

PREPARATION AND CHARACTERIZATION OF CHITOSAN / CELLULOSE BLEND FILMS USING $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ AS A SOLVENT

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Chitosan (CS)/cellulose (BC) blend films were successfully prepared using $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ as a solvent. Homogeneous structures without obvious phase separation between CS and BC for all blend films were observed by scanning electron microscope (SEM) analysis. The tensile strengths of CS/BC blend films decreased with the increase of chitosan content. The results of X-ray diffraction (XRD) analysis indicated that the crystal structures of BC and CS were disrupted during the processes of dissolving and regeneration. Also, the reformation of hydrogen bonds between CS and BC during dissolution and regeneration processes resulted in the shift of diffraction peaks. Fourier transforms infrared spectroscopy (FT-IR) and thermogravimetric analysis (TGA) analysis results confirmed this observation. Moreover, obvious antimicrobial capability of CS/BC blend films against *E. coli* has been observed, indicating that antibacterial activity of chitosan has not been significantly inactivated while using $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ as a solvent. Therefore, $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ can be regarded as a promising solvent to prepare degradable films with antibacterial properties.

Keywords: Chitosan; Cellulose; Blend film; $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$; Antibacterial activity; Characterization

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INTRODUCTION

Membrane separation technologies have attracted worldwide research attention due to their great potential for wastewater reclamation, separation of substances (Bruggen *et al.* 2003; Gotoh *et al.* 2004), drinking water purification (Wallace *et al.* 2008; Yangali-Quintanilla *et al.* 2011), sea water desalination (Wang *et al.* 2007, 2009; Choi *et al.* 2009; Peñate and García-Rodríguez 2012), and so on. However, most membranes are prepared with non-biodegradable petrochemical materials (Wei *et al.* 2012; Zhang *et al.* 2012; Venault *et al.* 2012). These non-degradable plastic materials used as disposable items are more evidentially disturbing and damaging the ecosystem (Lu *et al.* 2006).

Renewable resources can be regarded as ideal materials for membrane production. Cellulose, one kind of natural biomacromolecule, has often been used to prepare degradable membranes (Jie *et al.* 2005; Yamamoto *et al.* 2010; Madaeni and Heidary 2011). However, the antimicrobial properties of the cellulose-based membranes are very poor (Liu *et al.* 2010; Zhu *et al.* 2010). As we know, chitosan itself has antimicrobial properties (Alonso *et al.* 2009). To improve the antimicrobial performance of cellulose-based materials, some research has been conducted with directly mixed chitosan powder and cellulose solution through physical methods (Zhuang *et al.* 2002). Although the antimicrobial properties of blend films or membranes were more or less improved, the

surfaces of these membranes are comparatively rough. The leaching of chitosan will highly influence the antimicrobial properties of blend films during the process of commercial application. Thus, simultaneous dissolving chitosan and cellulose in a solution becomes the key problem for homogeneous composite membrane production from renewable materials.

Previously, the blend membranes were prepared from chitosan and cellulose using trifluoroacetic acid as a solvent (Wu *et al.* 2004). Unfortunately, the chains of both biopolymers were significantly depolymerized, and the deacetylation of chitosan was also evidently changed during the process of regeneration. Later, chitosan/bacterial cellulose composite films were prepared by means of adding 0.25% to 0.75 % (w/v) of chitosan with low molecular weight into the culture medium during biosynthesis by *Acetobacter xylinum* (Phisalaphong and Jatupaiboon 2008). However, the addition of chitosan showed little improvement on the films' water transmission rates, average crystallinity index, and anti-microbial ability. Meanwhile, Shih *et al.* (2009) had prepared a transparent blend film by simultaneously dissolving cellulose and chitosan in N-methylmorpholine-N-oxide (NMMO). Due to phase separation, the film became coarse once the content of chitosan was beyond 5% (w/w). Moreover, a mix solution of NaOH/thiourea was developed to prepare chitosan/cellulose biocomposite films (Almeida *et al.* 2010). However, the operating conditions used in this solution system were very harsh. For example, the solution temperature should be kept at about -12°C during the dissolving process. Recently, ionic liquids, such as 1,3-dimethylimidazolium chloride (DMImCl), butyl-3-methylimidazolium acetate (BMIMAc), and 1-H-3-methylimidazolium chloride (HMImCl), have been used to prepare the chitosan/cellulose-blended films (Xiao *et al.* 2011; Stefanescu *et al.* 2012). Although the resulted membranes have good performance, unfortunately, ionic liquids themselves are expensive and not easy to be recovered.

Recently, many reports have employed $ZnCl_2 \cdot 3H_2O$ to dissolve cellulose and its derivatives (Leipner *et al.* 2000; Fischer *et al.* 2003; Lu *et al.* 2011). Fortunately, chitosan is dissolved by similar hydrated salts (such as $AlCl_3$ and $FeCl_3$) (Hirase *et al.* 2010). These hydrated salts are cheap and have the potential to be extended to industrial processes. Few publications have used hydrated salts to dissolve both of them. Therefore, in this study, $ZnCl_2 \cdot 3H_2O$ solution was selected as a solvent to simultaneously dissolve chitosan and cellulose. The resulted solution was used to form blend films, and the properties of them were also characterized.

EXPERIMENTAL

Materials

Chitosan (abbreviated as CS, $M_w = 2 \times 10^5$ Da, degree of deacetylation = 90%) was purchased from Golden-Shell Biochemical Co., Ltd. in China.

The bamboo cellulose (abbreviated as BC) with a polymerization degree of 650 was generally provided by Shaowu paper mill at Fujian province in China. Both chitosan and cellulose were dried over night at 60°C and used without any further purification.

Zinc chloride ($ZnCl_2$) was purchased from Sinopharm Chemical Reagent Co., Ltd (China) and used as received.

Preparation of Films

The preparation of the CS/BC blend was carried out in $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ solution according to the procedure proposed in the literature (Lu *et al.* 2011). 7.2 g of ZnCl_2 was dissolved in 10 g of deionized water to obtain ZnCl_2 solution. In this solution, the content of ZnCl_2 in water was 72%. Then, a 0.4 g mixture of CS / BC (w/w = 1:4, 1:6, 1:10) was put into a 100 mL flask and further mixed with 10.0 g of prepared $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ solution at 80 °C for the desired time. During the process of dissolving, the mixture was heated and persistently stirred for a specific duration until a transparent homogeneous solution was obtained. The CS/BC blend films were prepared on a coater (GBC-A4, GIST, Korea). Typically, 2 g CS/BC blend in $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ solution was firstly poured and then manually casted onto a glass slide. After the evaporation of water from blend, the gel sheet was formed. The gel sheet was then immediately immersed in water at ambient temperature for 15 min. The resulted fresh films were washed with running water and then deionized water to remove the solvent from the films. Finally the films were air-dried at room temperature. The regenerated chitosan (RCS) and bamboo cellulose (RBC) were prepared by the same method as contrasts.

Characterizations

Scanning electron microscopy (SEM)

Scanning electron micrographs (SEM) were taken on a scanning electron microscope (JEOL JSM-7500F). The surfaces of the CS/BC blend films were metalized with gold by sputtering for 20 s.

Mechanical analysis

According to the ASTM D 882-02 standard (ASTM, 2002), films were cut into strip-shaped specimens with size of 10 mm width and 10 cm long. The specimens were measured on a universal tensile tester (CMT 6104, Shenzhen SANS Test machine Co. Ltd., China). The tensile strength of the same specimens was the average value determined from 10 specimens.

The X-ray diffraction (XRD)

The X-ray diffraction (XRD) measurements of the samples were conducted using a reflection method on a MiniFlex2 XRD diffractometer (Japan Rigaku) with a Cu K-radiation of 1.54 Å at 40 kV and 30 mA. Samples were cut into powders so as to erase the effect of the crystalline orientation. The patterns were collected in the region of 2θ from 5° to 85°.

Fourier transforms infrared spectroscopy (FT-IR)

The films were cut into very fine-ground powders and then freeze-dried. FT-IR spectra of samples were recorded on a Fourier Transform Infrared spectrometer (Thermo Nicolet 380) by the KBr-disk method.

Thermogravimetric analysis (TGA)

Material mass losses vs. temperature were determined with a TG-DTA instrument (Netzsch STA 449 F3) at the heating rate of 10 °C /min under nitrogen with a flow rate of 20 mL/min. Approximately 2 to 3 mg of sample was weighed as a standard and heated from 25 °C to 600 °C. TG-DTA data was recorded with the time interval of one second.

Antimicrobial test

Escherichia coli (*E. coli*) (ATCC 25922) was used as a test microorganism in the experiments. The selection of the bacteria was based on the consideration that *E. coli* is the most commonly found bacterium in water and wastewater. Tryptone Soya Broth (shorted as TSB) (30 g/L) was used for the cultivation of *E. coli* (Zhu *et al.* 2010).

The antimicrobial activities of the CS/BC blend films were tested by the disc diffusion method. Peptone (5.0 g), beef extract (3.0 g), and sodium chloride (5.0 g) were mixed in 1000 mL distilled water to make nutrient agar medium. The pH of this culture was adjusted to approximately 7.0. Then agar (15.0 g) was added to the solution. The agar medium was sterilized in a conical flask at a pressure of 15 lbs for 30 min. This medium was transferred into sterilized petri dishes in a laminar air flon (Krishna Rao *et al.* 2012). Bacteria in stationary phase were gradually diluted into certain concentrations at about 10^5 CFU/mL in NaCl solution (0.85 %, w/v). Diluted suspensions (0.1 mL) of *E. coli* were transferred and spread onto the solid surface of the media. In the inhibition experiment, the films were placed on the *E. coli* agar plate and incubated at 37 °C for 24 h. Finally, the inhibition zone was monitored.

RESULTS AND DISCUSSION

Morphology of BC/CS Blend Films

The surfaces of RBC and blend films were characterized by SEM. The corresponding images are shown in Fig. 1.

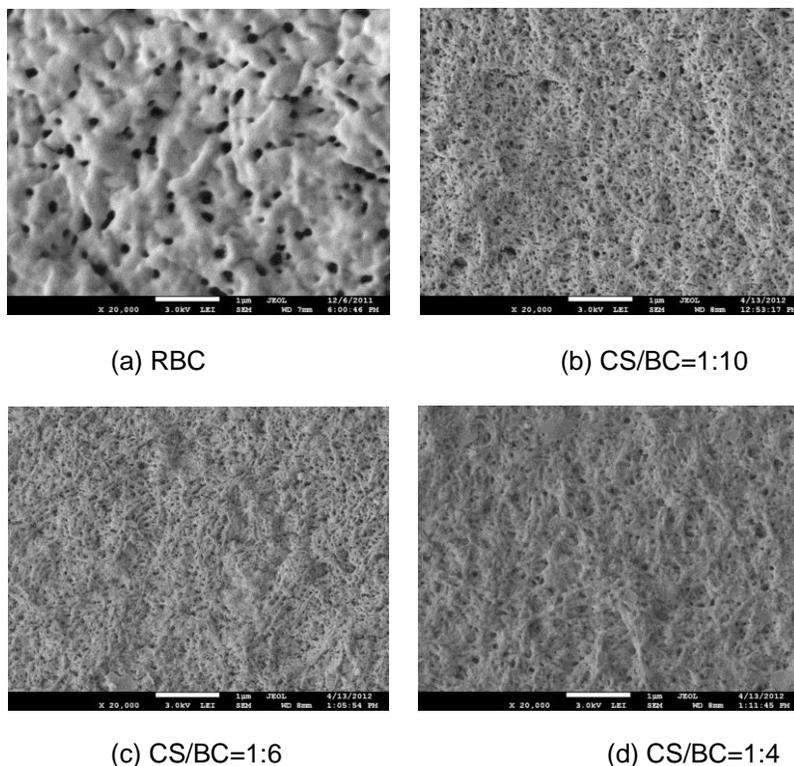


Fig. 1. SEM images of RBC and blend films. (a) RBC; (b) CS/BC = 1:10; (c) CS/BC = 1:6; (d) CS/BC = 1:4

All the films showed a homogeneous structure without obvious phase separation between CS and BC. Moreover, a porous structure and a well-organized network were observed in all of the blend films.

The pore formation may be caused by the leaching of $\text{Zn}(\text{OH})_2$ precipitate during the process of washing. A possible mechanism for this process may be described as follows (1) zinc ions react with hydroxide and form precipitate in the solution; (2) the precipitate is leached during tap water and deionized water washing process, which resulted in pore in films.

By blending with chitosan, the obtained CS/BC blend films become denser compared to the RBC film, as demonstrated in Fig. 1. The densities of apparent CS/BC blend films increased (was raised) with the increase of the chitosan content.

Mechanical Strength Analysis

Figure 2 shows the tensile strength of the blend films with different contents of chitosan. The tensile strength of RBC and RCS were 23.2MPa and 6.3 MPa, respectively. In comparison to that of RBC, the tensile strengths of CS/BC blend films decreased with the increase of chitosan content. This is mainly attributable to the low bonding strength of chitosan itself, although cellulose could combine with it (Wu *et al.* 2004).

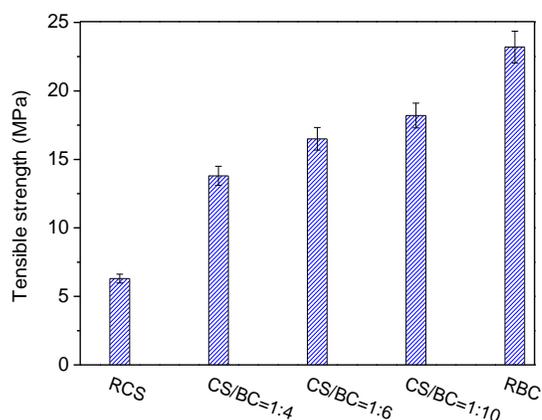


Fig. 2. The tensile strength of RBC, RCS, and blend films

XRD Characterization

The results of XRD tests of CS, BC, RCS, RBC, as well as CS/BC (w/w = 1/6) blend film are shown in Fig. 3. A typical diffraction pattern with prominent peaks at 2θ at 10.3° and 20.3° were found for CS, which are assigned to (0 2 0) and (1 0 0) reflections (Tian *et al.* 2003, 2004), respectively. Basically, there was no significant change for the diffraction pattern of RCS, but the intensity of it decreased. This indicated that inter- and intra-molecular hydrogen bonds of CS were destroyed during the process of dissolving in $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ solution. As a result, the crystal structure of RCS was reconstituted, which resulted in a remarkable decrease in its crystallinity compared to that of CS. Generally, the XRD profile of BC demonstrated that the peaks observed at $2\theta = 16.4^\circ$, 22.9° , and 35.2° were indexed as the cellulose crystalline plane (1 0 1), (0 0 2), and (0 4 0) (Zhao *et al.* 2006; Hameed and Guo 2010; Lu *et al.* 2011). However, the diffraction pattern of the RBC only showed a peak at $2\theta = 21.9^\circ$, indicating that the crystal type of BC was transferred from cellulose I to cellulose III (Yang 2005). Moreover, the crystallinity of

RBC also was decreased remarkably. The results revealed that not only inter- and intra-molecular hydrogen bonds but also the crystal structure of BC was disrupted during the processes of dissolving and regeneration. After simultaneously dissolving CS and BC, the diffraction peaks of generated CS / BC blend film (expressed as 2θ) were mainly found at 11.8° and 21.1° . The crystallinity of the blend film was between the corresponding values of CS and BC. According to the reports from Xu *et al.* (2005) and Luo *et al.* (2008), this result may be explained by the reformation of hydrogen bonds between CS and BC during dissolution and regeneration processes.

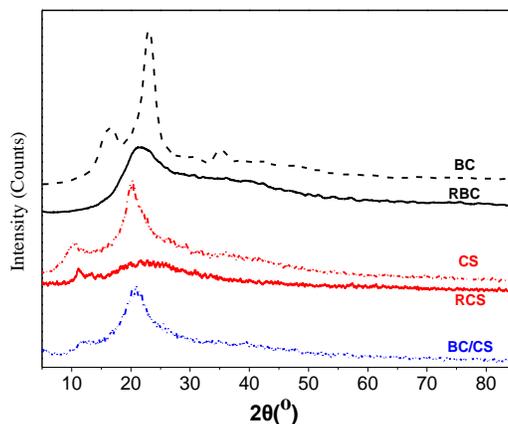


Fig. 3. XRD characterization results of original and regenerated cellulose and chitosan, also the blend film

TGA Analysis

The thermal stabilities of CS, BC, RCS, RBC, and CS/BC blend films were measured on a TG-DTA instrument in a nitrogen environment, and the results are shown in Fig. 4 and Table 1. It was found that CS and RCS started to degrade at the temperature of 279.0°C and 245.6°C , respectively. The temperatures corresponding to maximum degradation rate of CS and RCS were determined to be 297.8°C and 262.5°C , respectively. In the cases of BC and RBC, the onset of degradation started at 321.3°C and 211.7°C , respectively. The maximum degradation rates for both of them were observed at 341.7°C and 228.2°C due to the dehydration and decomposition reaction of the cellulose molecules. The results indicated that the thermal stabilities of the RCS and RBC were inferior to that of the CS and BC. However, the onset of thermal degradation of the CS/BC blend films was observed from 304.1°C to 316.8°C . The temperatures corresponding to the maximum degradation rates of these blend films thus ranged from 324.8°C to 331.3°C . The thermal stability of the CS/BC blend films was better than that of CS but worse than that of BC. Therefore, it was hypothesized that some interactions between CS and BC were formed while dissolving in the $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ solution and during the regeneration processes, which could affect their thermal decomposition properties.

Moreover, the effect of chitosan content on the thermal stability of CS/BC blend films was also investigated. From Fig. 4 (e, f), it was found that residual qualities of the CS/BC blend films increased with the increase of the chitosan contents. This mainly can be attributed to the greater interaction between amino groups of the CS and the hydroxyl groups of the BC (Luo *et al.* 2008; Phisalpong and Jatupaiboon 2008).

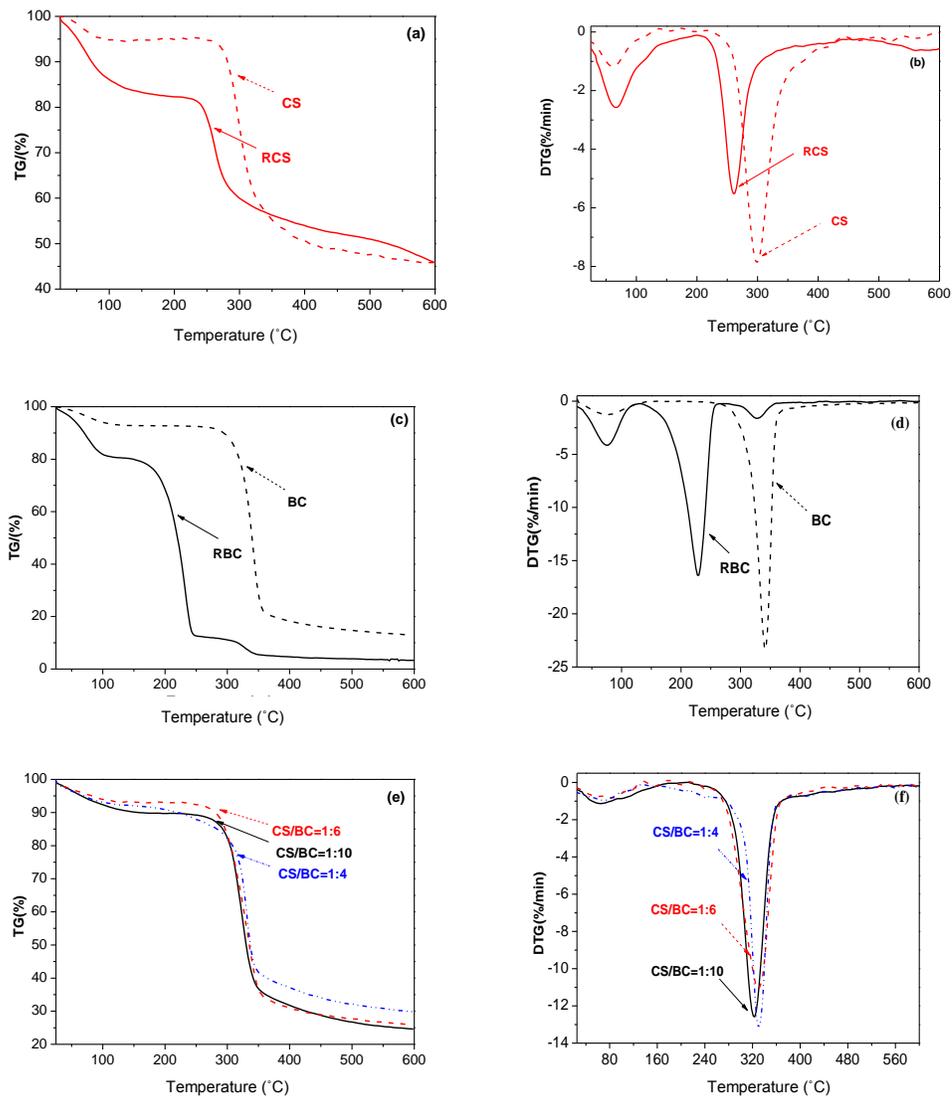


Fig. 4. TG and DTG analysis results of original and regenerated cellulose and chitosan (a, b, c, d), also the blend films (e, f)

Table 1. Characteristic Values of TG and DTG Curves

Samples	T_{onset} ($^{\circ}\text{C}$)	$T_{\text{maximum rate}}$ ($^{\circ}\text{C}$)	Residual quality (%)
CS	279.0	297.8	45.83
RCS	245.6	262.5	45.80
BC	321.3	341.7	12.85
RBC	211.7	228.2	3.26
CS/BC=1:10	304.1	324.8	23.59
CS/BC=1:6	310.6	328.5	25.93
CS/BC=1:4	316.8	331.3	29.67

FT-IR Analysis

The FT-IR spectra of the samples and analysis results are shown in Fig. 5 and Table 2. The results of FT-IR spectra for RBC and BC and RCS and CS differed little. The main change happened during simultaneous dissolution and regeneration of BC and CS. The O–H and N–H stretching and N–H bending vibrations in the BC/CS (w/w = 1/6) blend film were weaker than those of BC and CS. This is mainly because the H-bond networks in BC and CS were broken in the $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ dissolution process, but they might not be completely reconstituted during the regeneration process.

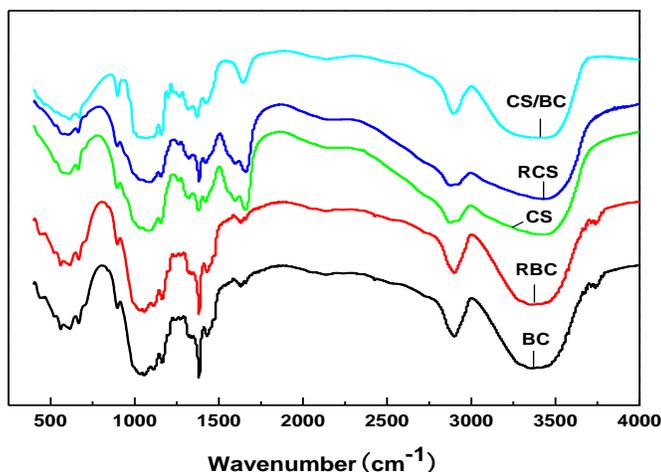


Fig. 5. FT-IR spectra of original and regenerated cellulose and chitosan, also the blend films

The absorption band of the RCS at 1659.1 cm^{-1} corresponds to the carbonyl stretch in amides. The carbonyl band of the CS/BC blend films shifted to a lower frequency (1646.6 cm^{-1}). Moreover, the –NH bending vibrations (1597.1 cm^{-1}) were not observed in the spectra of the CS/BC blend films. The band shifted to a higher frequency. The peak of carbonyl stretch vibration in amides of CS might also overlap it. A similar observation was also described earlier in blends of chitosan and cellulose using BMIMAc as the solvent (Stefanescu *et al.* 2012).

Table 2. Characteristic Values of FT-IR Absorption

	CS (cm^{-1})	RCS (cm^{-1})	BC (cm^{-1})	RBC (cm^{-1})	CS/BC (cm^{-1})
A	3432.7	3430.3	3372.6	3372.9	3419.3
B	2876.0	2875.0	2900.3	2900.8	2895.4
C	1659.3	1659.1	1650.3	1650.7	1646.6
D	1597.1	1597.6			
E	1420.6	1421.0	1430.9	1431.6	1420.9
F	1380.4	1379.8	1383.8	1382.6	1372.1
G	1154.5	1154.9	1113.7	1110.8	1158.7
H	1087.9	1085.4	1042.1	1040.7	1070.6

A: –OH and –NH stretching; B: –CH stretching; C: C=O stretching (amide I) and absorbed water in the amorphous region; D: –NH bending (amide II); E: –CH and –NH bending vibrations; F: –CH₃ bending vibrations; G: Anti-symmetric stretching of the C–O–C bridge; H: Skeletal vibrations involving the C–O stretching.

It has been proposed that the intermolecular H-bond of BC and CS was broken down. The BC–CS H-bond was formed, resulting in a good miscible film (Luo *et al.* 2008; Xu *et al.* 2005). Moreover, these results are consistent with that of XRD analysis. The hypothesis proposed in the section of XRD characterization can also be confirmed by the FT-IR analysis results.

Antimicrobial Activity Test

The antibacterial activity of the RBC films and the CS/BC blend films were tested by *E. coli* based on a disc diffusion method (Fig. 6). An inhibition zone was observed around the CS/BC blend films, while there was no inhibition zone observed for the RBC film.

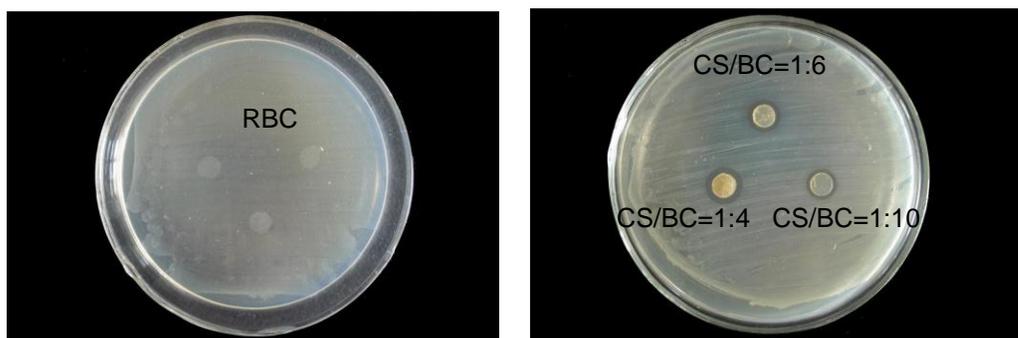


Fig. 6. The antibacterial activity of RBC films and CS/BC blend films against *E. coli*

Moreover, the inhibition zone became more obvious when the content of CS increased in blend films. This can be explained by the antibacterial activity of chitosan itself. It also indicated that dissolving chitosan, using $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ as a solvent, had not significantly inactivated its antibacterial capability. Many researchers have found that the cell wall of a bacterium can be disrupted by the chitosan via interaction between different charges; even the exact antibacterial mechanism of it is still debatable. However, it is clear that the positive charges in chitosan molecules can interact with the negative charges in the bacterial cell wall (Diana *et al.* 2009). The interaction leads to the leakage with protein and other intracellular constituents (Sajomsang *et al.* 2009), further inactivates the activity of bacterium.

CONCLUSIONS

Cellulose/chitosan blend films were prepared by simultaneously dissolving cellulose and chitosan in concentrated $\text{ZnCl}_2 \cdot 3\text{H}_2\text{O}$ solution. It was found that the CS/BC blend films are homogeneous with a significantly denser structure in comparison to the RBC film. The tensile strength of these films are weaker than that of RBC film, but better than that of RCS. Its crystallinity and thermal stability are between those of CS and BC. The FTIR spectra and TGA analysis of the blend films confirmed the intermolecular interaction between cellulose and chitosan, which also demonstrated the formation of homogeneous film while using BC and CS as materials. The effective antimicrobial activity against *E. coli* indicates that the antimicrobial activity of CS was not destroyed.

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