

PREPARATION AND CHARACTERIZATION OF A NOVEL DURIAN SEED STARCH-CELLULOSE NANOPARTICLE COMPOSITE FILMS

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ABSTRACT

Durian is a seasonal fruit widely grown in Thailand. Only one-third of durian is edible, whereas the seeds (20-25%) and the shell are usually thrown away. Fresh durian seed consists largely of starch (56% by dried weight) and might be considered such a suitable raw material for producing biodegradable films. However, plasticized starch still exhibits problems such as high water adsorption and the poor mechanical properties. To overcome these drawbacks, in this paper, the addition of cellulose nanoparticle (CN) as the filler for reinforcement of the durian seed starch (DSS) films was investigated. CN were prepared from a NaOH/urea/H₂O solution of microcrystalline cellulose using an ethanol/HCl aqueous solution as the precipitant. CN were obtained with the size in the range of 50-100 nm. SEM micrographs of the fractured surface of the composite films revealed the nonuniform distribution of CN in the DSS/glycerol matrix. With the increasing CN content from 0 to 5 wt%, the tensile strength increased but the water vapor permeability values decreased noticeably. The improvement of these properties may be attributed to the good interaction between the CN filler and the glycerol plasticized-DSS matrix because of the similar polysaccharides of cellulose and starch.

Keywords: Durian seed; Starch; Edible films; cellulose nanoparticles

INTRODUCTION

Chemically synthesized polymeric films are widely used for packaging in food industry, due to various advantages such as flexible, durable and inexpensive. Packaging materials account for approximately 30% by weight of municipal solid waste which 13% is due to plastic materials [1]. A serious disadvantage of these films is that they are not biodegradable. Incineration is a common method of disposing of polyolefins, but it results in high emissions of carbon dioxide.

Starch is a natural polymer which possesses many unique properties and some shortcomings simultaneously. Many efforts have been exerted to develop starch-based polymers for conserving the petrochemical resources, reducing environmental impact and searching more applications. Starch films have been used for various food applications. Films prepared from starches are isotropic, odorless, tasteless, colorless, non-toxic and biodegradable.

Starch is the major chemical component of durian seed flour, comprising around 56% of the dry weight. Native durian seed starch (DSS) with 25% amylose content was characterized by rounded granules ranging in size 2 to 4 μm in diameter with smooth surface [2]. It is potential to use DSS as a base raw material for production of biodegradable films. However, glycerol-plasticized DSS films exhibited poor mechanical and water barrier properties [3]. Thus, in this study, cellulose nanoparticles (CN) obtained by hydrolysis of microcrystalline cellulose (MC) were used as the reinforcing filler in glycerol plasticized DSS films with anticipation to improve these properties of the films.

MATERIALS AND METHODS

Preparation of cellulose nanocomposites (CN)

MC was dissolved based on the method of Cal and

Zhang [4] with some modification. An aqueous solution containing NaOH/urea/H₂O at the ratio of 7:12:81 by weight was used as a solvent for MC. The 2 g MC was added into the solvent (200 ml) under vigorous stirring until MC was completely dissolved in an ice bath. A solution (200 ml) containing HCl:ethanol (30:170 by volume) was dropped wise to the transparent MC solution with vigorous stirring. The suspensions were centrifuged and the settled CN were washed several times using distilled water to remove the salt and urea. Then CN were oven dried at 50°C and kept in desiccator until further use as the filler for the preparation of DSS/CN composite films.

Film formation

A simple extraction of durian seed starch was described by Pimpa et al. [5]. The concentrations of 5% (w/v) of DSS and 30% glycerol (w/w DSS) were used in all films formulations. These concentrations were chosen based on preliminary experiments. This suspension was mixed with 10% (w/w DSS) citric acid and heated at 90°C for 1 h with continuous agitation. After cooling, films were casted by pouring 5.0 ml of solution onto 8.6-cm internal diameter petridish and dried at the room condition (30 °C, 60% RH) for 24 h. Then, the films were peeled off. In order to study the effect of CN filler on the glycerol plasticized DSS/CN composite films, CN at the concentration of 0-5% (w/w DSS) were incorporated into the film matrix.

Film property measurement

Thickness of films was determined using micrometer at 10 random positions around the films, and average values were used in calculations. The gravimetric modified cup method based on ASTM E96-80 was used to determine water vapor permeability (WVP) and calculated as described by McHugh et al.[6]. The tensile strength (TS) and percentage of elongation at break (%E) as evaluated in a tensile test based on ASTM D882-95 were 8th TSAE International Conference (TSAE2015) March 17-19, 2015; Bangkok, Thailand

performed using an Instron Universal Testing Machine (Model 4414, Canton, Mass., USA). Initial gap separation and cross-headed speed were set to 50 mm and 0.5 mm/s and calculated as described by Pimpa et al. [5].

Electron microscope measurement

The size and morphology of the synthesized CN were evaluated by using a transmission electron microscope (JEOL, JEM-1011; Japan) operated at an accelerating voltage of 310, 500 and 650 kV. Samples were prepared by placing a drop of the colloidal AgNPs solution on a carbon coated sample grid in open air. Scanning electron microscope (SEM) was used to characterize the film surfaces and crossed sections. The samples were examined in a model Leo 1455 Vp scanning electron microscope. Pieces of 6 mm x 1 mm were cut from the film, mounted on stub, and gold coated by Sputter coating Sc-7620.

RESULTS AND DISCUSSION

Characterization of cellulose nanoparticles (CN)

CN particles were prepared from a NaOH/urea/H₂O solution of microcrystalline cellulose (MC) using a novel method of a drop-wise addition of an ethanol/HCl aqueous solution as the precipitant. The low temperature brought out a large inclusion complex associated with cellulose, NaOH, urea and H₂O clusters which improved the dissolution of cellulose in aqueous solution. The addition of HCl/ethanol solution resulted in the coagulation of CN from the NaOH/urea aqueous solution. The hydro-chloric acid component was used to neutralize NaOH in the aqueous solution. As shown in transmission electron microscope (TEM) micrograph (Fig. 1), CN particles were obtained with the size of about 50-100 nm. The interaction of the hydrogen bonds between the coagulated CN and the dissolved cellulose may play an important role in the stability of CN in the suspension. This method is different from CN prepared by classical acid hydrolysis. During the processing of acid hydrolysis, the degradation of amorphous cellulose resulted in the acicular or rod-like form of CN [7].

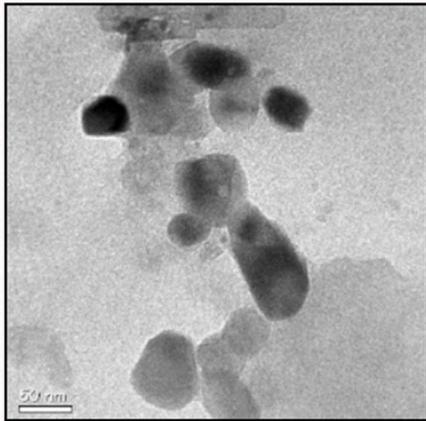


Fig.1. TEM image of CN particles

Microstructure of the DSS/CN composite films

The morphology of composites is a very important characteristic because it ultimately determines many properties of the composites. During the processing of glycerol plasticized starch films, water and glycerol are well known to disrupt inter- and intramolecular hydrogen bonds, physically breaking up the granules of starch and making the starch become a continuous phase [8].

As shown in Fig. 2, SEM micrographs at 2000x magnification of the surfaces and fractures of DSS/CN composite films revealed the distribution of CN in the film matrix, even at the low level (2%). At the higher loading of CN (5%) the distribution of CN were not uniform in the matrix and the severe aggregation was clearly noticed, although their appearances were not obviously different (Fig. 3).

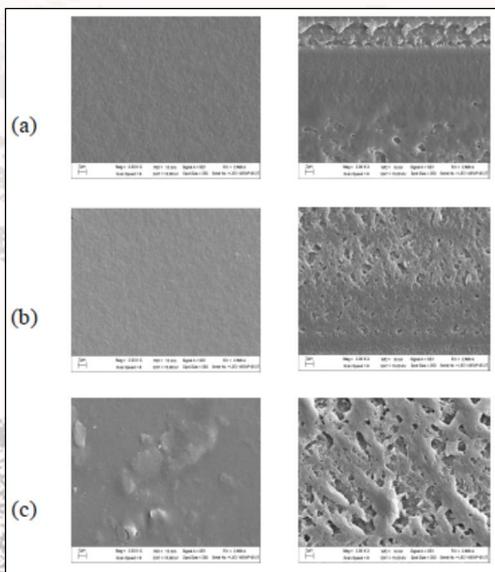


Fig. 2 SEM micrographs of DSS/CN composite films at (left) surfaces and (right) fractures incorporated with CN at levels of (a) 0%, (b) 2% and (c) 5% w/w DSS

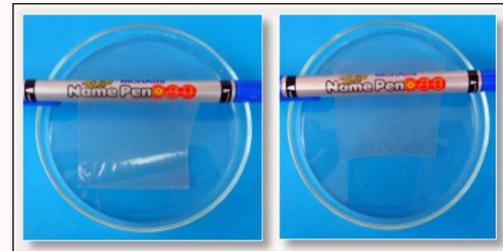


Fig. 3 The appearances of DSS/CN composite films with incorporation of CN particles at the levels of (left) 2% and (right) 5% w/w DSS

Mechanical properties of the DSS/CN composite films

Fig. 4 exhibits the effect of CN content on the mechanical properties of the DSS/CN composite films. As the filler in the film matrix, CN particles had an obvious reinforcement effect. In the processing of DSS/CN composite films, the amorphous section of CN could be easy to swollen and form the interfacial interaction with the matrix. With the increasing CN content, the tensile strength (TS) increased, but the elongation at break (E) of the composite films decreased. The incorporation of CN particles at 4% level could improve the film strength as shown by TS from 0.4456 to 0.9396 KgF/mm² as compared to that without CN addition, accounted by 110%. This may be ascribed to the good interfacial interaction between CN and the glycerol plasticized DSS matrix because of similar polysaccharide structures of cellulose and starch. CN could take effects of the physical joints, which could improve the tensile strength, but decrease the flexibility of starch molecules [9]. However, at higher CN content (5%), the TS value significantly decreased. This might be ascribed by the non-uniform distribution with severe aggregation of CN in DSS/CN composite films with high CN loading as shown in SEM image (Fig 2c).

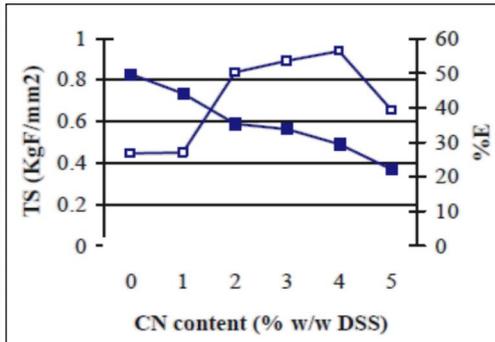


Fig.4 The effect of CN content on tensile strength (□) and Elongation at break (○) of the DSS/CN composite films

Water vapor permeability of the DSS/CN composite films

In food packaging applications, films should be avoid or at least decrease moisture transfer between food and surrounding atmosphere; water vapor permeability (WVP) value should be as low as possible. As shown at Fig. 5, higher CN content decreased the film's ability to act as a barrier to moisture. The WVP property of the DSS/CN composite film was noticeably improved by adding CN content at the level of 1-2% but gradually decreased when higher CN content (3-5%) were added. Water resistance of CN biopolymer is better than starch biopolymer. This could be attributed to the highly crystalline and hydrophobic character of cellulose in comparison to starch polymer. The addition of CN particles could introduce a tortuous path for water molecule to pass through [10]. At low CN content, CN particles could disperse well in the film matrix as shown in SEM image (Fig. 2b), which blocked the water vapor. However, excessive CN content was easily agglomerated (Fig 3c), which actually decreased the effective content of CN and facilitated the water vapor permeation.

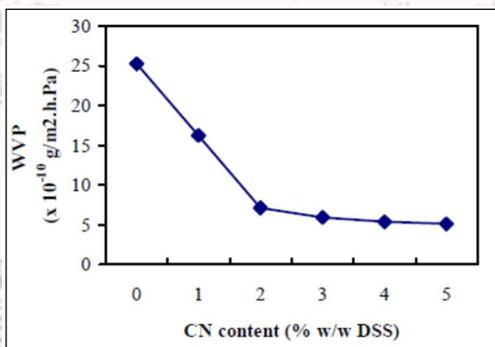


Fig.5 The effect of CN content on water vapor permeability of the DSS/CN composite films

CONCLUSIONS

The developed DSS/CN composite films could be easy form by casting method. The DSS/CN composite films were clear, smooth surfaced and flexible. As expected, increasing the CN content of the DSS/CN composite films made them stronger but less stretchable, especially higher than 4%. The incorporation of CN particles also improved water barrier property by greatly lowering WVP at the appropriate amounts of CN contents. Thus it can conclude that CN particle can be used as the filler for the DSS/CN composite films. It is a good alternative method to improve film strength and water barrier properties of the DSS films. Furthermore, CN particles could also be used as the filler for other natural polysaccharide matrixes. Thus, the effective polysaccharide/CN composites could be applied in the packaging fields as edible films, disposable or food packaging.

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