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Preparation of single or double-network chitosan/poly(vinyl alcohol) gel films through selectively cross-linking method

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ABSTRACT

A selectively cross-linking method, which is based on the “di–diol” interaction between poly(vinyl alcohol) and borate and the strong electrostatic interaction between chitosan and tripolyphosphate, was developed. Chitosan/poly(vinyl alcohol) films cross-linked separately with borate, tripolyphosphate and borate/tripolyphosphate were then prepared in terms of this method. Water vapor permeation, mechanical strength, surface morphology and molecular interactions of the films were studied by water permeation test, texture test, atomic force microscopy and ATR-FTIR spectroscopy. With the introduction of cross-linking structure, there is a large improvement in elastic modulus from 271 ± 14.2 to 551 ± 14.7 MPa and a large decrease in water vapor permeability from $(5.41 \pm 0.21) \times 10^{-7}$ g/m h Pa to $(3.12 \pm 0.24) \times 10^{-7}$ g/m h Pa of chitosan/poly(vinyl alcohol) films. The surface morphology of the cross-linked films exhibits a nanoparticle aggregation structure. The size and aggregation behavior of these nanoparticles are strongly related to the type of cross-linker. Furthermore, ATR-FTIR results indicate that strong interaction between polymer matrix and cross-linker exists in our system. This work provides a simple and efficient way to prepare chitosan/poly(vinyl alcohol) films with controllable network structure.

1. Introduction

As one of the most important blends of chitosan, chitosan/poly(vinyl alcohol) (PVA) blend have been widely investigated with an emphasis on its aggregation structure and properties in the past few decades (Arvanitoyannis, 1999; Barbani, Cristallini, Gagliardi, Guerra, & Silvestri, 2008; Chuang, Young, Yao, & Chiu, 1999; Jin & Bai, 2002; Ngah, Kamari, & Koay, 2004; Xiong, Liu, Zhang, & Zhu, 2008; Yang, Su, Leu, & Yang, 2004; Zhao et al., 2003). One of the hot and controversial topics about this system is its compatibility, which is closely relevant to the extent of polymer–polymer interactions. Strong evidences from accurate measurements have shown that this system is not fully miscible at molecular level, depending on the preparation processing and/or the fraction of a certain composition (Castro, Gargallo, Leiva, & Radic, 2005; Jawalkar, Raju, Halligudi, Sairam, & Aminabhavi, 2007; Nakano et al., 2007; Sandoval, Castro, Gargallo, Radic, & Freire, 2005). This special behavior of chitosan/PVA blend arises from the weak interaction between PVA and chitosan as a result of their tight intramolecular structure. However, it has been reported that, this problem could be addressed to some extent through modifying the basic interactions between chitosan and PVA using hydrogen bond forming plasticizer such as glycerol, sucrose and sorbitol. Effect of the plasticizers on structure and properties of the blends have been well explored (Arvanitoyannis, Kolokuris, Nakayama, Yamamoto, & Aiba 1997; Liang, Huang, Liu, & Yam, accepted for publication).

Furthermore, cross-linking treatment has emerged as another important strategy to improve the performance of chitosan/PVA films. It has been reported that, chitosan and PVA could be well cross-linked with some PVA-based cross-linkers (Luo, Yu, Qian, & Zhou, 2005) and chitosan-based cross-linkers (Schiffman & Schauer, 2007a, 2007b; Wang, Zhang, Hu, Yang, & Du, 2007). Those cross-linkers like borate (Miura, Kimura, Suzukia, Miyashita, & Nishio, 1999), tripolyphosphate (TPP) (Mi, Sung, Shyu, Su, & Peng, 2003) and glutaraldehyde (Schiffman & Schauer, 2007a, 2007b) can form cross-linking structure with PVA and chitosan chain by non-covalent or covalent bonds. So far, applications of those cross-linked PVA/chitosan products in separation process, drug delivery and water treatment have been explored (Abdelaal, Abdel-Razik, Abdel-Bary, & El-Sherbiny, 2007; Ignatova, Starbova, Markova, Manolova, & Rashkova, 2006; Wang, Du, & Fan, 2005; Zhang, Mardyani, Chan, & Kumacheva, 2006). However, an organic integrity of the merits of those developed cross-linking techniques remains necessary not only for designing chitosan/PVA blend with controlled network structure, but for expanding their practical applications.

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In this work, we attempt to develop a simple method, which possesses the merits of high efficiency and especially selectivity, to prepare cross-linked chitosan/PVA films. One of the main purposes for this method is to realize a selective and quick introduction of single and/or double-network structure to the films, which were initially prepared by solution casting method. Considering the molecular characteristics of chitosan and PVA, we prefer to use borate and tripolyphosphate as an example to establish this meaningful method. Borate has the special ability to cross-linking PVA through so-called "di–diol" reaction while tripolyphosphate can form cross-linked structure with chitosan by strong electrostatic interaction (Lin, Liu, Shen, Yu, & Cheng, 2003; Mi et al., 2003). This selective behavior of both borate and tripolyphosphate would enable us to design the film with controlled single- or double-network structure. The mechanical testing, water permeation testing, atomic force microscope (AFM) and ATR-FTIR spectroscopy were combined together for a further demonstration on the effect of different cross-linking treatment on the structure and properties of the films.

2. Materials and methods

2.1. Materials

Chitosan with the degree of deacetylation 98.0% and molecular weight of M_w = 330 kDa were purchased from Kunpoong Bio., Co., Ltd. (South Korea). Poly(vinyl alcohol) (PVA) (M_n = 61,000, degree of hydrolysis 98.0%) was purchased from Fluka. Glycerol (bp = 296 °C) was purchased from Fisher Scientific (Pittsburg, PA). Borate and tripolyphosphate were purchased from Sigma. All of these reagents were used as received. Milli-Q (18.3 MΩ) water was used in all experiments.

2.2. Sample preparation

Chitosan/PVA blending films with a weight ratio of W_{PVA}:$W_{Chitosan}$ = 50:50 were prepared by solution casting method in petri dishes. Twenty-four grams PVA was dissolved in 276.0 g deionized water to form 8.0 wt% polymer solution at 90 °C. The solution then was kept at room temperature for 24 h before used. Two weight percent chitosan was obtained by dissolving 4.0 g chitosan powder in 196.0 g 1.0 wt% acetic acid solution at room temperature. Prior to use, some impurities in the stock solution were removed by a centrifugation of 3000 rpm. Ten grams 8.0 wt% PVA solution was mixed homogenously with 40.0 g 2.0 wt% chitosan solution and 0.92 g glycerol to prepare composite film-forming solutions, which were then cast to a uniform layer of 5.0 mm onto each petri dish. The film-forming conditions were fixed at 40 °C and ambient relative humidity in a drying oven for 48 h. The dried films were peeled off the dish, and were kept in dried desiccators for the next experiments. The average thickness of the films is 0.15 ± 0.03 mm.

In cross-linking step, the above dried films were immersed in 1.0 wt% borate, 1.0 wt% tripolyphosphate and 1.0 wt% borate/tripolyphosphate solution, respectively, for designated time to introduce cross-linking structure. Here, the weight ratio between borate and tripolyphosphate in 1.0 wt% borate/tripolyphosphate mixture solution is 1:1. As a contrast, the films without cross-linking treatment are treated with deionized water for the same time. All of the treated films are then re-dried in an oven at 40 °C for the next experiments. Uncross-linked Chitosan/PVA film is denoted herein as CP-n. And the films cross-linked by borate, tripolyphosphate and borate/tripolyphosphate mixture are coded as CP-b, CP-t and PC-tb, respectively.

2.3. Performance and structure analysis of the films

Optical transmittances of the dried films were measured using a UV–vis spectrophotometer (Shimadzu UV-1601PC, Japan) with absorption wavelength fixed at 800 nm.

The tensile strength and elongation at break of the films were measured on a *TA.XT2i* Texture Analyzer (Texture Technologies Corporation, Scarsdale, New York) according to ISO527-3:1995 (E) at a speed of 5.0 mm/min. Rectangular specimens (1.0 × 10.0 cm) were cut using a precision double-blade cutter. Initial grip separation was set at 25.0 mm. The measurements were replicated at least four times for each sample.

Water vapor permeability (*WVP*) of the samples was measured and calculated using ASTM E-96 method and the *WVP* correction method, respectively (Maté & Krochta, 1996). Permeability cups, whose internal and external diameter are 44.2 and 54.2 mm, respectively, were firstly filled with 20.0 ± 0.5 g calcium chloride (RH = 0%), and then sealed by the tested samples. Silicon rubber sealant (Dow Corning, USA) and the ring covers were used for tightly attaching the films to the cups. First, the initial weights of the cups were recorded using a balance with a precision of 0.0001 g. Subsequently, the measured cups were then placed in an environmental desiccator set at room temperature and 90% relative humidity (RH). After an equilibrium state of the conditions in the desiccator was reached, cups were weighed seven times every 5 h. Following *WVP* determination, the thickness of each sample was taken immediately as the average of measurements taken at eight points of the film using a micrometer. Linear regression analysis of the weight increment versus time plots was performed using Origin 7 software to obtain the accurate steady-state slopes K_s (g/h). The actual *WVP* values of the films were calculated according to the following equation:

$$WVP = K_s L / \Delta P A \qquad (1)$$

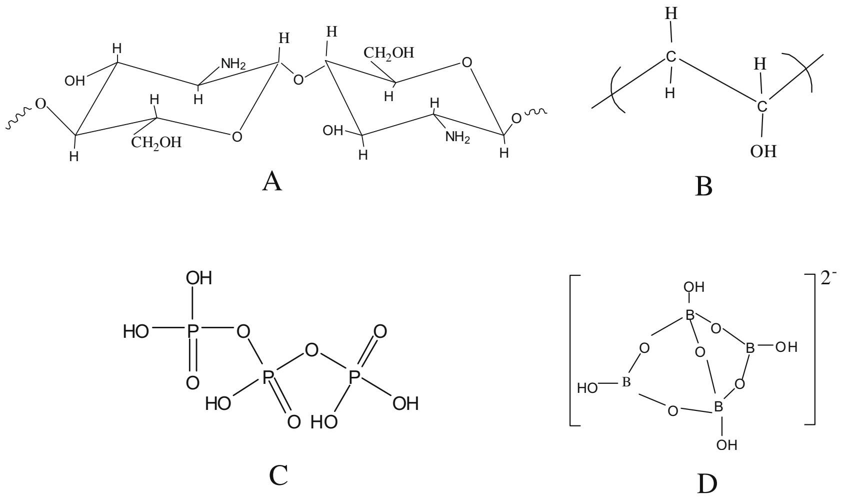
where, L is the thickness of the tested films; ΔP, which equals 2850.95 Pa, is the pressure difference between the inside cup and the outside of the cup; and A, which equals 1.53×10^{-3} m^2, is the effective permeability area of the tested films. The *WVP* values shown in this work were averaged from three parallel measurements.

The bottom surfaces of the dried films were imaged by tapping mode in air using a commercial Nanoscope IIIa Multi-Mode AFM (Veeco Instruments, CA). It was equipped with an *E* scanner which possesses the maximum *xy* range of 15.0 μm. The topographies were obtained at the scan size of 2.0 μm (data collection at 512 × 512 pixels) and the scan frequency of 1.2 Hz by a silicon nitride cantilever.

FTIR measurements of the dried films were performed by means of a Thermo Nicolet 670 FT-IR Spectrometer (Thermo Electron Corp., Madison, WI) at ambient temperature. Prior to the measurement, samples were further dried in a vacuum oven at 50 °C for 6 h. Data from the bottom sides of the films were collected over 128 scans at 4 cm^{-1} resolution using a Smart Miracle ATR (attenuated total reflectance) accessory and analyzed using the associated EZ-OMNIC software. The samples were taken at random from the flat sheet films, and were placed in direct contact with Ge ATR crystal.

3. Results and discussion

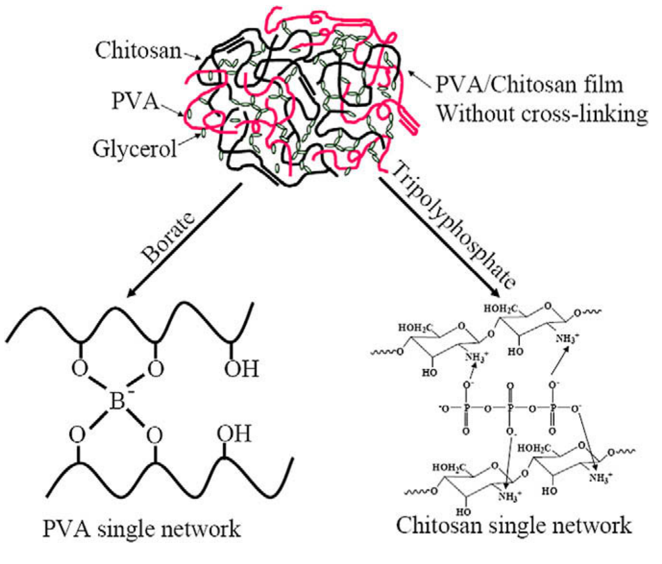
Scheme 1 presents the chemical structure of chitosan (A), poly(vinyl alcohol) (B), tripolyphosphate (C) and borate (D) for a clear view of their molecular characteristics. With main chain composed of β-(1–4)-2-acetamido-D-glucose (20%) and β-(1–4)-2-amino-D-glucose (80%) units, chitosan exhibits typical polycationic nature



Scheme 1. Chemical structure of chitosan (A), poly(vinyl alcohol) (B), tripolyphosphate (C) and borate (D).

in acidic media (Scheme 1(A)). The amino group $-NH_2$ in its backbone existed as protonated formation which has the ability to combine with negative charged ions through electrostatic interaction. Poly(vinyl alcohol) (Scheme 1(B)) is one of the most typical polymers which have the capability to form polymer-ion complexation with some small molecules such as citric acid (Bodugoèz, Pekel, & Guèven, 1999; Shi et al., 2008) and borate (Kim et al., 2005). Herein, we choose negative charged tripolyphosphate (Scheme 1(C)) and borate (Scheme 1(D)) as cross-linker for chitosan and PVA, respectively.

In terms of the above analysis, Scheme 2 presents the rationale of our selective method for preparing chitosan/PVA film with single- or double-network structure. As shown in the left of Scheme 2, the mechanism of the cross-linking reaction of borate ion with PVA is believed to be a so-called "di–diol" complexation, which is formed between two diol units and one borate ion (Keita, Ricard, Audebert, Pezron, & Leibler, 1995; Kurokawa, Shibayama, Ishimaru, Nomura, & Wu, 1992). The physical properties of such PVA gel have been studied extensively in recent (Keita et al., 1995; Lin, Liu, Yu, Liu, & Rwei, 2005). Investigations in the phase behavior and sol–gel transition of PVA–borate–water system indicated that, at a given combination of PVA concentration and ionic strength, the system exhibited a clear–opaque–clear transition with increasing boric acid concentration (Kurokawa et al., 1992). In our case, this cross-linking reaction will introduce PVA cross-linked network in chitosan/PVA film. The right part of Scheme 2 shows the cross-linking mechanism of chitosan and tripolyphosphate. Simply, this cross-linking treatment is based on the electrostatic interaction between negatively charged tripolyphosphate ion and protonated amino group in chitosan chain, which will cause the formation of chitosan cross-linked network in the film. Since it is easy to control, this electrostatic cross-linking strategy has been applied to prepare chitosan gel film and microgel spheres for bio-separation and drug delivery (Wang et al., 2005; Zhang et al., 2006). Therefore, PVA-based or chitosan-based single-network structure in the blending film is achievable by alternatively changing the type of cross-linker. Moreover, as contrast to the two-step method developed by Gong, Katsuyama, Kurokawa, and Osada (2003) and Nakayama et al. (2004), double-network structure in the chitosan/PVA film can be established in one-step *via* our method using borate–tripolyphosphate mixture cross-linker. Since both di–diol and electrostatic interaction are very strong and easy to operate, the cross-linking process here is of high efficiency.



Scheme 2. The rationale of selectively cross-linking method to prepare chitosan/PVA single- or double-network films by using borate and tripolyphosphate as cross-linkers.

According to the above selective rationale, chitosan/PVA films with single-network or double-network structure were successfully prepared by using 1.0 wt% borate, 1.0 wt% tripolyphosphate and 1.0 wt% borate–tripolyphosphate aqueous solution. Our result indicates that the cross-linking treatment does not lead to an obvious change in the appearance and transparency of the films as compared with that of without cross-linked one. All of the films keep a very high transparency of 95.4 ± 2.7% at 800 nm. Water vapor permeability of the films at room temperature as a function of cross-linker is shown in Fig. 1(A). The cross-linking time used here is 5.0 s. It is obvious that, *WVP* values of CP-b, CP-t and CP-tb are largely lower than that of CP-n. This result indicates that the introduction of cross-linking structure can effectively enhance water barrier property of the films. Usually, water vapor permeation through a hydrophilic film is closely related to the solubility and diffusivity of water molecules in polymer matrix. The *WVP* values of protein and polysaccharide films could be enhanced by incorporation of hydrophilic plasticizers into these biopolymer films due to the increase of free volume between polymer chains (Arvanitoyannis et al. 1997; Kołodziejska & Piotrowska, 2007; Turhan & Sah-

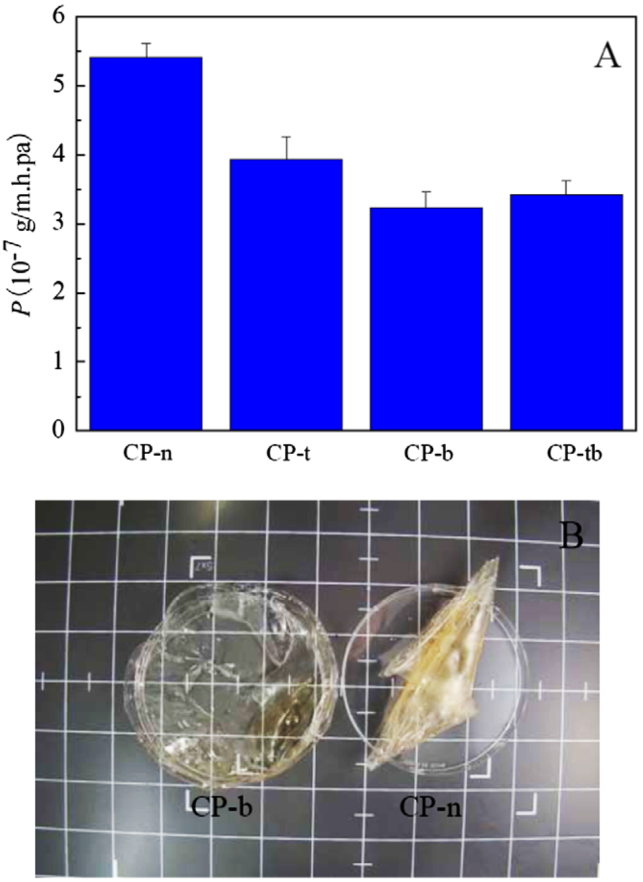


Fig. 1. Water vapor permeability of CP-n, CP-t, CP-b and CP-tb (A); and water-resistance capability of CP-b and CP-n (B).

baz, 2004). In the present case, the decrease of *WVP* is due to the formation of some densely cross-linked region. It decreases the free volume in the films and thereby increases the diffusion path of water molecules. Interestingly, some difference in *WVP* values can also be observed for the films cross-linked by different cross-linkers. Following by CP-tb [$(3.52 \pm 0.21) \times 10^{-7}$ g/m h Pa], CP-b possesses the smallest water vapor permeability of $(3.12 \pm 0.24) \times 10^{-7}$ g/m h Pa. This result demonstrates that the intrinsic nature of the cross-linkers has some ability to affect *WVP* of the films as a result of the formation of different cross-linking structure.

To further test water-resistance capability of chitosan/PVA films after cross-linked, we simply immersed CP-n and CP-b in deionized water for 20 min. The swelling results of the films are shown in Fig. 1(B). From the pictures, the film CP-b can still keep its smooth shape and does not roll or break after underwent an immersion in water. But, CP-n is rolled up and broke. This result indicates that the PVA-based single network is successfully introduced into the film. The introduction of cross-linking structure can improve the water-resistance capability of chitosan/PVA films. However, no obvious difference in the water-resistance capability presents among CP-b, CP-t and CP-tb.

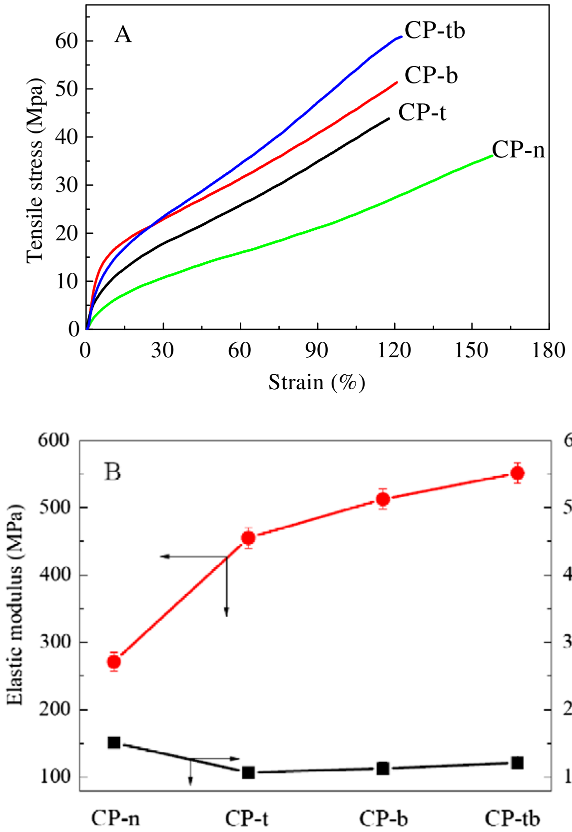


Fig. 2. Stress–strain curves of CP-n, CP-t, CP-b and CP-tb (A); and elastic modulus and strain of CP-n, CP-t, CP-b and CP-tb (B).

The mechanical performance of chitosan/PVA films selectively cross-linked by different cross-linkers was studied by texture testing. The stress-strain curves are shown in Fig. 2(A). The tensile strength at break of CP-b, CP-t and CP-tb is ranged from 43.1 to 60.9 MPa, which is much higher than 35.6 MPa of CP-n. All of the cross-linked films show a similar elongation at break of round 130%, which is slightly lower than 156% of CP-n. The result indicates that the introduction of cross-linking network can effectively improve the mechanical performance of chitosan/PVA films. This reinforcement effect of cross-linking network is quite different from that exhibited by plasticizer, which usually leads to a decrease in the mechanical performance of chitosan/PVA film (Arvanitoyannis et al., 1997). Moreover, under the same or similar weight ratio of chitoan and PVA in the films, both tensile strength at break and elongation at break of the films we developed here are at least two times higher than that observed in glutaraldehyde cross-linked chitosan/PVA films and pure chitosan/PVA films (Costa-Júnior, Barbosa-Stancioli, Mansur, Vasconcelos, Mansur, in press; Srinivasa, Ramesh, Kumar, Tharanathan, 2003). Synergistic effect of glycerol with cross-linking network may also play important role for this large improvement in the mechanical performance of the films. Furthermore, as can be seen from Fig. 2(B), the film CP-tb exhibits the highest elastic modulus of 551.3 MPa as compared to 512.3 MPa for CP-b and 455.1 MPa for CP-t. That is, the films with double-network structure exhibit somewhat higher ability to resist external force in comparison with that having single-network structure.

To study the effect of cross-linking treatment on surface morphology of chitosan/PVA films and also simply clarify the reason why cross-linking treatment can improve the mechanical performance of the films, AFM images from the bottom surface of CP-n, CP-t, CP-b and CP-tb are shown in Figs. 3(A–D) (height) and 4(A–D) (phase). All of the films are composed of nanoparticles but exhibit quite different particle size and particle aggregation structure. The surface morphology shown in Figs. 3(A) and 4(A) for CP-n indicates that the profiles of particles in its surface are not well shaped and the particle aggregation structure is not obvious. This result is different from that was found in our previous work, which indicated a well shaped particle aggregation structure in chitosan/PVA film containing 36.5 wt% glycerol (Liang et al., accepted for

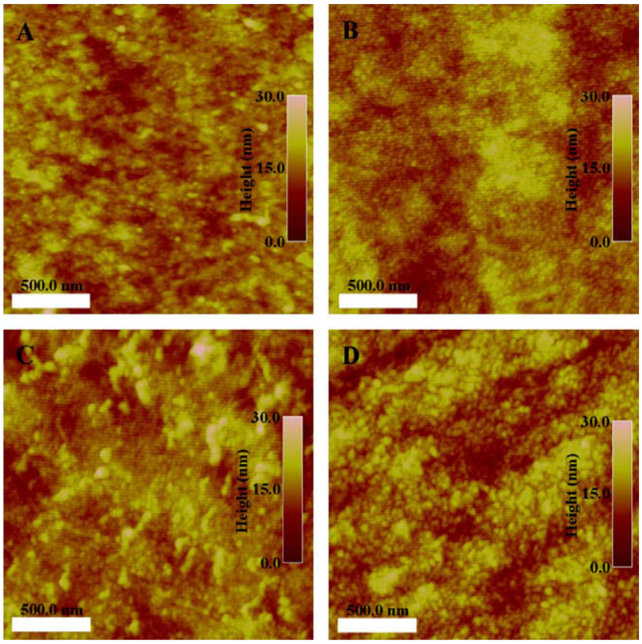


Fig. 3. AFM height images from the bottom surface of CP-n (A), CP-t (B), CP-b (C) and CP-tb (D).

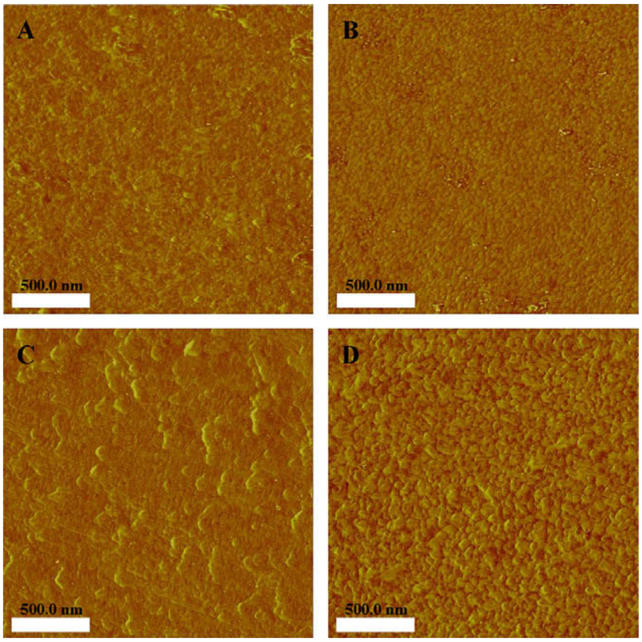


Fig. 4. AFM phase images from the bottom surface of CP-n (A), CP-t (B), CP-b (C) and CP-tb (D).

publication). This difference may arise from strong swelling capability of water to the film and diffusion of some glycerol to surrounding water during the immersion process. It leads to reorganization in surface structure of the film at highly hydrated state. However, after underwent a cross-linking treatment, the particle aggregation structure in CP-t, CP-b and especially CP-tb is quite obvious though there is a great different in particle size and aggregation fashion among them. These results indicated that, reorganization of the aggregation structure occurred in the films is mainly induced by the cross-linking interaction. CP-t possesses the smoothest surface with evenly distributed and well-shaped particles, which have the smallest average particle size of 24.6 nm. Roughness analysis indicates that the roughness factor in CP-t surface is 20.6 nm (Fig. 5). However, chitosan particle size we observed here is largely smaller than those tripolyphosphate cross-linked chitosan nanoparticles prepared in solution, which usually exhibits a diameter of several hundreds nanometer depending on the concentration of tripolyphosphate and chitosan (Jang & Lee, 2008; Qi, Xu, Jiang, Hu, & Zou, 2004). There is an aggregation structure with some protuberances on the surface of CP-b, which has the largest roughness factor of 31.3 nm. Combined with the result from Fig. 4(C), it is easy to see that the particles in CP-b show a densest aggregation, which may is attributed to its highest water barrier property. More striking result is observed from the surface of CP-tb as shown in Fig. 3(D) and Fig. 4(D). The average size of the particle is about twice larger than that of CP-t. All of the particles are aggregated uniformly with a roughness factor of 25.9 nm. This structure possibly is due to the synergistic effect of borate and tripolyphosphate that lead to a formation of double-network structure in CP-tb. The results disclosed by AFM indicate that the application of cross-linking treatment to the films can cause great difference in the surface structure of chitosan/PVA films.

ATR-FTIR spectra were used for a further study on the molecular interaction in chitosan/PVA films before and after underwent a cross-linking treatment (Fig. 6). CP-n was used as a comparison. In Fig. 6(A), the center of the peak located at 3286 cm^{-1} for CP-n is corresponding to the overlapped stretching of hydrogen bond bounded –OH and $-NH_2$. The stretching of its $-CH_2$ appears at 2921 cm^{-1}. Unexpectedly, both location and density of these two absorbance bands show no obvious changes for PC-b and PC-tb even though there is a cross-linking reaction between hydroxyl groups in PVA chains and borate molecules. This result indicates that the so-called "di–diol" complexation between borate and PVA may not take great changes in chemical or hydrogen bond environment of the films. A further proof for this assumption can be obtained from Fig. 6(B), which demonstrates the absorbance of the films at the wavenumber range of 1800 to 800 cm^{-1}. No shift or new peak corresponding to the "di–diol" interaction is observed for CP-b and CP-tb. However, strong shift of the characteristic absorption band (amide II) of chitosan is observed from 1568 cm^{-1} film CP-n to 1557 cm^{-1} for CP-t and CP-tb. Similar shift has also been found in the other tripolyphosphate cross-linked chitosan nanoparticle or fiber system, which indicates strong electrostatic interaction between chitosan and tripolyphosphate (Qi et al., 2004; Wang et al., 2007). Chitosan cross-linked network in

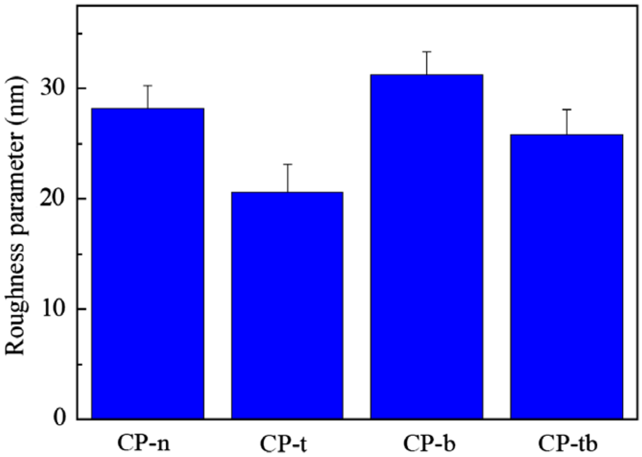


Fig. 5. Surface roughness factor of CP-n, CP-t, CP-b and CP-tb.

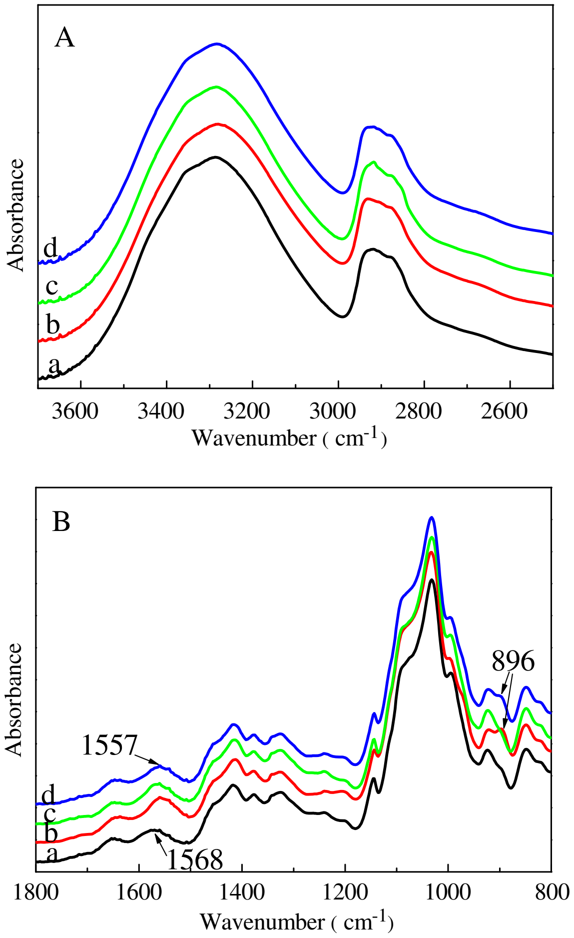


Fig. 6. ATR-FTIR spectra of CP-n (a), CP-t (b), CP-b (c) and CP-tb (d).

the films therefore is formed through strong electrostatic interaction.

4. Conclusions

On the basis of the "di–diol" interaction between borate and PVA as well as the strong electrostatic interaction between tripolyphosphate and chitosan, a selectively cross-linking method has been successfully developed to prepare chitosan/PVA films with single- and double-network structure. This selective method exhibited the features of simplicity, high-efficiency and controllability. Our results indicated that the introduction of single- or double-network structure could effectively improve water vapor permeation and mechanical strength of the films in comparison with the films without cross-linked. The highest tensile strength can even reach 60.9 MPa for CP-tb. AFM analysis on the surface morphology of chitosan/PVA films indicated that all of the films are composed of nanoparticles, which showed different size and aggregation fashion due to the use of different cross-linkers. The cross-linkers gave rise to different polymer–polymer interactions and thereby caused different reorganization dynamics in the film during the cross-linking process. ATR-FTIR results indicated that strong electrostatic interaction took place between chitosan and tripolyphosphate but no strong proof was observed for the so-called "di–diol" interaction between PVA and borate though the formation of PVA cross-linked network. However, the method we developed here would be meaningful to develop some biopolymer blending films with designed and controllable network structure.

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