films.

The researchers evaluated the results to determine if the varying starch and PVA ratios increased the mechanical properties of the product. They also evaluated the effect of the Chitosan coating concentration on its antimicrobial properties. Finally, the study suggested optimum settings for the desired application after evaluating the interactions among the three components.

5. RESULTS AND RECOMMENDATION

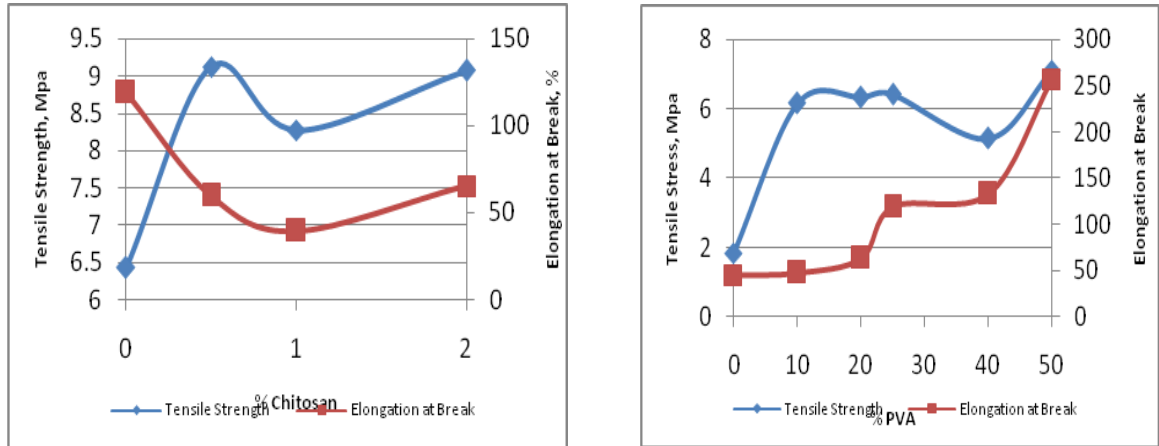
Starch-PVA-based films were successfully fabricated using the solution casting method, and coated with Chitosan to form a laminate film. Results showed that the mechanical properties of the films improved with increased PVA concentration and the addition of Chitosan layer. The films' tensile strength increased 284% max at 50:50 Starch-PVA ratios. Furthermore, a significant increase in the mechanical properties was also observed at the 75:25 Starch-PVA ratios. The Chitosan coating also increased the tensile properties of the films by 376.78%. ANOVA (one-way) showed the significance of both factors; moreover, ANOVA (two-way) showed higher significance for PVA. The researchers found antimicrobial properties on the coated films with the addition of PVA and Chitosan. Significant decrease in bacterial growth was observed starting at 1% Chitosan coating. The hydrophilic property of starch films remained even with PVA or Chitosan. The ANOVA identified increased PVA amount as a significant factor because it contributed to the decrease of the water absorbance and swelling degree of the film. No trend was observed with the Chitosan-coated samples.

It is important to note that mixing PVA and Starch, and adding a Chitosan layer to form films addressed the issue of starch brittleness. At 75:25 Starch-PVA ratios, the intended increase in mechanical properties was attained without having to add more PVA. In addition, though the process failed to address the hydrophilicity of starch, this finding provided a leeway to suggest other applications requiring both hydrophilicity and mechanical strength. The added Chitosan layer, though lacking total microbial inhibition, showed that it hindered the growth of both the *E. coli* and *S. typhimurium* bacteria.

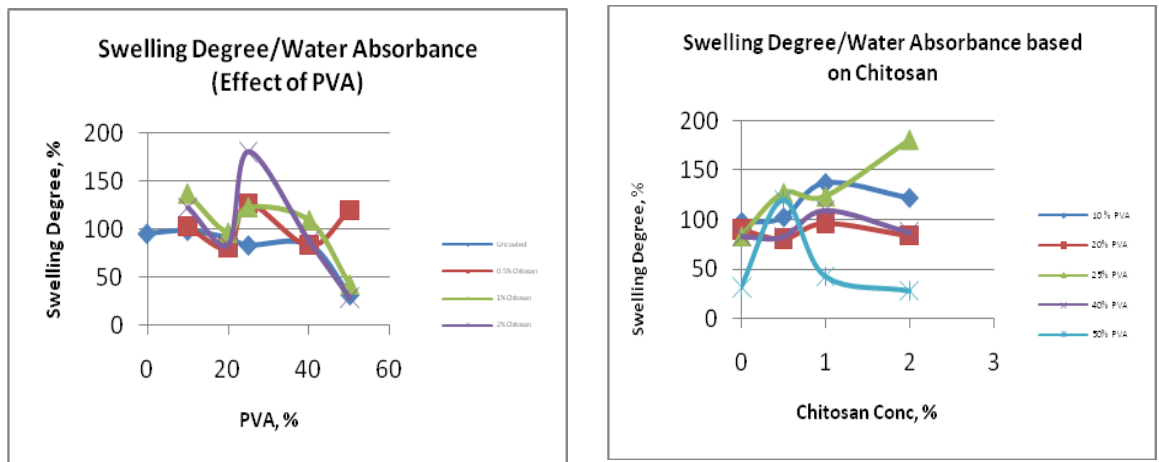
The researchers recommend further studies to develop and enhance the properties of starch-based films to suit the industries' demands. Chemical modification and addition of nano-

reinforcements may further improve both the mechanical and water resistance properties of starch-based polymers, permitting their use in food packaging. The researchers also recommend future studies to further improve the antimicrobial properties of the films to attain total inhibition of microbial growth.

Figures



Effect of %PVA and Chitosan Coating on the Tensile Strength and Elongation at Break of the Starch-based films.



Effect of %PVA and Chitosan Coating on the Swelling Degree/Water Absorbance of Film

Tables

Statistical Analysis Summary for Mechanical Properties

Table 1. ANOVA (One-way) for the Effect of PVA on the Tensile Strength of Starch Films

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	36.11287	5	7.222573	63.64105	4.07E-05	4.387374
Within Groups	0.680935	6	0.113489			
Total	36.7938	11				$\alpha = 0.5$

Remarks: $F > F_{crit}$, Therefore the amount of PVA is a significant factor in the Tensile Strength

Table 2. ANOVA (One-way) for the Effect of Chitosan on the Tensile Strength of Starch Films

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	9.538335	3	3.179445	9.647161	0.0265	6.591382
Within Groups	1.318293	4	0.329573			
Total	10.85663	7				$\alpha = 0.5$

Remarks: $F > F_{crit}$, Therefore the concentration of chitosan coating is a significant factor for TS

Table 3. ANOVA (One-way) for the Effect of PVA on the Elongation at Break of Starch Films

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	6.490944	5	1.298189	21.23145	0.000945	4.387374
Within Groups	0.366868	6	0.061145			
Total	6.857812	11				$\alpha = 0.5$

Remarks: $F > F_{crit}$, Therefore the amount of PVA is a significant factor in the Strain property of film

Table 4. Antimicrobial Test Results from the Microbial Test Assay conducted by NSRI.

Sample	Test Specimen	
	E. coli	S. typhimurium
Starch (100:0)	+++	+++
SPVA (75% Starch 25% PVA)	0.0% Chitosan	++
	0.5% Chitosan	++
	1.0% Chitosan	+
	2.0% Chitosan	+

Legend: (+++) – Heavy Growth; (++) – Moderate Growth; (+) – Slight Growth

ANOVA

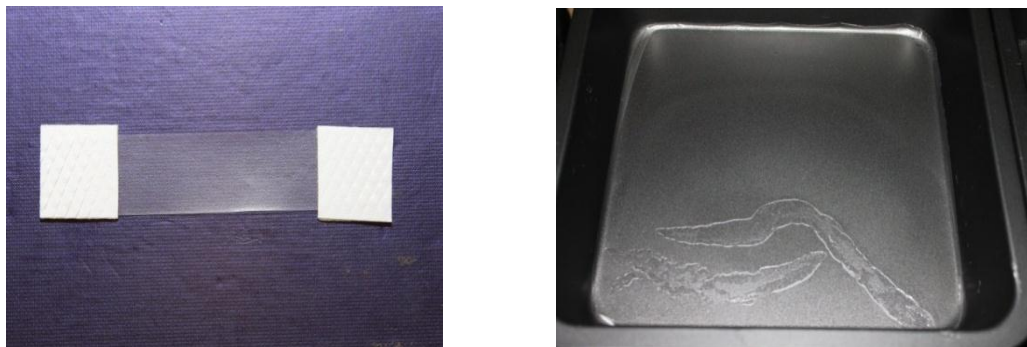
Source of Variation	SS	df	MS	F	P-value	F crit
PVA	12567.88	4	3141.971	3.826854	0.031421	3.259167
Chitosan	2254.365	3	751.4548	0.915256	0.462698	3.490295
Error	9852.389	12	821.0324			
Total	24674.64	19				

Photos

Experimental Set up



Product and Test Samples



REFERENCES

1. Anida M.M. Gomes, Paloma L. da Silva, Carolina de L. e Moura, Claudio E.M. da Silva, Na'gila M.P.S. Ricardo. "Study of the Mechanical and Biodegradable Properties of Cassava starch/Chitosan/PVA Blends." *Macromol.Symp.*2011, 299/300: 220–226.
2. Babak Ghanbarzadeh, Hadi Almasi, Ali A. Entezami. "Improving the barrier and mechanical properties of corn starch-based ediblefilms: Effect of citric acid and carboxymethyl cellulose." *Industrial Crops and Products* 33 (2011): 229–235.
3. Baofeng Lin, Yumin Du, Yanming Li, Xingquan Liang, Xiaoying Wang, Wen Deng, Xiaohui Wang, Lei Li, John F. Kennedy. "The effect of moist heat treatment on the characteristic of starch-based composite materials coating with chitosan." *Carbohydrate Polymers* 81 (2010): 554–559.

4. Fujun Liu, Bing Qin, Linghao He, Rui Song. "Novel starch/chitosan blending membrane: Antibacterial, permeable and mechanical properties." Carbohydrate Polymers 78 (2009): 146–150.
5. HongshengLiua, FengweiXie, Long Yu, Ling Chen, Lin Li. "Thermal processing of starch-based polymers." Progress in Polymer Science 34 (2009): 1348–1368.
6. Jiang Zhou, Yunhai Ma, LiliRen, Jin Tong, Ziqin Liu, Liang Xie. "Preparation and characterization of surface crosslinked TPS/PVA blend films." Carbohydrate Polymers 76 (2009): 632–638.
7. Jiang Zhou, Yunhai Ma, LiliRen, Jin Tong, Ziqin Liu, Liang Xie. "Preparation and characterization of surface crosslinked TPS/PVA blend films." Carbohydrate Polymers 76 (2009): 632–638.
8. Liqun Zhang, Wei Tian. "The effect of citric acid on the structural properties and cytotoxicity of the polyvinyl alcohol/starch films when molding at high temperature." Carbohydrate Polymers 74 (2008): 763–770.
9. MaolinZhai, Long Zhao, Fumio Yoshii, TamikazuKume. "Study on antibacterial starch/chitosan blend film formed under the action of irradiation." Carbohydrate Polymers 57 (2004): 83–88.
10. Melissa A.L. Russo, Cathryn O'Sullivan, Beth Rounsefell, Peter J. Halley, Rowan Truss,
11. Narendra Reddy, Yiqi Yang. "Citric acid cross-linking of starch films." Food Chemistry 118 (2010): 702–711.
12. P.C. Srinivasa, M.N. Ramesh, K.R. Kumar, R.N. Tharanathan. "Properties and sorption studies of chitosan–polyvinyl alcohol blend films." Carbohydrate Polymers 53 (2003): 431–438.
13. R. Jayasekara, I. Harding, I. Bowater, G.B.Y. Christie, G.T. Lonergan. "Preparation, surface modification and characterisation of solution cast starch PVA blended films." Polymer Testing 23 (2004): 17-27.
14. Rui Shi, Jingliang Bi, Zizheng Zhang, Aichen Zhu, Dafu Chen, Xinhua Zhou,
15. S. Tripathi, G.K. Mehrotra, P.K. Dutta. "Physicochemical and bioactivity of cross-linked chitosan–PVA film for food packaging applications." International Journal of Biological Macromolecules 45 (2009): 372–376.
16. S. Tripathi, G.K. Mehrotra, P.K. Dutta. "Preparation and physicochemical evaluation of chitosan/poly(vinyl alcohol)/pectinternary film for food-packaging applications." Carbohydrate Polymers 79 (2010): 711–716.
17. Sanjiv Arora, SohanLala, Chetan Sharmab and Kamal R. Anejab. "Synthesis, thermal and antimicrobial studies of chitosan/starch/poly(vinyl alcohol) ternary blend films." Der Chemica Sinica 2011, 2(5):75-86.
18. Shangwen Tang, PengZou, HanguoXiong, Huali Tang. "Effect of nano-SiO₂ on the performance of starch/polyvinyl alcohol blend films." Carbohydrate Polymers 72 (2008): 521–526.
19. William P. Clarke. "The anaerobic degradability of thermoplastic starch: Polyvinyl alcohol blends: Potential biodegradable food packaging materials." Bioresource Technology 100 (2009): 1705–1710.
20. Xiaozhao Han, Sensen Chen, Xianguo Hu. "Controlled-release fertilizer encapsulated by starch/polyvinyl alcohol coating." Desalination 240 (2009): 21-26.

21. Xiaozhi Tang, Sajid Alavi. "Recent advances in starch, polyvinyl alcohol based polymer blends, nanocomposites and their biodegradability." [Carbohydrate Polymers](#) 85 (2011): 7–16.
22. Zhao Guohua, Liu Ya, Fang Cuilan, Zhang Min, Zhou Caiqiong, Chen Zongdao. "Water resistance, mechanical properties and biodegradability of methylated-cornstarch/poly (vinyl alcohol) blend film." [Polymer Degradation and Stability](#) 91 (2006): 703-711.