Carbohydrate Polymers 78 (2009) 444–448

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Mechanical properties of chitosan/bamboo charcoal composite films made with normal and surface oxidized charcoal

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ARTICLE INFO

Article history:
Received 21 January 2009
Received in revised form 27 April 2009
Accepted 30 April 2009
Available online 7 May 2009

Keywords:
Chitosan
Bamboo charcoal
Composite
Film
Mechanical properties

ABSTRACT

Chitosan/bamboo charcoal composite films were prepared by blending chitosan with either virgin bamboo charcoal or bamboo charcoal modified by nitric acid oxidation to provide more hydrophilic regions on the bamboo charcoal surface. Investigation of the physical properties of these composite films revealed that the tensile strength and Young's modulus of the chitosan films were enhanced in a dose-dependent manner by the inclusion of modified bamboo charcoal at up to 1% (w/w), whilst the elongation at break was increased by inclusion of modified bamboo charcoal at up to 0.5% (w/w). In contrast, chitosan composites with virgin bamboo charcoal at up to 0.5% or 1.0% (w/w) showed no enhancement of the tensile strength or Young's modulus, respectively, and both parameters were reduced with higher levels of virgin bamboo charcoal. Oil, and especially water, absorption of the composite films displayed a marked and dose-dependent increase compared to those of the pure chitosan film.

1. Introduction

Chitosan, a polysaccharide composed mainly of β-(1,4)-linked 2-deoxy-2-amino-D-glucopyranose units, is the deacetylated product of chitin, poly (*N*-acetyl)-D-glucopyranose. Chitin and chitosan, which are extracted from various animals and plants, are the second most abundant natural biopolymers found on earth next to cellulose (Knaul, Hudson, & Creber, 1999; Zheng, Du, Yu, Huang, & Zhang, 2001). Because of its biocompatibility, biodegradability, antimicrobial activity and non-toxicity, chitosan has been extensively investigated for several decades for uses in biomaterials, wastewater treatment, cosmetics, food packaging, and textiles amongst others (Li, Dunn, Grandmaison, & Goosen, 1997). However, its properties, such as thermal stability, mechanical properties and gas barrier properties are frequently not sufficient to meet the requirements of these wide ranges of applications (Dilip, Annamalai, & Raj, 2006; Hoagland & Parris, 1996; King-Fu, Chi-Yi, Tzyy-Shyan, Wen-Yen, & Yuang-Haun, 2005; Pinotti, Garcia, Martino, & Zaritzky, 2007; Wong, Gastineau, Gregorski, Tillin, & Pavlath, 1992; Yixiang, Xi, & Milford, 2006). Developing chitosan/bamboo charcoal powder composite films by inserting bamboo charcoal powder in chitosan chains can enhance its properties (Ching-Wen et al., 2007).

Bamboo (*Dendrocalamus asper* Backer) charcoal powder contains many pores and gaps in its structure, making it excellent for absorption, electromagnetic shielding and infrared emission (Asada et al., 2002). Bamboo charcoal powder also contains ions, such as the anions calcium, sodium and iron, and is of use in water and air purification and improving the acidity condition (Asada et al., 2002; Mizuta, Matsumoto, Hatate, Nishihara, & Nakanishi, 2004), and is widely used in the fields of food cooking, baking, stocking, and keeping food produce fresh.

Both chitosan and bamboo are plentiful, relatively cheap, renewable, biodegradable, and relatively non-toxic and sustainable products. Therefore, the aim of this research was to evaluate if the incorporation of bamboo charcoal would lead to a high-performance chitosan composite film. Chitosan/bamboo charcoal composite films were prepared by the use of a spin coater machine and then the functional properties of these hybrid films were evaluated.

2. Experimental

2.1. Materials

Chitosan powder, with a deacetylation degree of 95% and a molecular weight = 10 kDa, was purchased from Seafresh Chitosan (Lab) Co., Ltd. (Thailand). Bamboo charcoal powder with particle size range 7–13 μm. Nitric (70% (v/v)) and glacial acetic acids were purchased from J.T. Baker (Thailand).

2.2. Modification of bamboo charcoal powder

Eight gram of bamboo charcoal powder was suspended in 600 ml of 70% (v/v) nitric acid in a 1000 ml flask and refluxed at

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doi:10.1016/j.carbpol.2009.04.027

130 °C for 2 h. The charcoal was recovered from the cooled mixture by centrifugation at 4000 rpm for 15 min with decanting of the supernatant. The charcoal pellet was washed by thorough resuspension in distilled water and pelleted by centrifugation as before. The pelleted washed charcoal powders were then harvested, dried in an oven at 80 °C overnight and further heated at 130 °C for 2 h to remove any residual nitrogen oxides.

2.3. Preparation of chitosan and chitosan/bamboo charcoal composite films

Pure chitosan films were prepared by dissolving 5 g of chitosan powder in 100 ml of 30% (v/v) acetic acid solution and stirring in a high speed mixer for 72 h. Chitosan films were then derived from this solution using a spin coater machine and dried at room temperature for 48 h.

Chitosan/bamboo charcoal composite films were prepared by mixing 5% (w/v) chitosan solution with various amounts, from 0.1% to 2% (w/w), of bamboo charcoal powder and then stirred at 2500 rpm for 1 h. The chitosan/bamboo charcoal composite films were likewise derived from the solution using the spin coater machine and dried at room temperature for 48 h.

Chitosan/modified bamboo charcoal composite films were prepared as above, except using modified bamboo charcoal in place of unmodified bamboo charcoal.

2.4. Characterization of the chitosan/bamboo charcoal composite films

2.4.1. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectra (transmission) were recorded on a Perkin–Elmer Model Spectrum One in the range of 4000–450 cm^{-1} at a resolution of 1 cm^{-1}. Bamboo charcoal powders were thoroughly mixed with KBr and pressed into pellet form.

2.4.2. Mechanical properties of films

The tensile stress at maximum load, tensile modulus, and percent elongation at break of the film samples were measured using a Universal Testing Machine (Model LLOYD LR 100K). Film samples of 150 × 15 mm were measured for thickness, and then conditioned for 24 h at 25 °C and 60% RH before testing. The test was carried out according to the ASTM D 882 standard method, with an initial grip separation of 100 mm, a crosshead speed of 10 mm min^{-1}, and load cell of 100 N.

2.4.3. Water absorption of films

Water absorption of films was determined by following the standard method of ASTM D 570-95. For water absorption, specimens of 76.2 × 25.4 mm were placed in a desiccator for 24 h, weighed, and immersed in distilled water at an ambient temperature for 24 h. The test specimens were removed, patted dry with a dry lint cloth and weighed immediately. Water absorption is expressed as the percentage increase in weight.

2.4.4. Oil absorption of films

Oil absorption was determined as the amount of sunflower oil absorbed by the chitosan and composite films under the same testing procedures as mention earlier for water absorption, except for changing distilled water to sunflower oil.

3. Results and discussion

3.1. FTIR spectroscopy

Bamboo charcoal particles are hydrophobic and stay in aggregated form in aqueous environments, which makes it difficult to be adsorbed onto the surface of and then diffuse into the chitosan film, particularly the more hydrophilic ones. Oxidative treatment of bamboo charcoal particles is one effective way to increase the hydrophilicity due to the generation of carboxylic acid groups (as well as other minor changes such as hydroxyl groups) on the particles' surface. Nitric acid, a strong oxidizing agent, can attack some imperfect areas of the bamboo charcoal particles during refluxing, which leads to the formation of carboxylic acid groups (—COOH) at these surfaces. This result was similar to that obtained from the modification of carbon black with nitric acid (Dapeng & Gang, 2007).

Comparing the FTIR spectra of untreated and modified (70% (v/v) nitric acid treated) bamboo charcoal particles revealed the likely presence of COOH (~1727 cm^{-1}), as well as other features typical of oxidation including —OH at ~3392 cm^{-1}, C═C at 1616 cm^{-1}, N═O at 1345 cm^{-1} and C—O at ~1216 cm^{-1}, in the modified bamboo charcoal particles (Fig. 1). These results supports

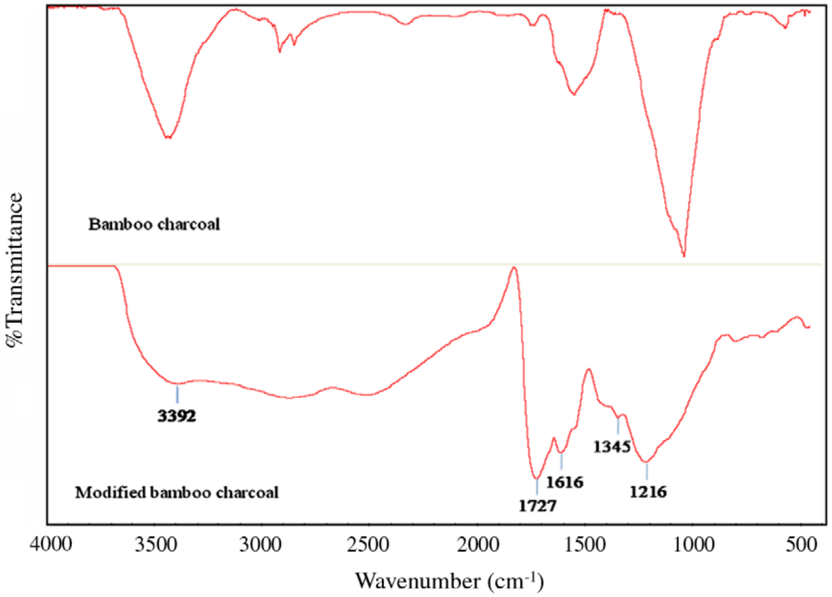

Fig. 1. FTIR spectra of unmodified and modified bamboo charcoal particles.

that nitric acid, used as an oxidizing agent, had oxidized some areas of bamboo charcoal particles during refluxing leading to formation of carboxylic acid groups (and other moieties) on the surface of the bamboo charcoal particles.

3.2. Mechanical properties of chitosan and chitosan/bamboo charcoal composite films

The effect of the inclusion of different bamboo charcoal contents on the tensile strength, Young's modulus, and elongation at break of the composite films are summarized in Figs. 2, 3 and 4, respectively.

The tensile strength of the chitosan/unmodified bamboo charcoal composite films decreased slightly but significantly with increasing unmodified bamboo charcoal contents in composite films up to 0.5% (w/w), and then decreased dramatically (~66%) at 1% and 2% (w/w) unmodified bamboo charcoal levels. This result may suggest that no reinforcement was obtained by the addition of unmodified bamboo charcoal, but rather that unmodified bamboo charcoal had a poor interfacial adhesion between itself and the composite matrix and possibly was more agglomerated when added at 1% and 2% (w/w), which weakens the stress distribution in the chitosan/unmodified bamboo charcoal composite film.

In contrast, the tensile strength of the chitosan/modified bamboo charcoal composite film increased in a dose-dependent manner with increasing levels of modified bamboo charcoal up to a maximum at 1% (w/w), at which level the increase in tensile strength attained over pure chitosan films was ~46%, and then fell slightly at 2% (w/w) modified bamboo charcoal. This result could be attributed to the presence of carboxylic acid groups (and perhaps to a lesser extent the other polar modifications such as hydroxyl groups) formed on the surface of the bamboo charcoal by nitric acid oxidation which provide a better interfacial adhesion with the chitosan through hydrogen and electrostatic bonding. However, that 2% (w/w) modified bamboo charcoal in the composite film slightly reduced the tensile strength, compared to 1% (w/w), may be due to agglomeration of bamboo charcoal with a resulting reduced stress distribution from chitosan to the modified bamboo charcoal.

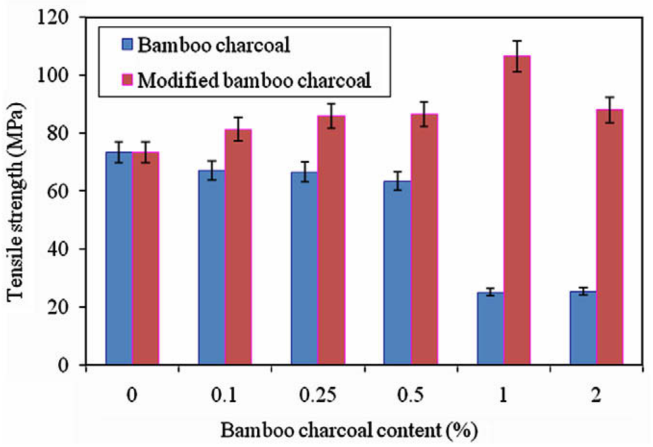

Fig. 2. The effect of unmodified and modified bamboo charcoal on the tensile strength of chitosan films.

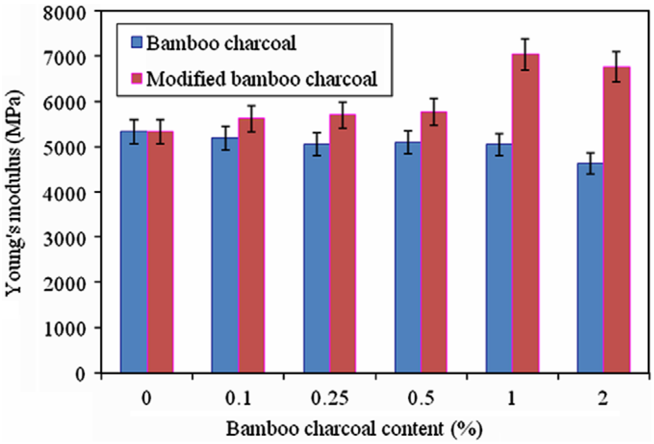

Fig. 3. The effect of unmodified and modified bamboo charcoal on the Young's modulus of chitosan films.

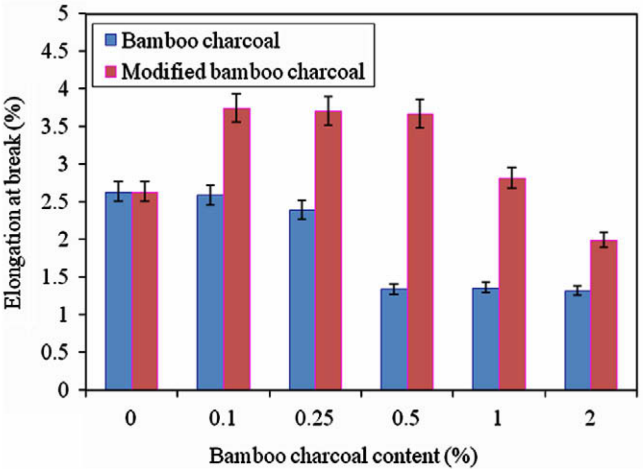

Fig. 4. The effect of unmodified and modified bamboo charcoal on the elongation at break of chitosan films.

Using Young's modulus as a marker of the rigidity of these films, the rigidity of the chitosan/modified bamboo charcoal composite films, somewhat akin to the tensile strength, was increased in a dose-dependent manner with increasing modified bamboo charcoal content up to 1% (w/w), at which level an ~30% increase in rigidity was observed compared to pure chitosan films. Thereafter, a slight reduction, compared to 1% (w/w) modified bamboo charcoal, in rigidity was observed with 2% (w/w) modified bamboo charcoal. In contrast, the rigidity of the chitosan films was decreased only slightly with increasing unmodified bamboo charcoal content up to 1% (w/w), and more so at 2% (w/w). These results of the changes in the composite film rigidity, as determined by Young's modulus, could suggest that the oxidative treatment of bamboo charcoal particles was effective in increasing the interfacial adhesion between bamboo charcoal and chitosan (such as electrostatic forces between amine and carboxylic groups), and also in providing more H-bonding between them, and thus leading to a higher rigidity of the composite film compared to either pure chitosan or chitosan/unmodified bamboo charcoal composite films.

The elongation at break of chitosan/modified bamboo charcoal films showed a slightly different trend to those seen for composite rigidity and tensile strength. Thus, the elongation at break increased essentially the same amount (~38%) with the addition of 0.1–0.5% (w/w) modified bamboo charcoal content, and then deceased rapidly with higher levels (1% and 2% (w/w)) of modified bamboo charcoal. At 2% (w/w) modified bamboo charcoal content, elongation at break value was lower than that seen with pure chitosan film. This may be because the reduction of extensible matrix in this type of composite film is reduced extremely when the content of modified bamboo charcoal is increased to 1% (w/w) and above. The elongation at break of chitosan/unmodified bamboo charcoal showed no increase relative to pure chitosan films but decreased slightly with increasing unmodified bamboo charcoal content up to 0.25% (w/w), and then markedly at 0.5% (w/w) where a reduction of ~46% compared to pure chitosan films was observed, and then remained at this low level with higher unmodified bamboo charcoal contents (at least up to 2% (w/w)). Presumably, the unmodified bamboo charcoal, without any enhanced compatibility (electrostatic and hydrogen bonds) with chitosan, will be less able to resist deformation of these composite films.

3.3. Water absorption

The influences of the different types and levels of bamboo charcoal content on water absorption of chitosan films are summarized in Fig. 5. Water absorption of the pure chitosan film was about 112% by weight. Pure chitosan film had good water absorption due to hydrophilic nature of chitosan. Water absorption was increased in a dose-dependent manner by inclusion of either unmodified or modified bamboo charcoal up to 1% (w/w), although the increase in water adsorption was more marked in modified than unmodified bamboo charcoal composites. The enhanced water absorption seen in modified bamboo charcoal composite films relative to the same (w/w) unmodified bamboo charcoal composite films would then be attributed to the formation of hydrophilic carboxylic groups on the surface of the modified bamboo charcoal by nitric acid providing stronger hydrogen bonding for water and thus a more hydrophilic surface nature than those of chitosan/unmodified bamboo charcoal film, whilst the negative surface charge would reduce the tendency of bamboo charcoal to agglomerate and thus account for the less extreme reduction in water absorption seen in the 2% (w/w) bamboo charcoal composites. When the content of unmodified or modified bamboo charcoal was increased to 2% (w/w), however, a marked and slight decrease in water adsorption levels, with respect to that observed at 1% (w/w), was seen, respectively. The amount of bamboo charcoal contents of 2% (w/w) in composite films may cause significant agglomeration of the bamboo charcoal reducing the pores and gaps in the bamboo charcoal structure. These may detriment the ability of water absorption of both types of chitosan/bamboo charcoal composite films, compared to that seen at 1% (w/w). Bamboo charcoal was not considered as a hydrophilic material, but the significantly increased water absorption in both types of chitosan/bamboo charcoal composite films may likely to be attributed to the many pores and gaps in the bamboo charcoal structure and hydrophilic character of chitosan itself. Both of chitosan/bamboo charcoal composite films have very good water absorption, compared with commercial plastic low density polyethylene film produced from SAN DIEGO PLASTICS, INC. having water absorption less than 0.01%. This may likely be explained by the nature hydrophilic or hydrophobic character of material.

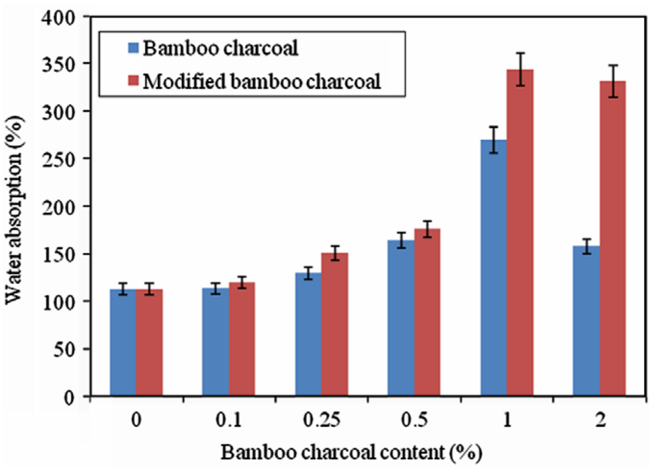

Fig. 5. The effect of unmodified and modified bamboo charcoal contents on water absorption of chitosan films.

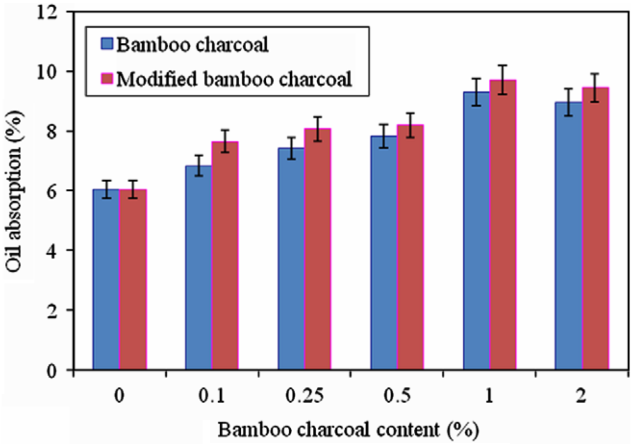

Fig. 6. The effect of unmodified and modified bamboo charcoal contents on oil absorption of chitosan films.

3.4. Oil absorption

The influence of bamboo charcoal content on the oil absorption of chitosan films is summarized in Fig. 6. In general, chitosan itself has good affinity with the oil and the bamboo charcoal is considered as a hydrophobic material. Therefore, inclusion of bamboo charcoal in chitosan composite films could enhance better oil absorption than that of pure chitosan film. The results shown in Fig. 6 could be concluded that oil absorption in the pure chitosan films was about 6% by weight, and both modified and unmodified bamboo charcoal composite films revealed a dose-dependent increase in oil absorption up to 1% (w/w) charcoal composition. The results of oil absorption of both types of bamboo charcoal composite films were in broad accordance with the results obtained for water absorption, except the magnitude was much lower. This again may reflect the presence of pores and gaps that bamboo charcoal introduces into the composite structure and also due to hydrophobic character of bamboo charcoal. Chitosan/modified bamboo charcoal composite film providing more oil absorption than that of chitosan/unmodified bamboo charcoal composite film would presumably be due to the reduced aggregation and more even dispersion of the charged modified bamboo charcoal particles throughout the composite matrix.

4. Conclusion

Chitosan/bamboo charcoal composite films were made by adding virgin (unmodified) or nitric acid oxidized (modified) bamboo charcoal into chitosan solution and forming the composite film by spin coating. The mechanical properties of these films were investigated and revealed that the tensile strength and rigidity (as defined by Young's modulus) of chitosan/1% (w/w) modified bamboo charcoal composite films were better than those of pure chitosan and chitosan/unmodified bamboo charcoal composite films. The elongation at break of chitosan/modified bamboo charcoal composite films were slightly higher than that of either pure chitosan film or chitosan/unmodified bamboo charcoal films, but were optimal at 0.5% (w/w) modified bamboo charcoal and reduced rapidly above this level. Incorporation of either unmodified or modified bamboo charcoal in chitosan films enhanced both the oil and, especially, the water absorption of the composite films. These effects are attributed to the induced surface charge and increased hydrophilic nature of the oxidized charcoal surface (e.g., carboxylic acid and hydroxyl groups) reducing agglomeration and maintaining a more homogenous dispersion in the composite matrix with hydrophilic pores and gaps.

Acknowledgement

The authors thank the 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund), Chulalongkorn University for the financial support.

References

Asada, T., Ishihara, S., Yamane, T., Toba, A., Yamada, A., & Oikawa, K. (2002). Science of bamboo charcoal: Study on carbonizing temperature of bamboo charcoal and removal capability of harmful gases. *Journal of Health Science, 48*, 473–479.

Ching-Wen, L., Ching-Wen, L., Ching-Hwan, L., Kuan-Hua, S., Chan-Hung, H., Zheng-Horng, L., et al. (2007). PET/PP blend with bamboo charcoal to produce functional composites. *Journal of Materials Processing Technology, 192–193*, 428–433.

Dapeng, Li, & Gang, Sun (2007). Coloration of textiles with self-dispersible carbon black nanoparticles. *Dyes and Pigments, 72*, 144–149.

Dilip, D., Annamalai, P. K., & Raj, P. S. (2006). Preparation and characterization of novel hybrid of chitosan-g-lactic acid and montmorillonite. *Journal of Biomedical Materials Research Part A, 78*, 372–382.

Hoagland, P., & Parris, N. (1996). Chitosan/pectin laminated films. *Journal of Agriculture and Food Chemistry, 44*, 1915–1919.

King-Fu, L., Chi-Yi, H., Tzyy-Shyan, H., Wen-Yen, C., & Yuang-Haun, L. (2005). A novel method to prepare chitosan/montmorillonite nanocomposites. *Journal of Applied Polymer Science, 98*, 2042–2047.

Knaul, J. Z., Hudson, S. M., & Creber, K. A. M. (1999). Improved mechanical properties of chitosan fibers. *Journal of Applied Polymer Science, 72*, 1721–1732.

Li, Q., Dunn, E. T., Grandmaison, E. W., & Goosen, M. F. (1997). Application and properties of chitosan. In M. F. A. Goosen (Ed.), *Applications of chitin and chitosan* (pp. 3–29). Lancaster, PA: Technomic Publishing.

Mizuta, K., Matsumoto, T., Hatate, Y., Nishihara, K., & Nakanishi, T. (2004). Removal of nitrate–nitrogen from drinking water using bamboo powder charcoal. *Bioresource Technology, 95*, 255–257.

Pinotti, A., Garcia, M. A., Martino, M. N., & Zaritzky, N. E. (2007). Study on microstructure and physical properties of composite films based on chitosan and methylcellulose. *Food Hydrocolloids, 21*, 66–72.

SAN DEIGO PLASTICS, INC.: UHMW-polyethylene. Available from http://www.sdplastics.com/polyeth.html. Accessed 22.04.09..

Wong, D. W. S., Gastineau, F. A., Gregorski, K. S., Tillin, S. J., & Pavlath, A. E. (1992). Chitosan lipids films: Microstructure and surface energy. *Journal of Agriculture and Food Chemistry, 40*, 540–544.

Yixiang, X., Xi, R., & Milford, A. H. (2006). Chitosan/clay nanocomposite film preparation and characterization. *Journal of Applied Polymer Science, 99*, 1684–1691.

Zheng, H., Du, Y., Yu, J., Huang, R., & Zhang, L. (2001). Preparation and characterization of chitosan/poly (vinyl alcohol) blend fibers. *Journal of Applied Polymer Science, 80*, 2558–2565.