

Bacterial Cellulose–Poly(vinyl alcohol) Nanocomposite Hydrogels Prepared by Chemical Crosslinking

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ABSTRACT: The bacterial cellulose–poly(vinyl alcohol) (BC/PVA) nanocomposite hydrogels using BC as the reinforcement and PVA as the matrix materials were formed in coagulating bath and crosslinked with formaldehyde, and characterized by attenuated total reflection Fourier transform infrared spectroscopy, mechanical properties tests, thermogravimetric analysis, and scanning electron microscope analysis. It was known that the chemical cross-linked

BC/PVA nanocomposite hydrogels exhibited some promising characteristics, such as appropriate mechanical strength and excellent thermal properties. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: BC/PVA nanocomposite hydrogels; chemical crosslinking; equilibrium swelling ratio; mechanical properties; thermal properties

INTRODUCTION

Cellulose is the most plentiful nature biopolymer on the Earth, being synthesized by plants and by some bacteria species, as well. In particular, bacterial cellulose (BC) composed of nano-sized fibril network is produced by some bacterial, such as *Gluconacetobacter xylinus*. The molecular formula of BC is $(C_6H_{10}O_5)_n$, having a β -1,4 linkage between two glucose molecules. BC has unique structural, functional, physical, and chemical properties. Recently, BC has gained increasing attention in the research realm due to the unique properties it possesses such as, its remarkable mechanical properties in both dry and wet states, porosity, high purity and crystallinity, water absorption, excellent biodegradability, and biocompatibility.¹ Therefore, BC has a wide range of applications in food, paper, and electronic industries,^{2–4} especially has potential application in biomedical engineering.⁵ For instance, bacterial cellulose has been used for wound dressings,^{6,7} vascular plants,^{8,9} artificial skin,¹⁰ and tissue engineering scaffold,¹¹ and applied actively in other areas. Lately, bacterial cellulose was functionalized to produce green nanocomposites,^{12,13} which exhibited some desirable properties.

Poly(vinyl alcohol) (PVA) is a representative water soluble polymer and its aqueous solution can form both chemical and physical gels depending on the

preparation conditions. It can be crosslinked with several methods, including chemical agents, electron beam or γ -irradiation, or physically using thermal cycling.^{14–16} Because of water solubility, no toxicity, and biodegradation by bacteria and fungi,^{17,18} it is a hydrophilic biocompatible hydrogel with several characteristics desired for biomedical application. In addition, PVA could be modified for preparing composites, for instance, it could be blended or grafted with starch and poly(vinyl pyrrolidone) (PVP); however, both PVA/starch and PVA/PVP composites exhibited low tensile strength.^{19,20}

BC/PVA nanocomposites have many advantages that make it valuable for biomedical engineering applications,^{21–23} for instance, it exhibits desirable properties as artificial cornea replacement biomaterial.²⁴ At present, the more popular method for preparing BC/PVA composite is freezing and lyophilization and freezing-thaw method.^{25,26} These methods present typical physical crosslinking, and have the advantages of no residual amounts of the toxic chemical crosslinking agents left, and the resulting BC/PVA composites demonstrated desirable properties. However, both freezing and lyophilization and the freezing-thaw method accompanies with high consumption of energy and time, and the methods required corresponding precision apparatuses to control the rate of heating and refrigerating. In addition, most of the BC/PVA composites were aquiferous, and the mechanical strength and toughness of these nanocomposites hydrogels were expected to be improved. Therefore, it is necessary to explore an economic way to get BC/PVA composites with promising properties.

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In this article, the BC/PVA nanocomposite hydrogels using BC as the reinforcement and PVA as the matrix materials were formed in coagulating bath and crosslinked with formaldehyde, and its equilibrium swelling ratio, FTIR spectroscopy characteristics, mechanical properties, thermal stability, and morphology properties were analyzed by gravimetric analysis, Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), mechanical tests, thermogravimetric analysis (TGA), and scanning electron microscope (SEM) analysis, respectively. The results showed the chemical cross-linked BC/PVA nanocomposite hydrogels exhibited some promising characteristics, such as appropriate mechanical strength, toughness, and excellent thermal properties.

EXPERIMENTAL

Materials

PVA (degree of polymerization 1750 ± 50 , hydrolysis degree 98%, content of PVA more than 99 wt %) purchased from Sinopharm Chemical Regent (Shanghai, China), was analytical reagent and used as received without further purification, and used in all solution preparation. BC was donated by YiDa Food Industry, HaiNan, and the BC pellicles were fibrillated using homogenizer and formed suspensions (2.42%). NaCl and formaldehyde (37 wt %), were purchased from Sinopharm Chemical Regent, were analytical reagent and used as received without further purification. Other reagents used in this work were of analytical grade.

PVA preparation

The 10 wt % PVA solution in distilled water was prepared in a Pyrex resin flask equipped with mixing and a reflux column, as described by Wan et al.²⁷ Dehydrated at room temperature, the PVA hydrogel were prepared and crosslinked with the 0.26 mol of formaldehyde (37 wt % aqueous solution) at 85°C in supersaturated solution of NaCl, the pH value of the solution was about 3.0. The chemical cross-linked PVA membrane was formed after crosslinked with formaldehyde. The nonchemical cross-linked PVA hydrogel prepared as follows: the 10 wt % PVA solutions dehydrated at room temperature to form PVA hydrogel. The PVA hydrogel was disposed in supersaturated solution of NaCl at 85°C for 30 min, and then the nonchemical cross-linked PVA membrane was formed. The chemical cross-linked and nonchemical cross-linked PVA membrane were immersed in deionized water to remove residual impurities, and then taken out, and

absorbed its water on surface by filter paper, respectively.

BC/PVA hydrogel preparation

Depending on the required concentration, 10 g PVA powder was added to the different volume of BC suspension with additional distilled water to obtain the solution composition, respectively. The mixture was then heated to 85°C and stirred for 2 h. Dehydrated at room temperature, the BC/PVA hydrogels were prepared and crosslinked with the 0.26 mol of formaldehyde (37 wt % aqueous solution) at 85°C in supersaturated solution of NaCl, the pH value of the solution was about 3.0. The chemical cross-linked BC/PVA membrane was formed after crosslinked with formaldehyde. The nonchemical cross-linked BC/PVA hydrogel prepared as follow: the BC/PVA solutions dehydrated at room temperature to form BC/PVA hydrogel. The BC/PVA hydrogel was disposed in supersaturated solution of NaCl at 85°C for 30 min, and then the nonchemical cross-linked BC/PVA membrane was formed. The chemical cross-linked and nonchemical cross-linked BC/PVA membrane were immersed in deionized water to remove residual impurities, and then taken out, and absorbed its water on surface by filter paper, respectively. The weight percentage of BC to PVA in mixture was designated as follow: 0, 0.99, 1.96, 2.91, 3.85, 4.76, 5.66, 6.54, 7.41, 8.26, and 9.09%, respectively.

The dissolve properties of BC in *bis*(1,2-ethylenediamine-*n,n'*)-copper(dihydroxide) solution

The *bis*(1,2-ethylenediamine-*n,n'*)-copper (dihydroxide) solution as the good solvent of cellulose was prepared by procedure of Barthel et al.²⁸ 0.05 g BC and 0.05 g BC chemical crosslinked with formaldehyde were immersed in 20 mL of *bis*(1,2-ethylenediamine-*n,n'*)-copper(dihydroxide) solution and stirred at 80°C for 2 h under a nitrogen atmosphere, respectively, and the chemical crosslinking between formaldehyde and BC was investigated.

Characterization of BC/PVA nanocomposite hydrogels

ATR-FTIR spectra were recorded with a Fourier transform spectrophotometer (NEXUS 670) averaging 64 scans at a resolution of 4 cm^{-1} in the range from 4000 to 400 cm^{-1} . The data were analyzed by means of software (OMNIC).

Equilibrium swelling ratio (ESR) of the PVA hydrogels and BC/PVA nanocomposite hydrogels in deionized were determined by gravimetric procedure, and calculated using the formula:

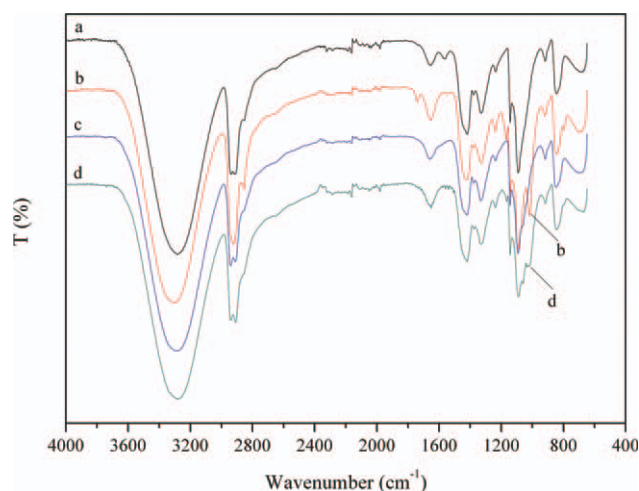


Figure 1 ATR-FTIR spectra of the hydrogels: (a,c) nonchemical cross-linked PVA hydrogel and 4.76% BC/PVA nanocomposite hydrogel, respectively; (b,d) chemical cross-linked PVA hydrogel and 4.76% BC/PVA nanocomposite hydrogel, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\text{ESR}(\%) = \frac{W_h}{W_d} \times 100$$

where W_h and W_d are the weight of swelling equilibrium hydrogel and dried hydrogel, respectively, the values were expressed as the means with standard deviation ($n = 5$).

The break elongation, strength, and modulus of the samples were conducted in accordance to BS EN ISO 527-1996 using a Universal mechanical testing machine (H5k-S, England) with an operating head load of 100 N. The tests were carried out at a condition of room temperature and 70% RH and repeated three times. Samples were strained to failure at a rate of 30 mm/min.

TGA was carried out by a STA-449PC/4/H Luxx simultaneous TG-DTA/DSC apparatus (Netzsch, Germany) with a heating rate of 10°C/min in the range of 25–850°C under a flowing N₂ at the rate of 20 mL/min. The percentage weight loss and derivative weight loss were plotted against temperature for all the samples. The thermal decomposition temperature was taken as the onset of significant weight loss, after the initial moisture losses.

SEM micrographs were taken with a scanning electron microscope (model JSM-5410LV, JOEL, Tokyo, Japan). The free surface of the sample was sputtered with a thin layer of gold to avoid electrical charging.

RESULTS AND DISCUSSION

ATR-FTIR spectroscopy

Figure 1 and Table I showed the ATR-FTIR spectra characteristics of nonchemical cross-linked PVA (a), 4.76% BC/PVA nanocomposite hydrogel (c), chemical cross-linked PVA (b), and 4.76% BC/PVA nanocomposite hydrogel (d), respectively. The absorption at 3280–3310 cm⁻¹ for all the samples, assigned to the O–H stretching vibrations, were showed wide peak. It was demonstrated that there were hydrogen bonds as the physical crosslinking in hydrogels because of abundant hydroxyl group. Two additional bands at 1167 and 1019 cm⁻¹ would be assigned to the C–O–C asymmetric stretching vibration²⁹ from Figure 1(b,d) compared with (a,c), and demonstrated that the chemical crosslinking from PVA hydrogel (b) and BC/PVA hydrogel (d) between PVA and formaldehyde. In addition, 2940–2850 cm⁻¹ corresponding to the -CH₂ stretching display an increasing intensity from (b,d) compared with (a,c). It is also confirmed the chemical crosslinking between PVA and formaldehyde. However, it did not indicate the chemical crosslinking reaction between BC and formaldehyde. Therefore, the swelling property of the BC/PVA nanocomposites hydrogel was investigated.

Equilibrium swelling ratio

Firstly, the effect of chemical crosslinking time using the formaldehyde on the ESR of the hydrogels was investigated, as shown in Figure 2. It was known that the ESR of the chemical cross-linked PVA and 4.76% BC/PVA nanocomposite hydrogel were decreased with crosslinking time. However, when it was longer than 30 min, the ESR was no longer decreasing. It means that the chemical crosslinking

TABLE I
ATR-FTIR Spectra Characteristics of Nonchemical Cross-linked PVA (a), 4.76% BC/PVA Nanocomposite Hydrogel (c), Chemical Cross-linked PVA (b), and 4.76% BC/PVA Nanocomposite Hydrogel (d)

Sample	Infrared group absorption wavenumber (cm ⁻¹)			
	-OH	-CH ₂ , -CH ₃	C-O	C-O-C
a	3281	2911, 2853	1143, 1090	-
b	3304	2922, 2854	1167, 1143, 1090	1019
c	3287	2941, 2911, 2853	1143, 1092	-
d	3284	2940, 2910, 2853	1165, 1143, 1089	1019

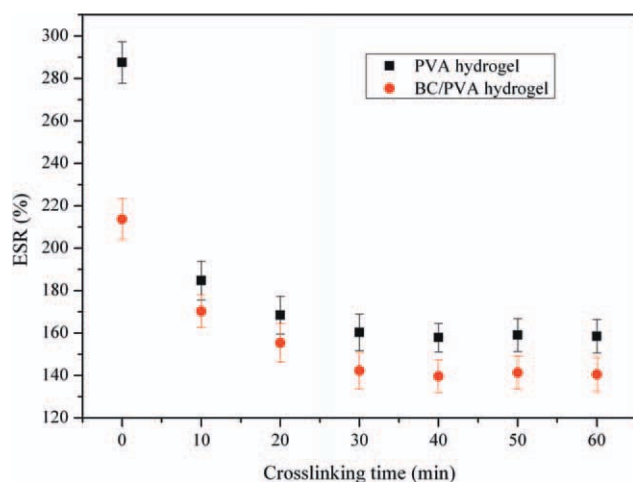


Figure 2 The effect of chemical crosslinking time on the ESR of the PVA hydrogels and 4.76% BC/PVA nanocomposite hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

has been completed. So 30 min of crosslinking time was used in next preparation.

Figure 3 showed the ESR of the nonchemical and chemical cross-linked PVA (a,b) and 4.76% BC/PVA nanocomposite hydrogels (c,d) at different temperature. From (a,c), not only the ESR of the nonchemical cross-linked PVA hydrogels and BC/PVA nanocomposite hydrogels, but also the ESR differences at same temperature were increased with the temperature, and started to dissolve when the temperature was higher than 70°C. It indicated that the hydrogen bonds between PVA chains, or PVA chains and BC, as the physical crosslinking in nonchemical cross-linked PVA and BC/PVA nanocomposite hydrogels, were gradually broken with the temperature, and the effect of BC nanofiber on physical crosslinking was apparent at lower temperature area. However, the physical crosslinking had been destroyed when the temperature was higher than 70°C. From (b,d), the ESR of the chemical cross-linked PVA hydrogel and BC/PVA nanocomposite hydrogel were also increased with the temperature, so did the ESR differences. However, the chemical cross-linked PVA and BC/PVA nanocomposite hydrogels did not dissolve even at 100°C. The ESR difference between the cross-linked PVA hydrogel and BC/PVA nanocomposite hydrogel were 87.5 and 105.2% when the temperature increased from 70 to 100°C. It was demonstrated that the effect of the BC nanofiber on chemical crosslinking was also obvious, and chemical crosslinking between PVA and BC with formaldehyde was achieved except physical crosslinking, respectively, as discussed in Figure 1 and Table I.

In addition, the solubility of the BC and the BC chemical crosslinked with formaldehyde in *bis*(1,2-ethylenediamine-*n,n'*)-copper(dihydroxide) solution was investigated. The BC was complete dissolved,

but the BC chemical crosslinked with formaldehyde was scarcely dissolved (residue was 91.7%) and form a cellulose hydrogel. It demonstrated that chemical crosslinking reaction was achieved between BC and formaldehyde. Therefore, the BC in BC/PVA nanocomposite hydrogel could form chemical crosslinking with formaldehyde, and had effect on the chemical crosslinking of BC/PVA hydrogel.

The ESR of nonchemical cross-linked BC/PVA nanocomposite hydrogel was decreased with the BC content at room temperature (Fig. 4). It showed that the ESR of the BC/PVA nanocomposite hydrogel was apparently affected by physical crosslinking. This might be interpreted by the change in network structure caused by BC integration and interactions formed between BC and PVA chain. Hydroxyl of PVA and BC could form strong inter- and intra-chain hydrogen bond between BC and PVA chain; the interactions between BC and PVA in a BC/PVA nanocomposite hydrogel could make the complex inter- and intra-chain hydrogen bond stronger and thus reduce the amount of bound water.²⁴ Therefore, the ESR of the BC/PVA nanocomposite hydrogel decreased with the BC content.

The ESR of chemical cross-linked BC/PVA nanocomposite hydrogels showed similar trends, and obviously lower than nonchemical cross-linked BC/PVA hydrogels; moreover, the differences of the ESR between chemical cross-linked BC/PVA nanocomposite hydrogels with different BC content were significantly different. It also indicated that the effect of BC content on chemical crosslinking was proved from the analysis of the ESR data. The mechanical properties and thermal properties of the chemical and nonchemical cross-linked nanocomposite

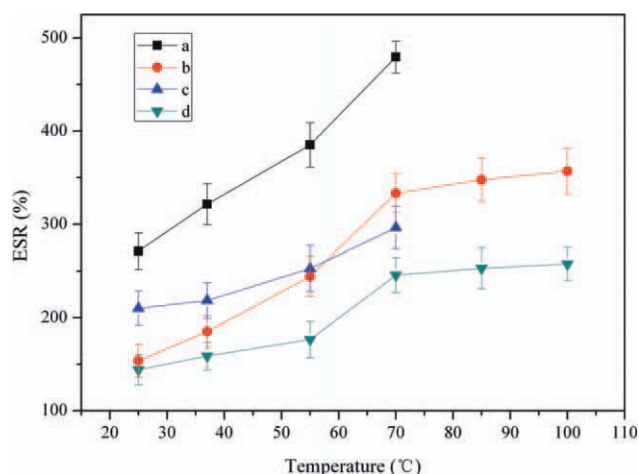


Figure 3 The ESR of the hydrogels at different temperature: (a,c) nonchemical cross-linked PVA hydrogels and 4.76% BC/PVA nanocomposite hydrogels; (b,d) chemical cross-linked PVA hydrogels and 4.76% BC/PVA nanocomposite hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

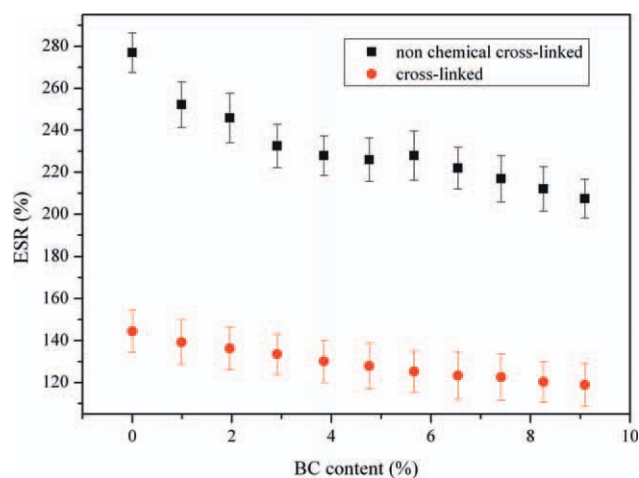


Figure 4 The effect of BC content on the ESR of the chemical and nonchemical cross-linked BC/PVA nanocomposite hydrogels at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrogels were also investigated to further confirm the chemical crosslinking between BC and PVA chains with formaldehyde, respectively.

Mechanical properties

The tensile strength, elongation at break, and Young's modulus of the BC/PVA nanocomposite hydrogels with various BC content were showed in Figures 5–7, respectively. According to the Figures 5 and 7, the tensile strength and the Young's modulus of the nonchemical cross-linked and chemical cross-linked BC/PVA nanocomposite hydrogels were increased and the elongation at break was decreased (Fig. 6) with BC content. The mechanical properties

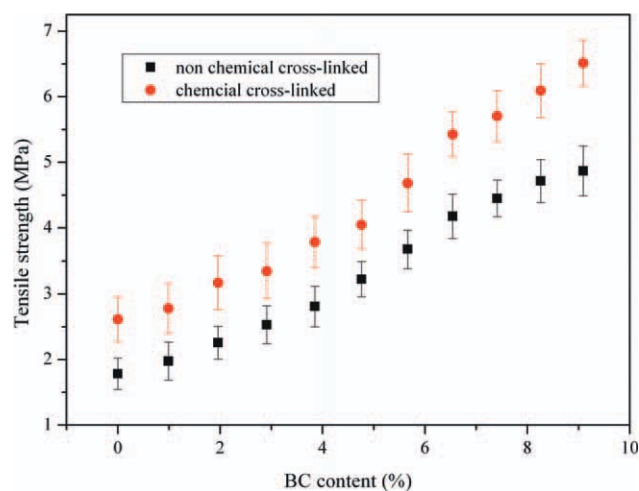


Figure 5 The effect of BC content on the tensile strength of the chemical and nonchemical cross-linked BC/PVA nanocomposite hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

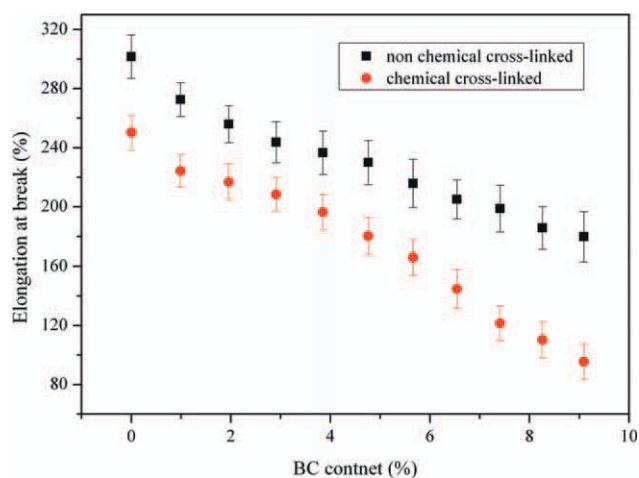


Figure 6 The effect of BC content on the elongation at break of the chemical and nonchemical cross-linked BC/PVA nanocomposite hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the nanocomposites hydrogel enhanced significantly because of BC's incorporation, which could be attributed to that the high strength and modulus of BC nano-fibrils. As both the PVA and the reinforcing components BC were hydrophilic in nature, the improvements observed in the tensile strengths and the Young's modulus of the nanocomposites hydrogel reinforced with BC could also be ascribed to the good dispersibility and excellent adhesion between BC and PVA.²⁴

The tensile strength and Young's modulus of the BC/PVA nanocomposite hydrogels were also enhanced because of chemical crosslinking. The differences of the tensile strength and the Young's modulus between chemical and nonchemical cross-

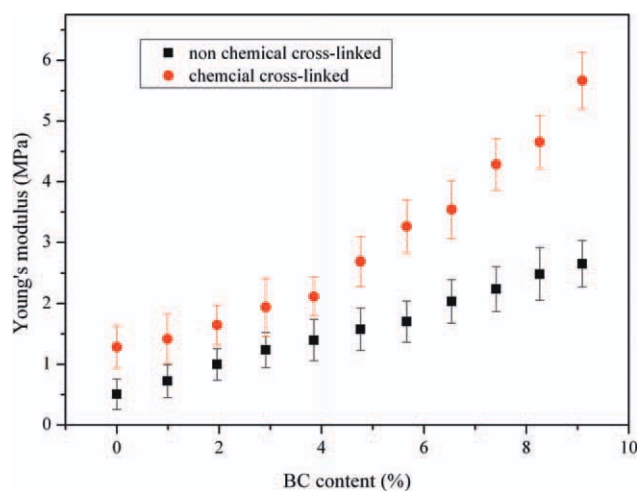


Figure 7 The effect of BC content on the Young's modulus of the chemical and nonchemical cross-linked BC/PVA nanocomposite hydrogels. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

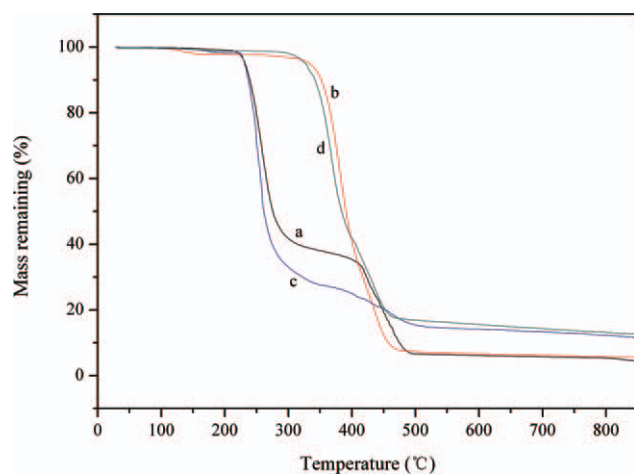


Figure 8 TG curves of the hydrogels: (a,c) nonchemical cross-linked PVA hydrogel and 4.76% BC/PVA nanocomposite hydrogel, respectively, (b,d) chemical cross-linked PVA hydrogel and 4.76% BC/PVA nanocomposite hydrogel, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

linked BC/PVA nanocomposite hydrogel were increased with BC content increasing. This behavior could be interpreted by the good interfacial adhesion and the formation of strong interactions between PVA chains, BC and PVA chains.²⁵ It also indicated that the chemical crosslinking between BC and PVA with formaldehyde was formed, respectively. In addition, it also indicated that chemical crosslinking was enhanced with increase of the BC content, as discussed in Figure 4. Therefore, the increase of the tensile strength and the Young's modulus, and the decrease of the elongation at break of the nanocomposite hydrogels were enhanced by BC content and chemical crosslinking.

Thermal properties

The effects of chemical crosslinking and BC reinforcing on the thermal stabilities of the PVA matrix were investigated by the TGA as shown in Figure 8. It was found that the thermal degradation of non-

TABLE II
Thermal Characteristics of TG Curves in Figure 8

Curve	T_{onset} (°C)	T_1 (°C)	T_2 (°C)	Residuals (wt %)
a	236.9	261.7	426.7	4.41
b	354.8	381.7	436.7	5.53
c	238.7	252.8	427.8	11.69
d	337.2	375.3	432.8	12.56

The thermal decomposition temperature was taken as the onset of significant (5%) weight loss, after the initial moisture losses. T_1 and T_2 obtained from the differential thermogravimetric curves of the samples. T_1 was the maximum decomposition temperature of the first weight-loss step. T_2 was the maximum decomposition temperature of the second weight-loss step.

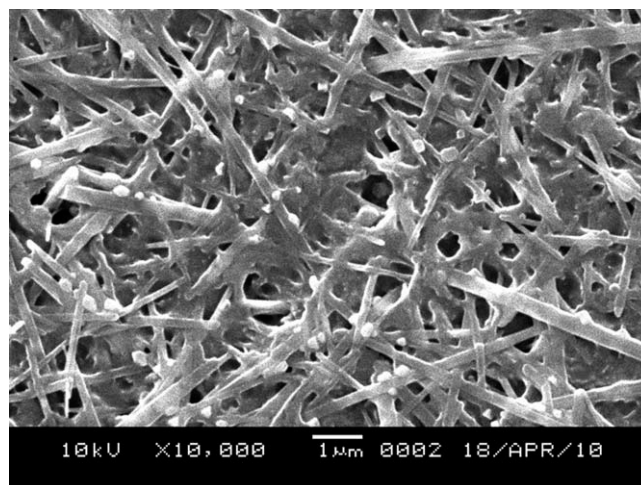


Figure 9 SEM image of 4.76% BC/PVA chemical cross-linked nanocomposite hydrogel.

chemical cross-linked PVA hydrogel revealed two main weight loss regions from Figure 8(a). The first region, at around 230–380°C appeared due to the degradation of the side-chain in the PVA matrix,²⁹ such as C–O bond. The weight loss occurred at 430–465°C was attributed to the second stage due to the cleavage of C–C backbone in polymer, the so called carbonization. In literature, the thermal degradation of the PVA^{24,29} exhibited similar thermo gravimetric behaviors.

The T_{onset} , T_1 , T_2 and residuals of the samples were determined from the TG curves as shown in Table II. It was found that the effect of BC reinforcing on the weight loss temperature of the PVA hydrogel may have slight effect from (a,c) or (b,d), respectively. There was slight increase of T_{onset} (a,c) of PVA hydrogel after BC's incorporation; it could be attributed to the formation of the hydrogen bonding between BC and PVA, which also indicated the good compatibility of BC and PVA. However, the T_{onset} and T_1 of the PVA hydrogels were remarkably increased with the chemical crosslinking comparing (b) with (a) or (d) with (c). It was demonstrated that the chemical crosslinking between PVA chains and formaldehyde was formed, and the structural stability of the PVA was enhanced because of chemical crosslinking. As a result, the thermal stability of the side-chain in the PVA matrix was remarkably enhanced with ether groups.³⁰ It was also found that the residuals of the PVA hydrogel were increased with BC reinforcing. The residual of the pure BC was about 14.96% in our test. Even if excluding the effect of BC on residuals, the residuals of the non-chemical cross-linked and chemical cross-linked 4.76% BC/PVA hydrogel were 10.98 and 11.85%, respectively. It was still higher than PVA hydrogel's. It also indicated that the global thermal stability of PVA matrix was enhanced with BC reinforcing.

Figure 9 presents the surface image of the chemical cross-linked 4.76% BC/PVA nanocomposite hydrogel. The image shows that PVA precipitated inside the BC micro-fibrils network, and BC appear well recovered and wrapped by PVA simultaneously.

CONCLUSION

BC/PVA nanocomposite hydrogels using BC as the reinforcement and PVA as the matrix materials were formed in coagulating bath and crosslinked with formaldehyde. The ATR-FTIR spectrum, ESR, mechanical, and thermal properties of the PVA and BC/PVA nanocomposite hydrogel revealed that chemical crosslinking between PVA and formaldehyde, BC and formaldehyde were achieved, respectively, and BC was conducive also to the chemical crosslinking. The ESR of the nanocomposite hydrogels were decreased after chemical crosslinking, and decreased with the BC content at room temperature. It was found that the mechanical properties of the nanocomposite hydrogels were apparently affected by chemical crosslinking and the content of BC. Tensile strength and the Young's modulus of the nanocomposite hydrogels were increased after chemical crosslinking and with BC content, the elongation at break was decreased. In addition, our result demonstrated that not only the PVA hydrogels, but also the BC/PVA nanocomposite hydrogels; the thermal stability were remarkably enhanced after chemical crosslinking. Briefly, the BC/PVA nanocomposite hydrogels, prepared by chemical crosslinking, exhibited promising mechanical properties and desirable thermal stability; so the nanocomposite hydrogels described in this study provides information for further development and optimization of a variety of nanofiber-polymer matrix composite hydrogels.

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