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Preparation and characterization of cellulose/chitosan blend films

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ABSTRACT

Cellulose and chitosan were mixed in *N*-methylmorpholine-*N*-oxide (NMMO) and heated to 100 °C, and then were processed under a pressure of 70 kg/cm^2 exerted by a compression molding machine at 100 °C for 8 min. As a result, transparent orange viscose films were obtained. After rinsing with deionized water and drying transparent yellowish blend films were obtained. Scanning electron microscope (SEM) indicated that when the chitosan content in the blend increased up to 3% the surface structure became smoother, but the film containing 5% (w/w) chitosan, became coarse again probably due to phase separation. Tensile strength test results were consistant with this. Antibacterial assessment proved that addition of chitosan to the films results in slight antibacterial properties. The halo zone test confirmed that the blend films made in this research have non-diffusible antibacterial properties.

1. Introduction

Chitin is consists of 2-acetamido-2-deoxy-β-D-glucose. Chitosan is the N-deacetylated derivate of chitin. Chitin and chitosan have a range of current and potential applications in photography, cosmetics, artificial skin, dressing, food and nutrition, ophthalmology, water engineering, metal capture from wastewater, paper finishing, solid-state batteries, drug delivery system, biotechnology, and cell-stimulating materials (Ravi Kumar, 2000). In recent years, chitosan films have mainly been applied to the pharmaceutical field. Generally, chitosan is dissolved in acetic acid or hydrochloric acid, then the solvent is removed by drying; or chitosan is precipitated by using coagulating agent (e.g., sodium hydroxide), and finally made into film. The relevant applications include bone cell adhesion and growth (Hamilton et al., 2007), blood compatibility (Yang, Zhou, Chuo, Wang, & Yu, 2007) and cell adhesion (Freier, Koh, Kazazian, & Shoichet, 2005). Chitosan film is biocompatible, biodegradable, and nontoxic, thus it is applicable to pharmaceutical and food industries. However, chitosan cost is high and thus importance is attached to the research on the combination of chitosan and other macromolecules. Examples are chitosan blends with hyaluronic acid (Xu, Ma, Shi, Gao, & Han, 2007), polyethylene glycol (Kiuchi, Kai, & Inoue, 2008; Wang, Dong, Du, & Kennedy, 2007), poly(vinyl alcohol) and alginate (Pei, Chen, Li, & Zhou, 2008), rice starch (Bourtoom & Chinnan, 2008), nylon 11 (Kuo, Sahu, & Yu, 2006), cellulose (Lima, Lazarin, & Airoldi, 2005; Twu, Huang, Chang, & Wang, 2003; Wu et al., 2004), poly(lactic acid) (Sébastien, Stéphane, Copinet, & Coma, 2006), collagen (Lima et al., 2006; Sionkowska et al., 2006), poly(*N*-vinyl-2-pyrrolidone) (Çaykara, Alaslan, Eroğlu, & Güven, 2006), polyanilne (Thanpitcha, Sirivat, Jamieson, & Rujiravanit, 2006), acrylic resin (Wada & Uragami, 2006), poly(ε-caprolactone) (Honma, Zhao, Asakawa, & Inoue, 2006), konjac glucomannan (Ye, Kennedy, Li, & Xie, 2006), clay (Xu, Ren, & Hanna, 2006), oleic acid (Vargas, Albors, Chiralt, & González-Martínez, 2009), and caseinate (Pereda, Aranguren, & Marcovich, 2008).

The ability of *N*-methylmorpholine-*N*-oxide (NMMO) to directly solvate cellulose has been known for a number of decades. The work of Canzy et al. (Chanzy & Dubé, 1979; Chanzy & Peguy, 1980) is today widely regarded as basis for the developments that later resulted in the Lyocell process. The molecular structure of chitosan is quite similar to that of cellulose. Only the functional groups connected to the second carbon in the repeating units differ from one another. The gel forming ability of chitosan in *N*-methylmorpholine-*N*-oxide has been reported (Dutta, Viswanathan, Mimrot, & Ravi Kumar, 1997; Ravi Kumar, Singh, & Dutta, 1999). In addition, NMMO was used as the common solvent for both chitosan and cellulose to produce chitosan/cellulose complex dope, and compound granules were obtained through processing, coagulating, and washing (Twu et al., 2003). In this research, NMMO is mixed with chitosan and cellulose; films are produced by compression molding machine; and blend films are obtained by rinsing with water and drying. This research explores the physical property and antibacterial properties of blend films.

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2. Materials and methods

2.1. Materials

Chitosan (Mv = 960 kDa, degree of deacetylation = 88.7%) was obtained from QBAS Co. The cellulose of hardwood pulp with DP = 1100 was obtained from Sappi Saiccor Ltd. (Umkomaas, Republic of South Africa). Chitosan and cellulose were dried overnight under vacuum at 80 °C prior to dissolution. Ninety-three percentage of (w/v) *N*-methylmorpholine-*N*-oxide (NMMO) was obtained by rotary vacuum evaporation of NMMO 50% (w/v) aqueous solution (BASF Co., Ludwigshafen, Germany). The *Staphylococcus aureus* subsp. *aureus* (ATCC 6538P) was purchased from the Bioresoure Collection and Research Center (BCRC, Hsin-chu, Taiwan), and was stored at 4 °C before it was used. Biochemical reagents of nutrient agar and nutrient broth were purchased from DIFCO Laboratories (Detroit, USA). All other chemicals were used as received. The water used on this experiment was purified by deionization of reverse osmosis water.

2.2. Preparation of chitosan/cellulose blend films

To accelerate the dissolution of cellulose in NMMO, cellulose was placed in a ball mill (BM-052, Yeong-Shin Co. Ltd., Taiwan), ground with yttria-stabilized zirconia grinding ball (diameter: 2 mm, Jeng-Bo Co. Ltd., Taiwan) for 3 h, and sieved with a 200 mesh sieve. Superfine cellulose powder was obtained. In this research, six formulations with different proportions were used (see Table 1). A total of 90 g 93% NMMO was used as the solvent, and both chitosan and cellulose powder were put into NMMO and churned continuously at room temperature. In the mixture, the solid content accounted for 10% (w/w), while chitosan accounted for 0–5% (w/w) of the total weight of solid matter. Five grams of mixture was then placed between two stainless steel sheets (10 cm × 10 cm, 1 mm thick). Teflon tape cloth (type: #970, Long-Cheng Co. Ltd., Taiwan) was placed between the stainless steel sheets as the lining. In this way, the molded film could be taken out easily. Then, 70 kg/cm^2 pressure was applied with CH-10 compression molding machine (Tian-Fa Ltd., Taiwan). The mixture was continuously heated at 100 °C and compressed for 8 min. Then, the transparent orange viscose film together with steel sheets and Teflon tape cloth was immersed in deionized water immediately. The NMMO was removed by rinsing the viscose film with deionized water, and cellulose and chitosan were made to coagulate. With respect to the blend films obtained after rinsing thrice, dried filter paper (type: 5A, diameter: 185 mm, Toyo Roshi Kaisha Co. Ltd., Japan) was used at normal temperature to remove the water on the surface and inside the films. To prevent the films from curving during drying, the films with most water removed were put between 10 pieces of dried filter paper, and 2 kg/cm^2 pressure was applied at normal temperature using a compression molding machine to remove the residual water. All flattened films (No. M1–M6) were placed in a desiccator for drying and stored for later use.

2.3. Scanning electron microscopy

The surface morphology of the chitosan/cellulose blend films was observed using a TOPCON AB-150S SEM. The films were deposited onto a copper holder with conductive carbon paint and coated with gold under vacuum before observation.

Table 1
The charged composition of cellulose/chitosan blend solutions and product code.

Blend solution	1	2	3	4	5	6
Chitosan (g)	0	0.03	0.05	0.2	0.3	0.5
Cellulose (g)	10	9.97	9.95	9.8	9.7	9.5
NMMO (g)	90	90	90	90	90	90
Code	M1	M2	M3	M4	M5	M6

2.4. Mechanical test

Mechanical test was measured by using a SUN Rheo Meter (controller: CR-10, detector: CR-200D, and adapter: No. 21) (SUN Scientific Co., Ltd., Tokyo, Japan). Blend films were cut into 25.4 mm × 100 mm, according to the ASTM D 882-02 standard (ASTM, 2002). Grip separation was set at 50 mm, with a cross-head speed of 50 mm/min. Each sample was tested repeatedly for eight times.

2.5. Antibacterial assessment

Antibacterial assessment gauges the antibacterial ability of samples (Jung et al., 2007). In this research, *S. aureus* (ATCC 6538P) was selected as the bacteria in tests. A total of 0.4 g sterilized M1–M6 were mixed with 100 mL 10^6 CFL/mL bacteria solution, respectively, and then the mixture was placed in conical flask and cultured in an orbital shaker incubator (Shang-Mei, CWF) at 37 °C and 100 rpm for 24 h. M1 was used as the control group, while M2–M6 were used as the experimental groups. The bacteria culture solutions were diluted by a factor of 10^4 by the 10 times dilution method. Then, 1 mL of each diluted bacteria solution was used to mix with 15 mL nutrient agar and then placed into petri dishes. After they were mixed evenly and became coagulated, they were cultured at 37 °C for 24 h; the colony count on the plate was then calculated. Experiments were done in triplicate. The percentage of viable cells was calculated using the following formula:

$$\text{percentage of viable cells} = \frac{K}{K_0}$$

where K_0 is M1 colony count and K is M2–M6 colony count.

2.6. Fatigue test

This test consisted of taking 5 g of M1–M6 films, mixing them with 100 mL deionized water, putting the mixture into conical flask, and churning it with stirring at 90 °C for 20 min. After replacing the water, the test was repeated for another five times. After the films were dried, the antibacterial test was conducted in accordance with Section 2.5.

2.7. Halo zone test

Halo zone test is used to test whether releasable antibacterial agent is contained in the samples (Park et al., 2001). In this research, *S. aureus* (ATCC 6538P) was selected as the bacteria in tests. Cellophane was taken and immersed in 5% tetracycline hydrochloride; this was treated as the control group after drying. A film from the control group and from M1 to M6 were taken, cut into 28 mm round films, and sterilized in high-temperature steam (121 °C, 15 min). The sterilized films were stuck to the central part of petri dishes which contain 15 mL nutrient agar with 10^6 CFU/mL *S. aureus* and cultured at 37 °C for 24 h. The release of antibacterial agent from the films on the plate could be determined according to the size of the inhibitory zone.

3. Results and discussion

3.1. Preparation of chitosan/cellulose blend film

NMMO is a direct solvent used for dissolving cellulose. The structure of chitosan is quite similar to that of cellulose. Only the

functional groups connected to the second carbon in the repeating unit differ from one another, that is, hydroxy group in cellulose, and amino group in chitosan. NMMO could also work as a direct solvent for chitosan. It has been shown from early studies that chitosan could dissolve in NMMO (Twu et al., 2003). Only after chitosan, cellulose, and NMMO are placed in a vacuum environment at 85 °C and churned continuously for 1 h could chitosan and cellulose totally dissolve in NMMO and a blend dope could be obtained. When the dope was examined under a microscope, it was found that the dope transmitted light and no dispersed phase was observed.

Since the specific surface area of pulp is small, the process for it to dissolve is very long. In this research, powder with grain size smaller than 75 μm was obtained after the pulp was ground and sieved. In this way, the speed for it to dissolve in NMMO was increased. Chitosan and cellulose could dissolve within a very short period if the samples are treated in high pressure. Furthermore, if polymer material is dissolved without contacting oxygen, the possibility of degradation of polymers will be reduced greatly. Take the M1 sample for example. The degree of polymerization cellulose changes only from 1100 to 1050. That is why no thermal stabilizer and antioxidant was added in this process.

After viscose films are rinsed with deionized water, the blend films could be separated from stainless steel sheets. To prevent the films from curving during drying, the films were put between dried filter paper, and 2 kg/cm^2 pressure was applied at normal temperature using a compression molding machine to remove the residual water. All flattened films were placed in a desiccator for drying. In general the obtained dried blend film thickness ranges from 0.08 mm to about 0.1 mm. Blend films are transparent and yellowish, and their color becomes darker with the increase of chitosan content in blend films. If chitosan and pulp powder are roasted at 100 °C, chitosan turns yellow more quickly than pulp powder. It is shown that degradation of chitosan in a high temperature environment causes blend films to turn yellow.

3.2. Morphology of chitosan/cellulose blend films

Fig. 1 shows the SEM images that magnify the samples 100 times, while Fig. 2 shows the images that magnifies the samples 500 times. M1 does not contain chitosan and its surface is cavernous (Figs. 1 and 2a); M3 contains 0.5% chitosan and its surface is coarse but no longer cavernous (Figs. 1 and 2b); M5 contains 3% chitosan and its surface is smooth (Figs. 1 and 2c); M6 contains 5% chitosan and its surface becomes coarse again (Figs. 1 and 2d). If films are produced by the high-pressure method, the water molecules in the solvent will vaporize immediately after the pressure is relieved and a cavernous structure forms on the M1 surface. When chitosan content in blend films increases, their surface tends to become smoother. Since the molecular weight of chitosan is up to 960 kDa, but that of cellulose is only 178 kDa, the change of viscosity of viscose films caused by chitosan cannot be overlooked. When the viscosity of viscose films increases, it will suppress the water molecules from vaporizing, causing M3 and M5 to lose the cavernous structure and their surface to become smoother. However, the surface of M6, which contains more chitosan, becomes coarse again probably because chitosan agglomerates and causes phase separation.

3.3. Mechanical property of chitosan/cellulose blend films

Fig. 3 shows the relationship between the tensile strength and chitosan content of blend films. The strength and morphology of the pure cellulose film is inferior to that of a cellophane film. Most commercial films are produced utilizing a biaxially oriented process which results in film having superior mechanical properties. However, the M1 film is weak because of its lack of orientation. Fig. 3 shows that the tensile strength of blend films increase with increasing chitosan content up to 3%. The tensile strength of M1, whose surface is cavernous, is the lowest owing to its incomplete structure and shape. The tensile strength of M4, which contains 2% chitosan, is four times higher than that of M1. It is deduced that

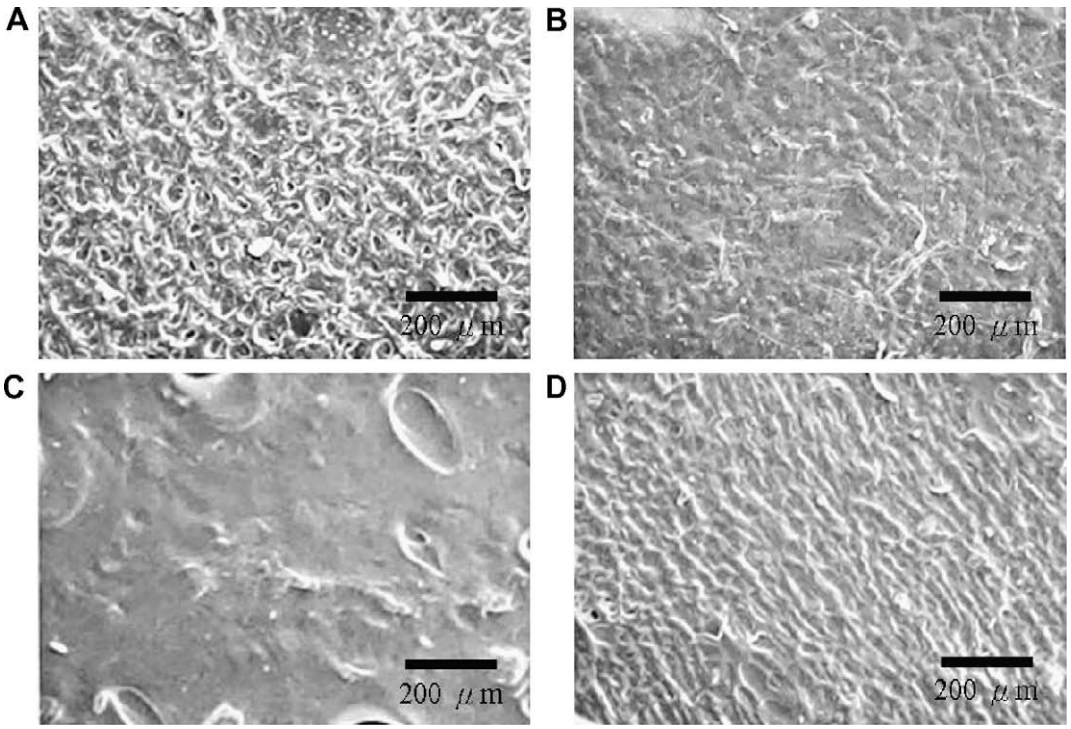

Fig. 1. SEM micrographs of cellulose/chitosan blend films (100×): (A) M1, (B) M3, (C) M5, and (D) M6.

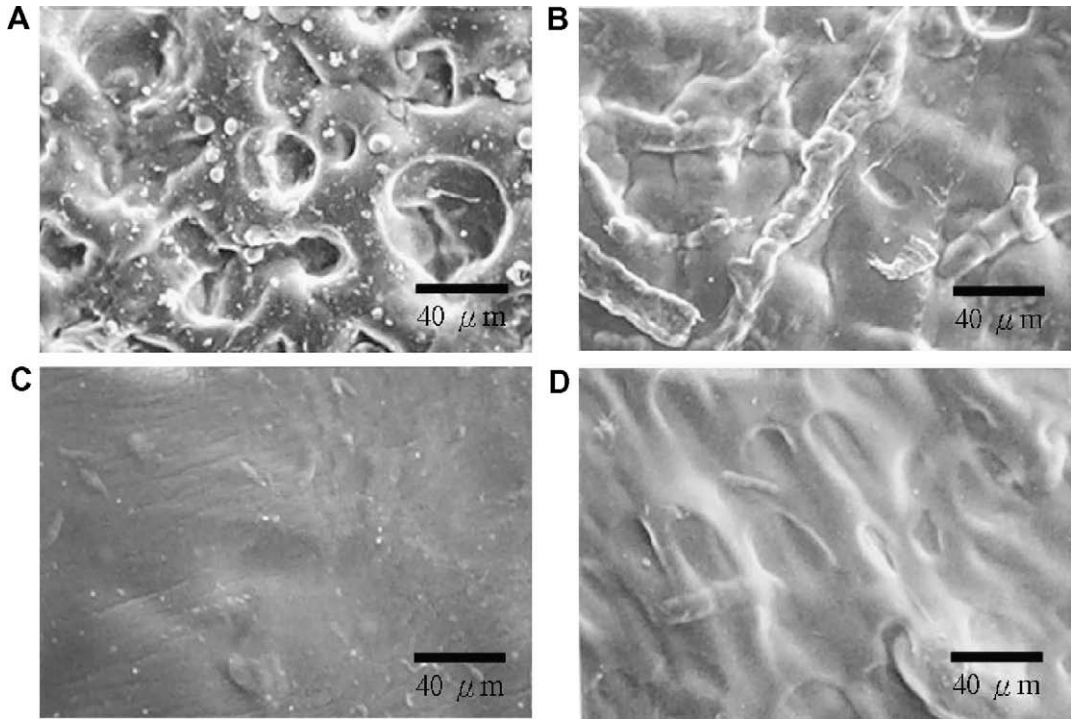

Fig. 2. SEM micrographs ofcellulose/chitosan blend films (500×): (A) M1, (B) M3, (C) M5, and (D) M6.

the molecular chain of chitosan, which has large molecule weight, is entangled with that of cellulose, changing the structure and shape of films and increasing the tensile strength of films accordingly. The tensile strength of M5, which contains 3% chitosan and has the smoothest surface, is the highest. In this film, chitosan and cellulose are compatible with one another.

However, the tensile strength of M6, which contains 5% chitosan, reduces dramatically. Generally speaking, when two macromolecules are mixed, phase separation occurs and results in sharp reduction in tensile strength. The SEM images indicates that the surface of M6, which contains the most chitosan, is coarse, thus it differs greatly from M5, whose surface is the smoothest. Observed results of both tensile strength and SEM indicate that chitosan and cellulose cannot dissolve in one another in the production process for M6, and phase separation occurs.

3.4. Antibacterial assessment of chitosan/cellulose blend films

It is learned from literature that the antibacterial mechanism for chitosan falls into two types. First, the positively charged chitosan could combine with the negatively charged bacterial surface, causing the permeability of the bacterial surface to increase, leading to leaching of intracellular components to the outer environment and causing the death of the bacteria. Secondly, chitosan oligomer could come into contact with bacteria directly and combine with DNA of bacteria to suppress the generation of mRNA (Sudarshan, Hoover, & Knorr, 1992). Fig. 4 shows the relationship between the percentage of viable cells in the blend films and the chitosan content. The viability of *S. aureus* reduces with increasing chitosan content in the blend films. Increasing chitosan content in films shows slight antibacterial properties. In the samples without

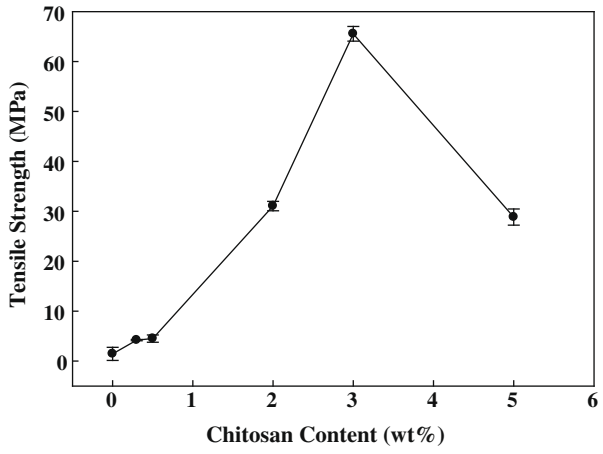

Fig. 3. Effect of chitosan content on mechanical properties of blend films (mean ± SD, $n = 8$).

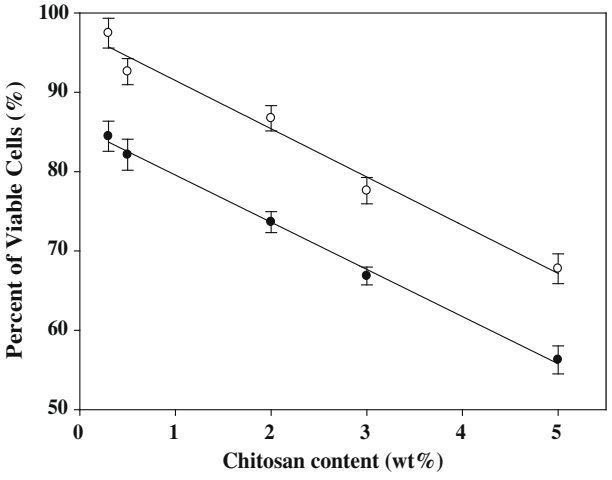

Fig. 4. Effect of chitosan content on percentage of viable cells of blend films with (○) and without (●) fatigue test (mean ± SD, $n = 3$).

fatigue test, the percentage of viable cells is low. Among them, the percentage of viable cells of M6 has reduced to 54%. A 0.25 log reduction. This is a small reduction.

When antibacterial test are conducted on the blend film that have been rinsed with 90 °C deionized water five times, the results indicate that its antibacterial ability has been reduced by 10% as compared with the blend film without the fatigue test. After the fatigue test, the following are observed: (1) the antibacterial ability of M6 is still higher than that of M2 without the fatigue test; (2) the antibacterial ability of M5 is only a little lower than that of M2 without the fatigue test; and (3) part of chitosan on the surface of blend film is dissolved, causing the reduction of its antibacterial ability to *S. aureus*. The fatigue test results prove that chitosan and cellulose blend films are resistant to rinsing with water.

3.5. Halo zone test of chitosan/cellulose blend films

Halo zone test is meant to assess the antibacterial ability of samples by measuring the size of the halo zone, and identify whether the samples contain releasable antibacterial agent. Fig. 5a shows the result of the test on M1. It is observed that there are a lot of colonies on either the plate or the surface of film, and the halo zone does not appear. It indicates that the M1 is not able to suppress the growth of *S. aureus*. Fig. 5b shows the result of the test on M6. It is observed that there is colony on the plate but not on the surface of the film. It proves that M6 is able to suppress the growth of *S. aureus*. Since no halo zone appears around the M6 film, it proves that chitosan of M6 will not diffuse onto the plate. Fig. 5c shows the result of the test on cellophane that is immersed in 5% tetracycline hydrochloride. It is observed that a halo zone has appeared around the film. It is the antibacterial agent contained by cellophane, and it diffuses to the surrounding area of the film, suppressing the growth of *S. aureus*. It forms the halo zone around the film. Fig. 5b and c represent the non-diffusible and diffusible antibacterial mechanism, respectively. Antibacterial assessment indicated that cellulose/chitosan blend films show only slight antibacterial properties. However, the blend films made in this research contains the non-diffusible antibacterial agent, chitosan, which is able to suppress the growth of *S. aureus*, and will not diffuse to the surrounding environment.

4. Conclusions

When chitosan and cellulose were dissolved in NMMO, a transparent orange viscose film could be obtained within a very short period if compression molding machine was used for processing. After the viscose films were rinsed with deionized water and dried, transparent yellowish blend films were obtained. It was indicated from both SEM and tensile strength test that the surface of blend films tended to become smoother and the strength of films was enhanced with the increase of chitosan content in blend films. However, the surface of M6, which contained more chitosan, became coarse again because the change of proportion in the receipt led to phase separation, which caused the tensile strength to reduce greatly. It was proven from antibacterial assessment and halo zone test that the blend films made in this research had non-diffusible

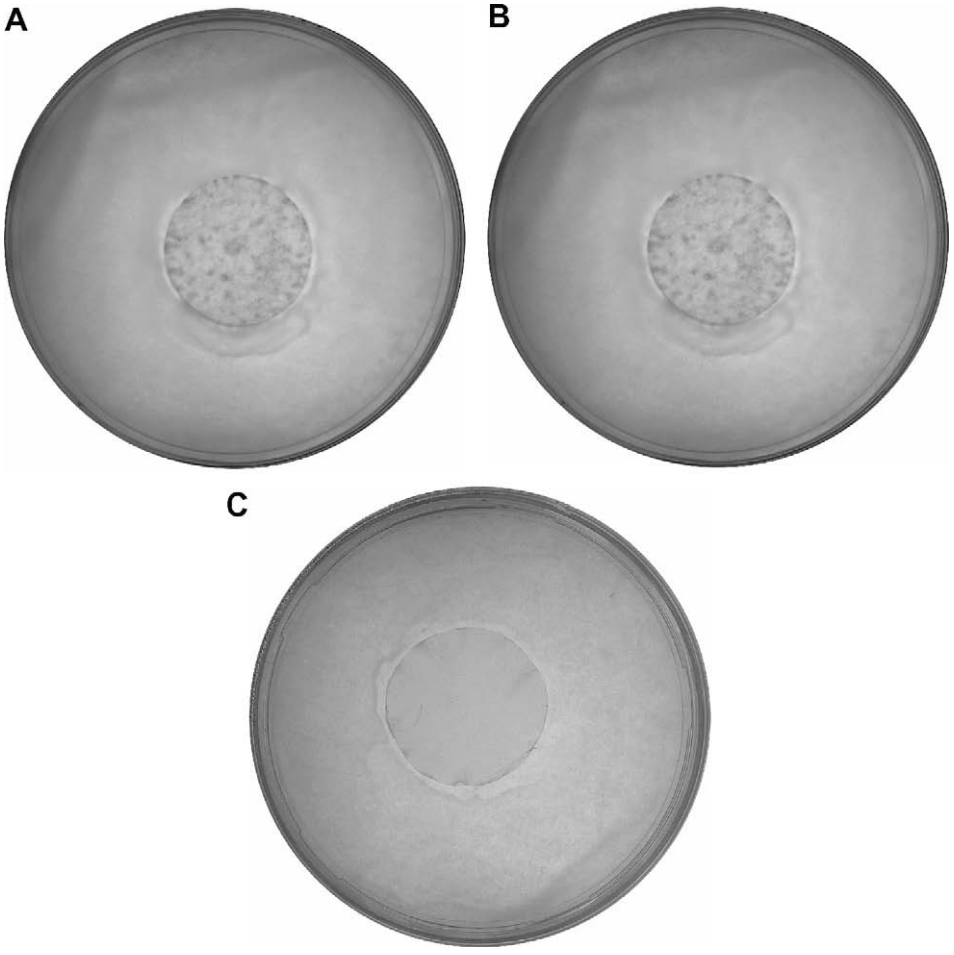

Fig. 5. The photographs of cellulose/chitosan blend films by the halo zone test: (A) M1, (B) M6, and (C) control.

antibacterial properties. In this research, chitosan was mixed with cellulose and compression molding machine was used to produce films. The raw material cost was low and the production method was simple, thus this is worth further study and development.

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