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Research Article

The effect of the crosslinking agent on physical and mechanical properties of Chitosan / Banana flour sheet

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Abstract

This research studied the effect of the cross-linking agent on physical and mechanical properties of Chitosan / Banana flour sheets. The Chitosan / Banana flour sheets were prepared by compression molding at 130°C for 2 minutes, using 15% gelatinized banana flour with propane 1,2-diol (plasticizer) mixed with 1.5% chitosan solution and boric acid used as the cross-linking agent with varied amounts (0%, 0.5%, 1%, 1.5% and 2%) based on dry starch content. The mixture was stirred until compatible and then dried and reduced in size at room temperature. For the final step, the product was prepared by compression molding in order to study physical (compatibility, humidity and color parameter) and mechanical properties (tensile testing) of the sheets. The Chitosan / Banana flour sheets mixed with boric acid showed an increase in miscibility between banana flour and chitosan as seen in the SEM images and improved flexibility of the sheets. The results presented show that the incorporation of boric acid into the Chitosan / Banana flour sheet improved the compatibility, mechanical properties, humidity stability and appearance of the material, a cross-linking content of 1.5% gave the best overall improvement. With these improved properties this Chitosan / Banana flour sheet can be applied to be used as a biodegradable food packaging material.

Keywords: plasticizer, cross-linking agent, Banana flour

Introduction

Currently, environmental pollution is a great concern for many people and results from various causes, both industrial and community sourced. Across the world about 1-million tonnes of single-used food packaging are used produced from polymer materials such as polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and polystyrene (PS). Most of these non-biodegradable materials are dumped into the environment (landfill sites) or burnt and this causes significant pollution. Starch is one of the possible alternative materials for producing biodegradable packaging. Starch has good potential as it is both renewable and biodegradable, however, starch-based films (Martin et al., 2001; Corradini et al., 2006), are brittle and hydrophilic, which limits their processing and applications. Starch can be blended with various synthetic and natural polymers in order to improve its properties. One of these natural polymers is chitosan (Aider, 2010), which is one of the most abundant polysaccharides in nature, it is also non-toxic, biodegradable, and has antimicrobial activity. Chitosan is however,

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more hydrophobic in nature when compared to starch. Most work related to the production of biodegradable films based on starch has studied to improve the biodegradable properties using synthetic polymers, such as producing starch film from sweet potato starch with glycerol as a plasticizer; the starch film produced had high flexibility and a decreased T_g than films without the plasticizer (Mali et al., 2005). Other work produced biodegradable polymer blends based on corn starch and thermoplastic chitosan extrusion processed, the resultant material presented a homogeneous fracture surface without the presence of starch granules or chitosan aggregates. Although the incorporation of thermoplastic chitosan caused a decrease in both tensile strength and stiffness, films with better extensibility and thermal stability were produced (Mendes et al., 2016). The previous research found that surface structure of chitosan/banana flour without cross-linking and prepare by casting method was exhibit big gel matrix particle because of retrogradation forms granula (Pitak & Rakshit,2011).

This research was interested to improve the surface structure of Chitosan / Banana flour sheets (CBFS) by use of a cross-linking agent and studies the effect of the cross-linking agent on physical and mechanical properties of CBFS.

Materials and methods

2.1 Materials

Banana flour (c.v.Kluai Namwa from local market in Phitsanulok, Thailand), commercial high molecular weight chitosan powder 40 mesh from shrimp shell (TA MING ENTERPRISES), Propane 1,2-diol (Asia Pacific Specialty Chemicals Ltd.), Boric acid (Fisher Scientific UK.)

2.2 Preparation of Banana flour

Banana flour was produced from fresh green bananas (c.v.Kluai Namwa). First, the bananas were removed from their bunches, washed before being placed into boiling water for 30 mins, after they were cooled, peeled, sliced and dried at 60ºC in oven 24 hours. Second, the dry bananas were sliced and milled by moulinex food processor (600w) and ball mill, respectively. Then banana flour powder was finally sieved using a 90 mesh.

2.3 Preparation of Chitosan / Banana flour sheet

The CBFS were prepared using 15%w/w gelatinized banana flour with propane 1,2-diol (plasticizer) at 30% based on the dry starch content mixed with 1.5%w/w chitosan solution (1.5%w/w of Chitosan powder dissolved in 1% acetic acid solution) and boric acid as the cross-linking agent, whose content was varied at 0%, 0.5%, 1%,1.5% and 2% again calculated on dry starch content and stir until compatible. Dried at room temperature 48 hours and reduced in size by moulinex food processor (600W). For the final step, the product was prepared by compression molding at 130ºC, 110 kg/cm^2 for 2 minutes in 15.0 x 15.0 cm^2 mold with a thickness of 1.00 mm. The Chitosan / Banana flour sheets were kept in a closed environment at room temperature at 50.0% humidity before studying the physical and mechanical properties.

2.4 Physical and Mechanical testing

Morphology was analyzed using scanning electron microscope (SEM, model Leo 1455VP, CARL ZEISS CO., LTD.) at Naresuan University, Thailand. 1.00 x 1.00 cm^2, for surface morphology samples were mounted with carbon tape on stubs. For the cross-section analysis samples from tensile testing were mounted with the cross-section positioned upward on the

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stubs in order to analyze the cross-section morphology, all specimens were sputter-coated with gold.

Humidity stability was studied by cutting 2.00 x 2.00 cm^2 from 3 positions in the sample and measured by digital vernier caliper. Moisture removed in sample was placed on tray in an oven at 105^{o}C for 4 hours. This experiment was carried out in a closed system (under 60% humidity and temperature range was 28^{o}C-36^{o}C). To measure the percent moisture content, the specimens were weighed every day for 14 days and the percent weight loss (W_1) was calculated based on the original weight (W_2). The temperature was around 28-36^{o}C.

$$\text{moisture content}=\left(\frac{W_2\text{-}W_1}{W_1}\right)\times 100$$

Colorimeter (Hunter Associates Laboratory, Inc.) was used to measure the color parameters of the specimens. Three readings on the surface of the specimens were taken using the CIE Laboratory L* (lightness), a* (redness), b* (yellowness) system in daylight conditions. The specimens were prepared by sampling 8 positions (2.00 x 2.00cm^2) per sample; each position was measured in 4 positions and averaged.

Tensile testing (Electronic Universal Testing Machine model WDW-5E) was performed to determine the mechanical properties of the CBFS. The specimens were determined according to ASTM D638. Five positions per sample were chosen and prepared by cutting strips of the sheets 168 mm long with gage length of 50 mm. The width and thickness of specimens were measured before each measurement and measured by 1 KN load cell, at a speed of 20 mm/min, at room temperature, and a humidity of 50.0% ±0.2.

Results and discussion

3.1 Physical and mechanical properties

3.1.1 Morphology of the chitosan / banana flour sheets

The surface morphology of the CBFS showed smooth surfaces as shown in figure 1. The CBFS without boric acid (30PD) has a very smooth surface because of banana flour and chitosan are both hydrophilic natural polymers, and they show good compatibility. The 30PD_0.5BR has roughest surface because of the incompatibility between chitosan and boric acid, however, when boric acid content was higher than 0.5% the CBFS gave smoother surfaces again. Overall, the surfaces are similar when different ratios of boric acid were added into the CBFS. Figure 2 shows the cross-section morphology of CBFS and shows the absence of starch granules after processing, present between gelatinized banana flour and chitosan. The result of 30PD was rough with large amount cracking in cross-section, which is greater than present in the cross-linked samples because when increasing the cross-linker content, there is an increase in the compatibility of sheets, as seen in the morphology in figure 2. Thus, the addition of boric acid into the mixture helped the compatibility of banana flour and chitosan.

3.1.2 Color parameter of the chitosan / banana flour sheets

The color parameters in Table 1 show L*, a* and b* values of cross-linked CBFS. 30PD sheet is without any cross-linker and presented the following color parameters; 5.73±0.62, 2.67±0.41 and 1.21±0.89. When boric acid was added to the mixture and increased from 0.5 to 2 %, there is approximately a twofold increase in all values, boric acid at 2% gives causes L* value increased to 14.96±0.46. This is due to the free volume between polymer chains from

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cross-linking causes an increase in transparency of CBFS and therefore, an increase in a* and b*.

3.1.3 Humidity stability of the chitosan / banana flour sheets

Figure 3 shows the percent moisture absorption of the CBFS. The moisture absorption ability of CBFS without cross-linker (30PD) was higher than with cross-linker by 4 times. The results show that a high proportion of free hydroxyl groups increases the amount of H-bonding with free water in the environment. When the humidity of system was increased the moisture absorption rate of sample was also increased, and the trend was the same as when the humidity of system was lower. The absorption moisture sensitivity of non-cross-linked was higher than cross-linked and moisture absorption values were dependent on the humidity of the system. These results show boric acid decreases the hydrophilic properties of CBFS and may be able to form cross-links between banana flour or banana flour and propane 1,2-diol. According to a previous report about hydrogen bonding interactions between hydroxyl groups on nanofibrillated cellulose (NFC), PVA, and trigonal borate complexes can occupy that would provide potential crosslinking (Spoljaric et al., 2014). Therefore, the banana flour structure contains hydroxyl group was similar to the NFC, and should also be able to utilize the same cross-linking mechanism. Therefore, the data indicated that cross-linking the CBFS with boric acid increases the humidity stability greater than non-cross-linking.

Table 1. Color values of the chitosan / banana flour sheets

Sample name	L*	a*	b*
30 PD	5.73±0.62	2.67±0.41	1.21±0.89
30PD_0.5BR	10.11±0.32	6.53±0.37	4.96±0.26
30PD_1BR	10.60±0.39	7.35±0.67	4.87±1.11
30PD_1.5BR	11.13±0.57	7.71±0.50	5.89±0.51
30PD_2BR	14.96±0.46	7.38±0.31	8.08±1.18

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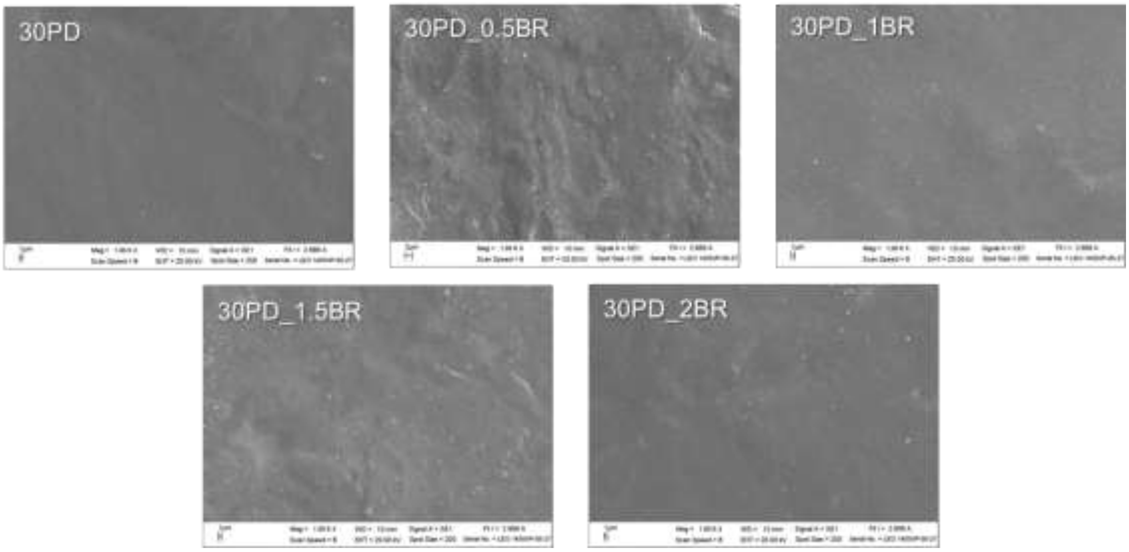

Figure 1. Surface morphology of the CBFS without cross-linker (30PD), cross-linked CBFS (30PD_0.5BR, 30PD_1BR, 30PD_1.5BR and 30PD_2BR)

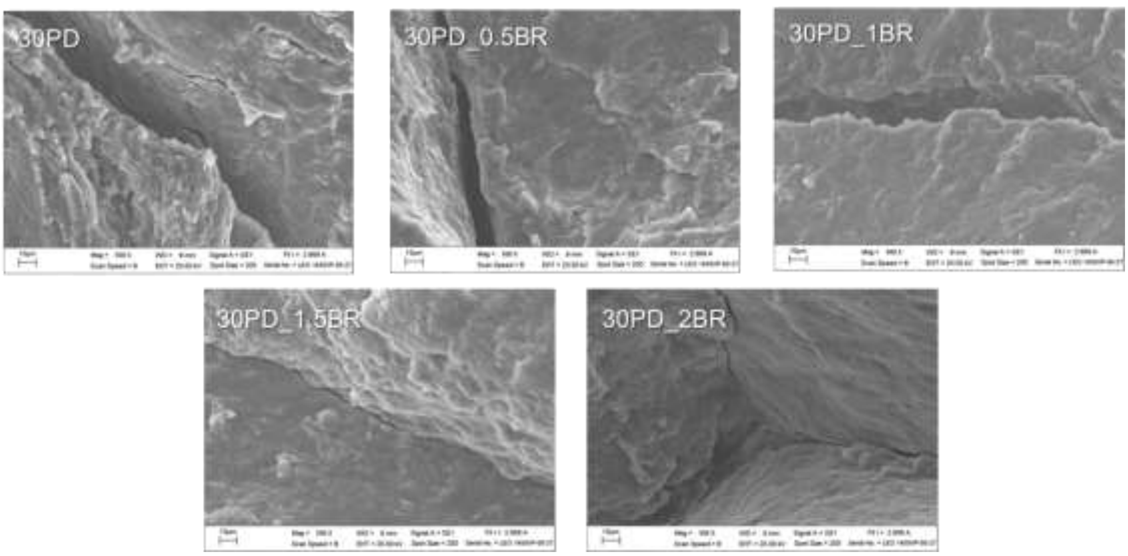

Figure 2. Cross-section morphology of CBFS without cross-linker (30PD), cross-linked CBFS (30PD_0.5BR, 30PD_1BR, 30PD_1.5BR and 30PD_2BR)

3.1.4 Mechanical properties of the chitosan / banana flour sheets

In order to examine the mechanical performance of the sheets the tensile strength, %Elongation at break and Modulus at break were measured and the results are shown in figure 4, 5 and 6, respectively. Figure 4 presents the tensile strength in MPa, from this figure the

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tensile strength value of 30PD_0.5BR was similar to 30PD but when boric acid was greater than 0.5% the trend was to get higher tensile strength values. In figure 5 the results showed that that when the boric acid content was 1%, there was a sudden increase in %Elongation, but %Elongation decreased with further increase in boric acid content as 2% of boric acid was too high and made to loss %Elongation in the CBFS. Figure 6 shows that the modulus at break decreases when the percentage of cross-linking agent was greater than 0.5%, there was decreased in the hardness of the CBFS. Therefore, in summary of the mechanical data, tensile strength and %Elongation increased, while modulus at break decreased when boric acid content was higher than 0.5%. This increased flexibility of sample was because of the percentage increase in cross-linker in the CBFS. The maximum force required to break the higher cross-linked samples was higher than low cross-linked samples. These results indicated that appropriate amount of cross-linking agent to increase flexibility of material was 1.5%.

Conclusion

In this research the aim was to study the effect of the cross-linking agent on physical and mechanical properties of Chitosan / Banana flour sheets. An increase in cross-linker (boric acid) content increased the miscibility between banana flour and chitosan as shown in the SEM images, as well as increases the humidity stability and flexibility. The mechanical properties were increased when appropriate amounts of cross-linking agent were used. A cross-linker content of 1.5% produced a material with the best overall balance of properties. With these improved properties this Chitosan / Banana flour sheet can be applied to be used as biodegradable food packaging materials.

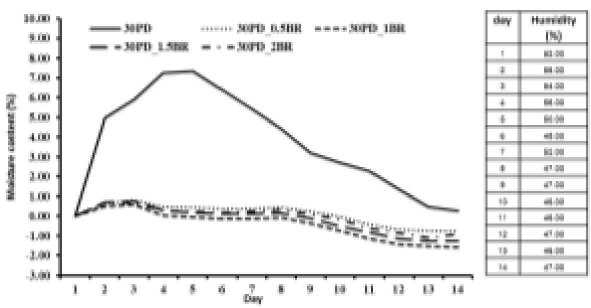

Figure 3. Average moisture content (%) of CBFS

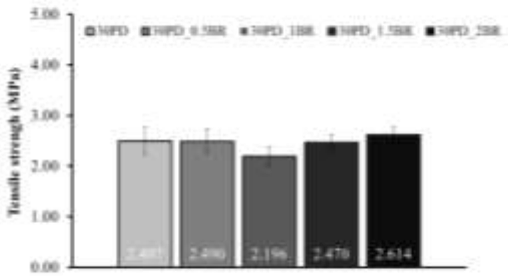

Figure 4. Tensile strength of CBFS

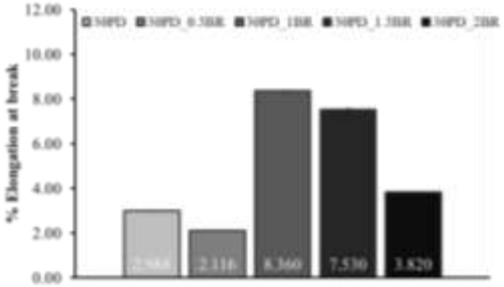

Figure 5. % Elongation at break of CBFS

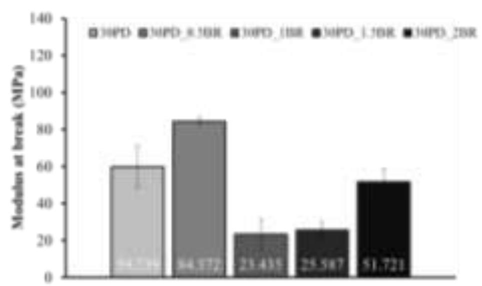

Figure 6. Modulus at break of CBFS

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