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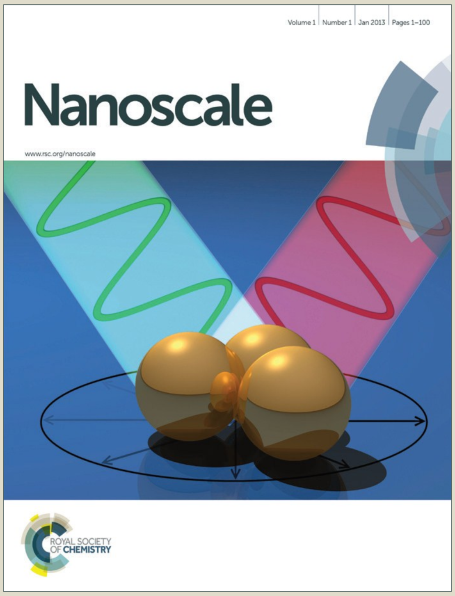

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Article

Water-soluble nanocrystalline cellulose films with highly transparent and oxygen barrier property

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By mixing guar gum (GG) solution with nanocrystalline cellulose (NCC) dispersion with a novel circular casting technology, we manufactured biodegradable films as packaging materials with improved optical and mechanical properties. These films could act as barriers for oxygen and could completely dissolve in water within 5 h. We also compared the effect of nanocomposite film and commercial food packaging materials on the preservation of food.

Introduction

It has been surveyed that non-biodegradable synthetic polymer films are estimated to be approximately 20.0% of the volume of municipal solid waste in North America and Germany. The presence of these non-biodegradable materials bring about many problems, such as the pollution of water, flash floods, disposal problems, global warming and so on[1]. Non-biodegradable packaging materials can cause serious "white pollution". Over the last few decades, there has been an increasing interest in development and application of sustainable and environmental friendly biodegradable polymer films due to the concerns of the limitation of natural resources and environmental problems caused by the non-biodegradable films[2].

Within the broad family of biodegradable film-forming polymers, xylan[3], gelatin[4], agar, salep glucomannan[5], chitosan, chitin, starch and pectin are the most attractive sources for their ability and applicability for food packaging. But there still are many limitations for their applications, e.g. gelatin, a collagen-derived material made from animal skin and bones, is not suit for Buddhism, Islam and vegetarians. And since 2012, a series of gelatin safety scandals emerge in an endless stream[6]. The starch based films are mechanically not strong enough and optically not sufficiently transparently, the metal ions in chitosan exceed the standard which could be imparted to food products. So these polymers must be replaced.

Guar gum (GG) is a kind of environmentally friendly natural polymer that can be extracted from endosperm of guar seeds produced in India and Pakistan. GG has a long polymeric chains, high molecular weight as compared to other biopolymers[7]. It consists of mannose backbone linked by (1-4)β-D-mannopyranose with galactose as a side group linked by (1-6)α-D-galactopyranose side group, with the ratio of mannose to galactose～1.6-1.8:1. GG can be widely used in pharmaceutics, food packaging, cosmetics and other fields as the stabilizer and adhesive because of its water solubility, and the ability to form aqueous solution of high viscosity at low concentration[8].But the overall properties of the GG film, such as the strength properties, the light transmittance and the barrier properties, should be improved in order to meet the International Standard Organization (ISO) of food packaging film.

Nanocrystalline cellulose (NCC), also called cellulose whisker, has gained prominence as a nanostructured material[9-12]. It is a highly crystalline nanometer sized rod-like particle, with the average length of 100-400 nm long with a width of 5-10 nm[13-14]. NCC can be extracted from cellulose sources, such as soft wood bleached kraft pulp, after the cellulose fibers are digested by a controlled acid hydrolysis process. Due to the grafting of sulfate groups on the surface of the NCC, the use of sulfuric acid in the hydrolysis process leads to a more stable dispersion[15-17].

NCC has received much attention in the last decades, particularly as reinforcement or nanofiller in polymer

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x composites due to the formation of a network structure that connect with each other by hydrogen bonds[18-20]. The presence of NCC reinforcing fillers in the polymer matrix provides superior performances, such as improved mechanical properties and barrier properties, leading to the next generation of biodegradable materials[21-23].

The main objective of this work is to develop a sustainable, biodegradable and environmentally friendly film. To fulfill this purpose, we develop a new circular casting method to prepare GG based film incorporated with NCC. The effect of NCC loading on the optical, mechanical, oxygen barrier and swelling properties of the hybrid films were evaluated.

Experimental

Materials

GG (surface charge density: -0.565mmol/g, purity: ≥99%) was purchased from Tianshi chemicals Co. Ltd., China. Northern bleached hardwood pulp（NBHK）was received from Canfor Co. Ltd., Canada. NCC was prepared from NBHK by sulfuric acid hydrolysis according to the method described by Junyong Zhu[24]. All other reagents were of analytical grade and used without further purification.

400 mesh cell sieve was purchased from Beijing zhongke ziyuan Co.Ltd., China.

Preparation of the films

5.0 g GG power was added into 245.0 g stiring water to obtain the GG water solution with the mass fraction of 2.0%. The NCC solution also had the mass fraction of 2.0%. Then calculated grams of the GG solution were added to the NCC suspensions resulting in a final NCC content from 5.0% to 60.0%(w/w). The GG-NCC solution was then homogenized by using homogenizer at 11000 rpm for 15 min and degassed for 2 min with conditioning mixer. Then the film-forming solution was casted on the baseband of polyethylene terephthalate（PET）which was adhered on the recyclable casting machine with the speed of 0.2 m/min and the heating temperature of 30℃. The GG-NCC film would be took up after dried by the infrared lamp. The casting process is shown in Fig.1.

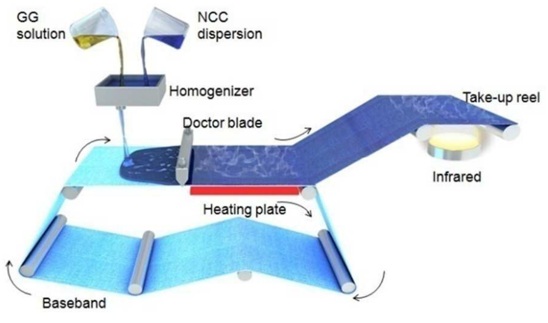

Fig. 1. The casting process. The mixture of GG solution and NCC dispersion was cast on the baseband after homogenization. The film will be winded by the take-up reel. The baseband is recycled for the endless use.

Characterisation of the GG/NCC hybrid films

Film samples were prepared for scanning electron microscopy (SEM) by dropping a 5 mm×5 mm piece cut from the center of the film in conducting resin. The samples were deposited on an aluminum holder and sputtered with ion sputtering instrument (model ACS-4000-C4, Ulvac, Japan), The spraying time of 20 seconds equivalent to coating thickness of approximately 4 nm. The morphology of the film's surface was characterized by SEM operating at 15 kV.

The hardness and elastic modulus were investigated by nanoindenter (G200, Agilent technologies, USA) according to ISO 14577. The film thickness was measured using a digital micrometer (Mitutoyo Series227, Mitutoyo, Tokyo, Japan)at five random positions along the film[25].

The Oxygen barrier property was determined using Isopiestic method, with a permeability testing apparatus (OTR-X1,Harke, China) according to ISO 15105-1. The film sample, with the surface area of 100 cm^2, was placed between the top and bottom part of the permeation cell.Test condition is 23℃, 0% RH.

Light transmission of the films in visible range were characterized at the wavelengths between 400 and 700 nm using a UV/Visible/near-infrared spectrophotometer (Lambda-950, Perkin Elmer Instruments Co. Ltd., America).

The gloss of the films was measured at 75° incidence angle, using a XGP portable mirror gloss meter (Xintong Guangda Science and Technology Co. Ltd., China), according to the ISO 8254-1. The measurements were performed on both surfaces of the films.

The test films were immersed in water (10 ml) for 5-40 min. The wet weight of the films was measured by taking out the films from the water and blotting with a filter paper to remove the surface adsorbed water followed by immediately weighing the films. The water uptake or swelling property of the films was calculated by the following equation:

$$S=(W_S-W_d)W_d\times 100\%$$

where, S is the percentage of water absorption of the films at equilibrium;W_s and W_d are the weights of the samples in the swollen and dry states, respectively.

100 mL water was added into a beaker. Then put the film samples of 23 mm×23 mm into the water which was stirred with a magnetic stirring agitator at the speed of 500 r/min. Filter the films with 400 mesh cell sieve after the films been stirred for 1, 2, 3, 4 and 5 h. Weigh the films that were on the sieve after drying.

The cake samples coated with GG-NCC films and preservative film were analyzed for total colonies and escherichia coli counts. Total colonies counts were determined from Plate Count Agar (Fluka, USA) incubated at 36°C for 1, 3 and 5 days. Escherichia coli counts was grown on Lauryl Sulfate Tryptose (Fluka, USA) at the same condition.

Results and discussion

Optical properties

Transparency and gloss are paramount to the film suitability as food coating, due to the impact of such properties on the appearance of the coated products. The optical properties of the GG-NCC film is directly related to the degree of homogeneity of the film, the internal microstructure of the matrix and the distribution of NCC, therefore depends on the formulation and fabrication procedures of the film[26-29]. The transparency of the films was evaluated through the internal transmittance (T), directly correlated to the transparency of the films (Figure 2a). The addition of NCC dramatically increased the transparency of GG based films. The results showed that the transparency of the films slightly increased with the addition of NCC up to 5.0% (w/w %). but, it dramatically increased at higher content (25.0 w/w %) of NCC. This phenomenon suggesting an occurrence of microphase separation due to the aggregation of NCCs within the GG matrix[8,30-31].

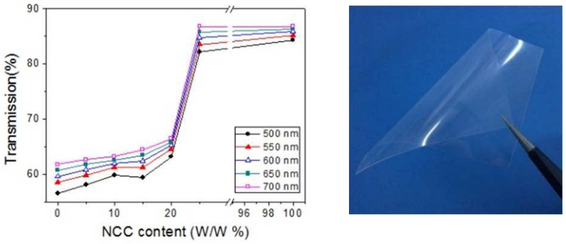

Fig. 2. a) Effect of NCC content on the optical properties of the films at the wavelength ranging from 500 nm to 700 nm. b) The GG-25.0% NCC film.

Fig. 3a shows the effect of NCC content on the surface gloss of the films. It can be seen that, the GG film had the most gloss. However, the films became less glossy when NCCs were added. This can be due to the presence of NCC particles on the film surface which contributes to increase the surface roughness, thus decreasing the gloss and masking the glossiness effect of GG. But when NCC content continued to increase, the film became glossy again, which could be ascribed to the formation of continuous phase of NCC.

The gloss of the films can also be directed determined by the morphology of the films (Figure 3b-d). The GG and NCC film exhibited a smooth surface, but the GG-20.0%NCC film looked rougher.

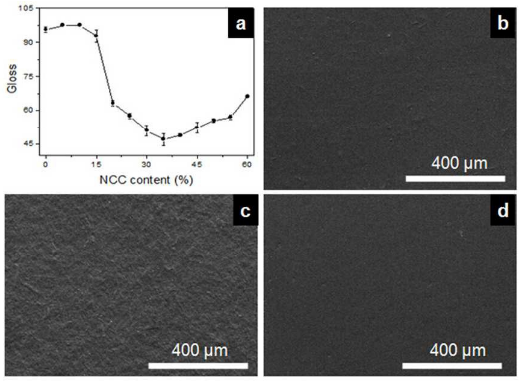

Fig. 3. a) Effect of NCC content on the surface gloss of the films. b)-d)the surface morphology of GG,GG-20.0%NCC and NCC film.

Mechanical properties

In our experiment, we exploited the hardness and elastic modulus of the GG, NCC and GG-NCC nanocomposite films (Figure 4). With the addition of 5.0% NCC (W/W%), the hardness and elastic modulus of the GG film both increased (hardness from 184.0 Mpa to 268.7 Mpa and elastic modulus from 5450.0 Mpa to 6876.5 Mpa). When the content of NCC increased to 30.0% and 25.0%, respectively, the hardness and elastic modulus of the composite film reached the peak (at 360.95 Mpa and 8206.6 Mpa). When the content of NCC reached about 30.0%, a relatively good balance of tensile strength and bursting strength was achieved (Figure S1a).This phenomenon may be attributed to two factors, e.g., (1) the formation of hydrogen bonds between GG-NCC[32], (2) the reinforcing effect occurred through effective stress transfer at the GG-NCC interface[32]. But when the NCC content continued to increase, the hardness and elastic modulus value decreased. There are three possible reasons, (1) the potential aggregation of NCC particles after a certain content is reached[33], (2) heterogeneous NCC size distribution in polymer matrix[34], (3) the rigid nature of NCC[8]. Elongation at break of the films continue decreasing all the time with the addition of NCC may also attributed to these three factors(Figure S1b).

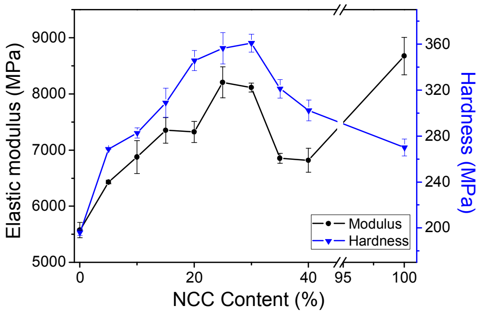

Fig.4. Effect of NCC content on the hardness and elastic modulus of the films.

Oxygen barrier property

Reducing the oxygen transmission rate in food packaging is important because it is related to the decrease in the development of off-flavors, off-odors and nutritional loss associated with oxidation in food stuffs[35-36].In this sense, the development of low oxygen transmission films is an important means to reducing food oxidation. The addition of NCC to a polymer is one of the methods to lower its oxygen transmission rate[37](Figure 5a). We can see that the oxygen transmission of composite film obviously reduced with the addition of 5.0%NCC. This results shows that the oxygen barrier property of the GG film was improved after addition of NCC. It was reported that NCC was selected as the green barrier of xylan/sorbitol/NCC film by casting the aqueous solution into polystyrene petri dishes. The oxygen transmission of xylan/sorbitol/NCC film decreased drastically with 25% and 50% dosage of NCC[38].

The oxygen barrier phenomenon can also be deduced from the size of the holes in the film. In order to enlarge the effect of the holes on the films, we immersed the films in water to make it fully swollen, then freezed the film with liquid nitrogen to shape the morphology of the holes (Figure 5b-d).The holes of the GG film were very big, but the holes became small after NCC was added into GG film. The reason of the GG film against oxidation increased when NCC was added into can be ascribed to the following reasons. In blended films, GG might crosslink with NCC by intermolecular bonding (i.e. electrostatic and hydrogen bonding). Furthermore, a decrease in the free volume or a densification of the network of the polymeric matrix occurred.The NCC particles incorporated into a polymeric matrix would generate a tortuous path for oxygen and, consequently, the permeability would decrease[39].As a result, the oxygen transmission of the blend films was lowered.

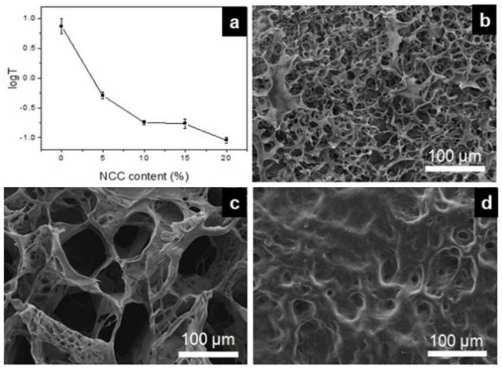

Fig.5. a) The oxygen permeability of the films. The logT was plotted against the logarithm of the oxygen transmission to establish a calibration curve based on the experimental data obtained. b)–d) The holes morphology of NCC,GG and GG-20.0%NCC film.

Swelling properties and water soluble properties

To a certain extent, the swelling properties can reflect the hydrophilic ability of the film.The swelling properties of NCC reinforced GG based films are presented in Figure 6. Incorporation of NCC significantly reduced the swelling percentage of GG based films. After 40 min, the swelling percentage of the neat GG films was found to be 39.5%, whereas due to the incorporation of 5.0%, 10.0% and 40.0% NCC, the swelling percentage of the composite films were found to be 34.8, 29.8 and 24.0%, respectively. This phenomenon of decreased water uptake can be ascribed to the fact that highly crystalline NCC is less hydrophilic than GG and the formation of strong filler-matrix interactions.the swelling percentage of the NCC film has no obvious change all the while.

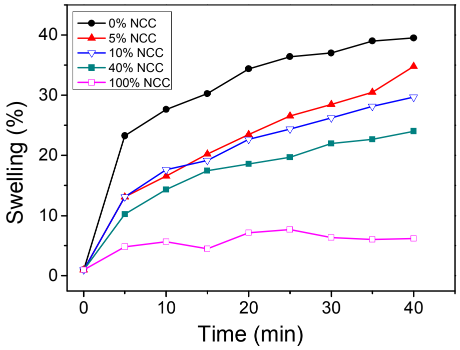

Fig. 6. Swelling ratio of different films in water.

In the process of experiment, we found that the film can be completely dissolved in water (Figure 7). After 1 h, NCC film, GG film, GG-40.0%NCC film and GG-30.0%NCC film dissolved by 96.4%, 60.9%, 88.4% and 80.7%, respectively. After 4 h, GG film and GG-30.0% NCC film had been completely dissolved. GG-40.0% NCC film can be completely dissolved after 5 h. And NCC film dissolved by 86.3% after 5 h which could ascribe to the highly crystalline of NCC.

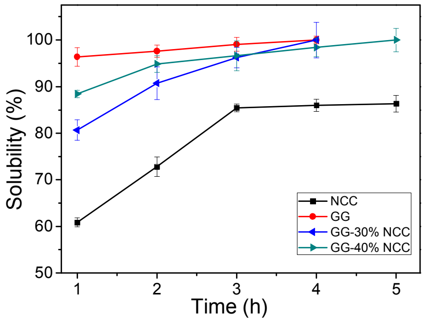

Fig. 7. The solubility of NCC, GG, GG-30.0%NCC and GG-40.0%NCC film.

Microbiological analysis

In order to examine the effect of GG-NCC film on the preservation of food, We made a comparison between the GG-NCC film and the preservative film. Changes in total colonies and escherichia coli count (log cfu/g) in cake during 5 days are shown in Figure 8. Total colonies and escherichia coli count of all samples both increased during storage.The total colonies of the sample packaged by GG-20.0% NCC film increased by 250.1% after 5 days, and the sample packaged by preservative film increased by 242.6%, there is no obvious difference between the two kinds of films.

The escherichia coli count of the sample packaged by GG-20.0%NCC film increased by 860.8% after 5 days, and the sample packaged by preservative film increased by 621.8%, the preservative film is slightly better than the GG-20.0%NCC film at this point. But the difference between these two films was not significant, either.

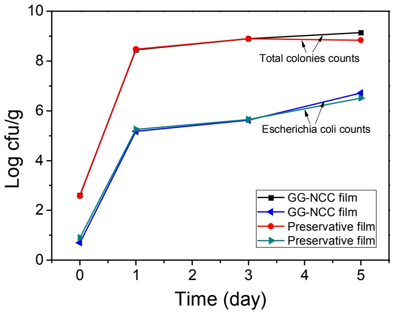

Fig.8. Effects of GG-20.0%NCC film and preservative film on cake preservation.

Conclusions

In this study, we prepared a biodegradable GG based film incorporated with NCC by using a new cycle casting method. NCC acted as a good reinforcing agent with the hardness and modulus of GG film increased by 96.2% and 50.6%, respectively. At the same time, the transmittance of the film increased by 50.0% and the air permeability decreased by 65.3%. The composite film can be completely dissolved in water after being stirred for 5 h. Microbial growth of samples packaged with GG-NCC films and preservative film were almost the same. The hybrid film has a great application prospect in the packaging field.

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