

Bacterial cellulose-based membrane-like biodegradable composites using cross-linked and noncross-linked polyvinyl alcohol

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Received: 18 January 2012 / Accepted: 19 April 2012 / Published online: 4 May 2012
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Abstract Bacterial cellulose (BC)-based membrane-like biodegradable composites were produced by immersing wet BC pellicles in polyvinyl alcohol (PVA) solution. The BC content in the BC–PVA composites can be adjusted by varying the concentration of PVA solution. Chemical cross-linking of PVA was carried out using glutaraldehyde to increase the mechanical properties of the composites as well as to make the PVA partially to highly water insoluble. Examination by scanning electron microscopy indicated that the PVA not only penetrated the BC network, but also filled the pores within the BC pellicle. Attenuated total reflectance-Fourier transform infrared spectroscopy showed that acetal linkages could be formed in the BC–PVA composites by a cross-linking reaction. Sol–gel results indicated that cross-linking reaction increasingly made PVA insoluble in water resulting in higher gel (cross-linked fraction) content in the PVA. Wide-angle X-ray diffraction results showed decreased crystallinity in cross-linked BC and PVA, as expected. It was also found that crystal size was smaller in PVA after cross-linking. The BC–PVA composites had excellent tensile properties and cross-linking increased these properties further. Thermogravimetric analysis showed higher thermal stability for BC–PVA composites compared to PVA. The cross-linked specimens, especially the highly cross-linked ones, showed even higher thermal stability. The methods developed in this study make it possible to control the PVA content in the composites as well as the cross-linking level of PVA. These composites could be good candidates for replacing traditional non-biodegradable plastics.

Introduction

The past several decades have seen rapid development of advanced composites with excellent mechanical properties that have replaced metals in many applications. Most of these composites are made using petroleum-derived non-degradable fibers, such as carbon, aramid and polymers/resins such as polyetheretherketone (PEEK) and epoxy. These composites are difficult to recycle or reuse, and hence pose a serious solid waste disposal problem due to decreasing landfill space, widespread litter, and pollution of land, air, and marine environments [1–3]. As a result, significant interest has been generated in developing fully biodegradable bio-based composites in the past few years [4–10].

Bacterial cellulose (BC) is a promising biodegradable green material with excellent potential as reinforcement for composites. BC is a specific cellulose primarily produced by *Acetobacter xylinum*, a Gram-negative, obligately aerobic bacterium, in a nutritional fermentation medium at 30 °C. The medium requires carbon sources (mannitol, sucrose, fructose or, others) and nitrogen sources (peptone, typtone, yeast extract, etc.), with optimum pH of 5.0. BC has the same chemical structure as other plant-based cellulose and is produced as fibers with diameters in the range of 70–90 nm. It displays many unique properties including higher purity, higher degree of polymerization, higher crystallinity, higher tensile strength and modulus, and stronger biological adaptability [11–15]. The BC material is already being used in many applications including artificial skin and blood vessels, binding agent for fibers and other materials, loud speaker diaphragms, high quality paper, foods, textiles, composite membranes, etc. [15–20].

Polyvinyl alcohol (PVA) is a thermoplastic, biocompatible, and biodegradable polymer. With hydroxyl groups

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in its structure, it is hydrophilic and expected to form hydrogen bonds and acetal linkages with other materials, such as cellulose and aldehydes [21, 22]. Therefore, BC–PVA is an excellent reinforcement and resin combination for fabricating biodegradable composites. BC–PVA-based composites have been developed previously [21–25]. Hydrogen bonds formed between hydroxyl groups on BC and PVA have been shown to facilitate fabrication of homogenous composites [21]. However, BC content in those composites was low and as a result the properties were not ideal to replace most of the traditional plastic materials. If the desired mechanical properties are achieved, such composites can have great potential for applications as articular cartilage [22] and aortic heart valve prosthesis [23, 24].

Both cellulose and PVA have been studied in the past and shown to be fully biodegradable [26–28]. As a result, their composites made using the two are also biodegradable. However, biodegradation investigation experiments involving BC–PVA composites, particularly those using cross-linked PVA are currently ongoing in our lab, will be the subject of our next paper.

Research in chemical cross-linking of PVA and cellulose fabrics has been reported earlier [29–36]. PVA can be cross-linked using glutaraldehyde (GA) in the presence of a strong acid [29–34]. PVA contains hydroxyl groups that form acetal linkages with aldehyde groups in the GA [29–34]. Cotton fibers (cellulose) and cellulose nanofibers from softwood which are chemically identical have also been cross-linked using GA to modify their properties [35, 36]. Recently, some research for cross-linking BC and BC/fibrin using glyoxal or GA has also been reported [37, 38]. However, effects of cross-linking of membrane-like BC–PVA composites have not been investigated yet.

In the present study, three types of thin membrane-like BC-based biodegradable composites; BC–PVA composites and partially and highly cross-linked BC–PVA composites were developed and characterized. The BC content in these composites could be easily controlled as desired, by varying the concentration of PVA solution. A simple immersion method was used to cross-link the BC–PVA composites. Further, the extent of cross-linking could be controlled. The membrane-like composites prepared had smooth surfaces; their tensile and thermal properties were excellent, especially those that were highly cross-linked.

Materials and methods

Microorganism and culture media

A. xylinum, ATCC 23769, obtained from the American Type Culture Collection (ATCC, Manassas, VA) was used

as the model strain and maintained on agar plates containing 25 g/L D-mannitol, 5 g/L yeast extract and 5 g/L tryptone, and 20 g/L agar. The mannitol culture medium used for BC production consisted of 25 g/L D-mannitol, 5 g/L yeast extract, and 5 g/L tryptone.

Preparation of BC pellicles

The strain from the agar plate was inoculated into a conical flask containing mannitol culture medium as the seed culture. The initial pH value of the medium was adjusted to 5.0 and was not regulated during the culture. The seed culture was incubated at 30 °C and 130 rpm on a rotary shaker for 2 days and 9 mL of this seed culture was inoculated into a 150-mL culture medium in 1000-mL conical flask for production of BC. The cultivation was carried out at initial pH 5.0 and 30 °C in a static incubator for 10 days. After incubation, the BC pellicles produced on the surface of mannitol culture medium were harvested and washed successively with water and 1 % (w/v), aqueous NaOH at 90 °C for 15 min, washed with deionized water to remove all microbial product contaminants, and obtain purified pellicles.

Preparation of BC–PVA composites

PVA powder (M_w 31,000–50,000, 98–99 % hydrolyzed, Aldrich, St. Louis, MO) was added to deionized water in 3.2 w/v % concentration, and the mixture was then stirred at 80 °C for 30 min to form the PVA solution. The purified BC pellicles were immersed into the PVA solution and kept in a water bath at 80 °C for 2 h, and were then allowed to remain in the PVA solution at room temperature for 12 h. The PVA-containing BC pellicles were then transferred into deionized water for 30 min to remove superfluous PVA on the surface of the BC pellicles to obtain BC–PVA prepregs. The BC–PVA prepregs were dried on a Teflon[®] plate in an oven at 45 °C for 12 h until the weights of the BC–PVA composites remained constant. The BC content in these composites was in the range of 50 %. The percentage BC content mentioned in the manuscript has been calculated on dry weight basis. The BC–PVA composites with varying BC content could be obtained, if desired, by simply adjusting the concentration of the PVA solution. BC mass was weighed after removing PVA from the BC–PVA composites by hot water washing. BC content in the composites was calculated using PVA and BC dry weights. BC and PVA were prepared by drying BC pellicles and casting PVA solution as control, for comparison. All composites, BC and PVA specimens prepared in this study were thin, membrane-like. The PVA solution concentrations used and the resulting BC content obtained in BC–PVA composites are presented in Table 1.

Table 1 BC content in BC–PVA composites

Concentrations of PVA solution for BC pellicle treatment (w/v%)	BC content in BC–PVA composites (wt%)
1.5	75 ± 4
3.2	50 ± 4
6.0	25 ± 3

Preparation of cross-linked BC–PVA composites

Partially cross-linked BC–PVA composites were prepared by immersion method using GA–acetone solution. The BC–PVA composites with 50 % BC content were initially immersed into the GA–acetone solution which contained 10 % by volume GA solution (25 % solution in water, Aldrich, St. Louis, MO) and 90 % by volume acetone (Mallinckrodt Baker, Phillipsburg, NJ). The pH of the GA–acetone solution was adjusted to around 1.0 using hydrochloric acid to trigger the cross-linking reaction. The reason for using acetone as a solvent was to prevent the PVA from dissolving in water during the cross-linking reaction [30]. After carrying the cross-linking reaction for 12 h at room temperature, the partially cross-linked specimens (prepregs) were taken out from the GA–acetone solution and rinsed with water to remove the residual GA and acetone. The partially cross-linked BC–PVA composites were then dried in an oven at 45 °C for 12 h until their weights were stabilized. Same process was used to partially cross-link BC and PVA specimens individually, to compare their properties.

Highly cross-linked BC–PVA composites were prepared in GA–water solution using similar method described above. The BC–PVA prepregs initially were partially dried at room temperature for 8 h before immersing into the GA–water solution, and water content in the partially dried specimens was around 50 %. The partially dried BC–PVA prepregs were then immersed into the GA–water solution containing 10 % by volume GA solution (25 % solution in water, Aldrich, St. Louis, MO) and 90 % by volume deionized water. The pH value of the GA–water solution was adjusted to around 1.0 using hydrochloric acid to trigger the cross-linking reaction. The incomplete drying of BC–PVA prepregs was to make sure the GA–water solution penetrated into the inner structures of BC–PVA prepregs and triggered the cross-linking reaction to as complete as possible. Our preliminary test results had indicated that the completely dried BC lost a majority of its porous structure as the individual nanofibers stuck to each other reducing the penetration of the GA–water solution. After 12 h of cross-linking reaction at room temperature, the highly cross-linked BC–PVA prepregs were taken out from the GA–water solution and rinsed with deionized

water to remove the residual GA. The highly cross-linked BC–PVA prepregs were then dried between two steel plates, to retain their flatness, in an oven at 45 °C for 12 h until the weights were stabilized. Highly cross-linked BC specimens and highly cross-linked PVA films were also prepared using the same method to compare their properties.

Characterization

Scanning electron microscopy analysis

Freeze-dried BC and freeze-dried BC–PVA composites (50 % BC) were sputter coated with gold and their surface topographies were observed with scanning electron microscope (SEM, LEO 1550 FESEM, Oberkochen, Germany) at an accelerating voltage of 15 kV.

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy

The BC–PVA composites, the partially cross-linked BC–PVA composites and the highly cross-linked BC–PVA composites were characterized using an FTIR spectrophotometer (Nicolet Magna-IR 560, Thermo Scientific, Waltham, MA). ATR-FTIR spectra were taken in the range of 4000–800 cm^{-1} wavenumbers using a split pea accessory. Each scan was an average of 64 scans obtained at a resolution of 4 cm^{-1} . BC content in all the composite specimens was in the range of 50 % and the specimens were dried in an oven at 45 °C for 12 h before spectroscopy. Reproducibility was confirmed for each type of specimen by repeating the experiment three times.

Sol–gel analysis

The cross-linked PVA, either in the form of cross-linked PVA film or the cross-linked BC–PVA composites (50 % BC), was dried in a moisture-meter (CW Brabender Instruments, Inc., South Hackensack, NJ) at 105 °C for 12 h before conducting the sol–gel test. The specimens were weighed to obtain their initial dry weights and then immersed in distilled water in 150-mL glass bottles. The mixtures in the glass bottles were then placed on a shaker table (MAXQ 4450, Thermo Scientific, Waltham, MA) at 80 °C and 175 rpm for 12 h. The solid contents for all specimens were then washed three times and filtered using a Whatman® filter paper (Number 4, 20–25 μm pore size, qualitative) to obtain final residues. The water-soluble portion (sol) and particles smaller than the pore size of the filter paper were removed. The final residues of the cross-linked PVA, either in the cross-linked PVA or the cross-linked BC–PVA composites, were kept in the moisture-meter at 105 °C

for 12 h again to obtain their final dry weights (gel). Ratios of the gel weights of the cross-linked PVA to their corresponding initial dry weights were used to determine the PVA gel (cross-linked) percentages. The BC weights in the cross-linked BC–PVA composites were regarded as constant values before and after the test.

X-ray diffraction (XRD) studies

Wide angle X-ray diffraction (WXR) was used to evaluate the crystallinity and/or crystal sizes of the BC, the PVA, the highly cross-linked BC and the highly cross-linked PVA. All specimens were dried in an oven at 45 °C for 12 h before WXR studies. The general area detection diffraction system (GADDS, Bruker-AXS, Inc., Madison, WI) was used at 45 kV and 40 mA. The XRD patterns of all the specimens were obtained using a Scintag theta–theta powder diffractometer (PAD X, Scintag, Inc., Cupertino, CA) with a solid-state intrinsic germanium detector. All specimens were scanned from 2° to 30° at 3°/min employing the Cu K_{α} X-ray radiation with a wavelength of 1.54 Å.

Tensile property characterization

Tensile tests of various specimens were performed using an Instron tensile testing machine (Instron, model 5566, Canton, MA). The specimens for BC, PVA, BC–PVA composites and their corresponding cross-linked specimens at different levels of cross-linking were cut into 10-mm wide and 60-mm long strips using a precise cutter. Young's moduli of all specimens were determined from the tensile test results conducted according to ASTM D-882-02. Two ends of the specimens were placed between the upper and lower grips of the Instron, leaving a gauge length of 30 mm. The strain rate of 0.02/min was maintained for all specimens. All specimens were conditioned at 21 °C and 65 % RH for 3 days before tensile test.

Thermogravimetric analysis (TGA)

TGA (TA instrument, Model No. 2050) was used to analyze the thermal properties of BC, PVA, BC–PVA composites (50 % BC) and their corresponding cross-linked specimens at different levels of cross-linking. All specimens were dried in an oven at 45 °C for 12 h before conducting the test. All TGA analyses were performed between 25 and 600 °C, and at a ramp rate of 20 °C/min under a nitrogen atmosphere by maintaining a flow rate of 10 mL/min.

Results and discussion

SEM images of BC and BC–PVA composites

Figure 1a, b show the SEM images of freeze-dried BC and freeze-dried BC–PVA composite (50 % BC) specimens, respectively. Both specimens were not hot pressed to preserve their structure. In Fig. 1a, the porous BC network structure is clearly visible. Since these specimens were freeze dried, the porous structure has been maintained. Based on the diameter measurements of 100 BC-nanofibers and 100 pores in the SEM image of the BC, the mean diameter of BC-nanofibers was found to be less than 100 nm and the pore diameters ranged from several dozens to several hundred nanometers. It is clear from Fig. 1b that the PVA penetrated the BC network structure and filled many of the pores. The diameters of the BC-nanofibers became larger since they were covered by the PVA. Many BC-nanofibers were embedded within the PVA layers, thus forming uniform composite structures with excellent properties. Similar surface topography of BC–polyethylene glycol (PEG) composite reported previously showed that PEG not only coated the surface of BC pellicles but also penetrated into the BC fiber network [39]. It has also been reported that structural modification can occur as the water surrounding polyglucosan chains are displaced and

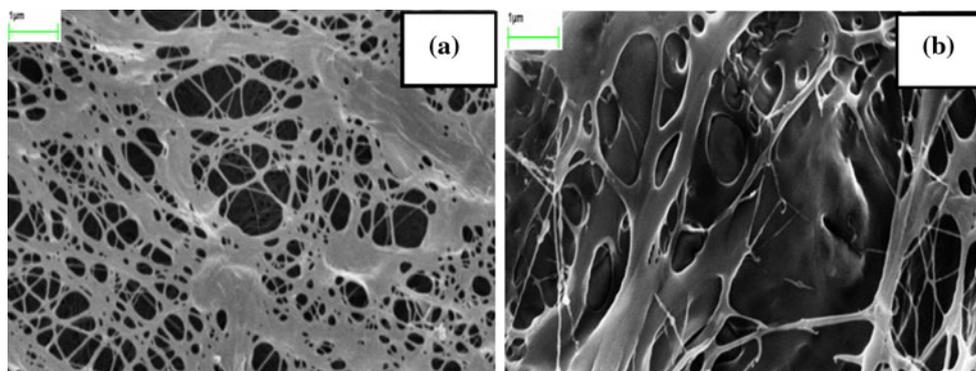


Fig. 1 SEM images of freeze dried BC (a) and freeze dried BC–PVA composite (b)

hydrogen bonds are formed between the hydroxyl groups of BC and PEG and of BC and PVA [21, 40, 41].

ATR-FTIR analysis of BC–PVA composites and cross-linked BC–PVA composites

Figure 2 shows the ATR-FTIR spectra of the BC–PVA composites (50 % BC) and BC–PVA composites cross-linked to different levels. All spectra were normalized based on bands observed at 1058 cm^{-1} wavenumber associated with C–O stretching. ATR-FTIR spectrum 2(a) is for the BC–PVA composite. ATR-FTIR spectrum 2(b) is for the partially cross-linked BC–PVA composite using the GA–acetone solution, while spectrum 2(c) is for the highly cross-linked BC–PVA composite using the GA–water solution. As mentioned earlier, the BC content in all three specimens was around 50 %. A broad band at $3200\text{--}3500\text{ cm}^{-1}$, wavenumber seen in all three spectra, is a result of the hydroxyl (O–H) stretching vibration resulting from the strong hydrogen bonds of intra-molecular and inter-molecular type [31, 32]. The absorption band observed between 2820 and 3000 cm^{-1} wavenumber is due to the stretching of aliphatic C–H bond [32]. Compared to spectrum 2(a), the absorbance intensity at $3200\text{--}3500\text{ cm}^{-1}$ band in the spectrum 2(b) is much lower. The normalized absorbance intensity ratio of bands for O–H to C–H decreased from 1.60 for spectrum 2(a) to 1.20 for spectrum 2(b). In the spectrum 2(c), the absorbance intensity ratio of bands for O–H to C–H decreased even further to 0.83. This spectral change indicates reduction in the O–H groups on the specimens as a result of cross-linking reaction with the GA [32]. Normalized absorbance of bands at $1700\text{--}1750\text{ cm}^{-1}$ in the spectra 2(a) and (b) were 0.13 and 0.20, respectively. While they are not sharp, they still demonstrate the presence of carbonyl (C=O) group in the composites from the remaining non-hydrolyzed vinyl acetate group of the PVA [31, 42]. In

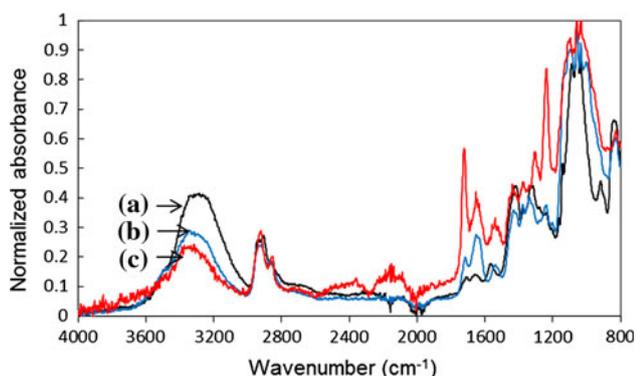


Fig. 2 Normalized ATR-FTIR spectra for BC–PVA composites (a), partially cross-linked BC–PVA composites (b) and highly cross-linked BC–PVA composites (c)

spectrum 2(c), however, a significantly sharp absorption (normalized absorbance of 0.57) observed at $1700\text{--}1750\text{ cm}^{-1}$ wavenumber indicates stronger stretching vibration of C=O in the composites. This means that in addition to the remaining non-hydrolyzed vinyl acetate groups, some residual aldehyde groups from the GA also existed in the highly cross-linked BC–PVA composites, both of them contributing to the stronger C=O absorption. This confirms the earlier observation that the GA–water solution can penetrate into the inner cavities of the BC–PVA composites network and part of the residual GA may still be trapped in the highly cross-linked BC–PVA composites even after wash. This is very likely when only one aldehyde group from GA reacts and the other end remains unreacted. The absorption at $1050\text{--}1150\text{ cm}^{-1}$ wavenumber seen in spectrum 2(a) is due to the presence of C–O stretching vibration from the acetate group [31, 32, 42]. The same absorption band for

C–O stretching vibration was much broader in spectrum 2(b) than in spectrum 2(a), resulting from the formation of the acetal linkages upon reaction of the PVA with the GA. In the spectrum 2(c), the band of C–O stretching vibration became the broadest one in three spectra due to the high cross-linking level and the formation of more acetal linkages.

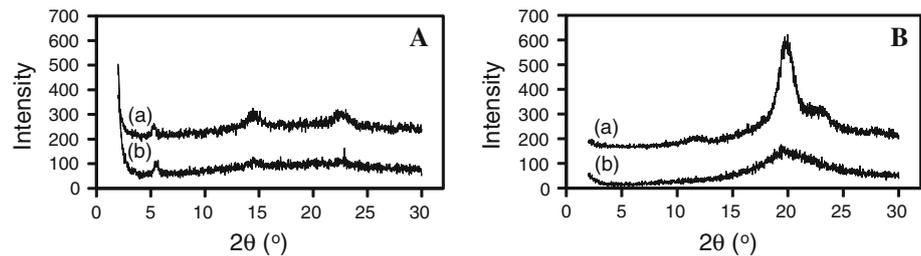
Overall, the ATR-FTIR results indicate that the BC–PVA composites were partially or highly cross-linked based on the decreased intensity of bands for O–H stretching vibration combined with the increased intensity of bands for C–O stretching vibration. Our preliminary ATR-FTIR study had shown that both BC and PVA are able to be cross-linked using either GA–acetone or GA–water solutions. The cross-linking reactions can occur between hydroxyl groups of the BC, between hydroxyl groups of the PVA, or between BC and PVA. These results also confirm that a higher cross-linking level can be achieved for BC–PVA composites with GA–water solution. This is mainly because the GA–acetone solution can hardly penetrate into the fully dried BC–PVA composites, whereas the GA–water solution has the ability to penetrate the BC–PVA preregs well and trigger a cross-linking reaction inside the BC–PVA preregs and form highly cross-linked BC–PVA composites.

Sol–gel analysis of cross-linked PVA and BC–PVA composites

Sol–gel analysis was performed for PVA as well as for the resin in BC–PVA composites that were cross-linked to different levels. Table 2 presents the sol–gel test results for partially and highly cross-linked PVA (the resins from partially and highly cross-linked BC–PVA composites) as well as control PVA. The results indicate that the gel (cross-linked) percentage of the partially cross-linked PVA was about 10 %. The values were close in both the partially

Table 2 Sol–gel test results of PVA at different levels of cross-linking

Specimens	PVA	Partially cross-linked PVA	PVA in partially cross-linked BC–PVA composites	Highly cross-linked PVA	PVA in highly cross-linked BC–PVA composites
Gel percentage in specimens	0	10.8	9.6	90.2	88.9

Fig. 3 WXR D patterns **A** BC (a) and highly cross-linked BC (b); **B** PVA (a) and highly cross-linked PVA (b)

cross-linked PVA and the resin present in the partially cross-linked BC–PVA composites. Approximately 90 % of the PVA was noncross-linked, and thus could be dissolved in deionized water during the sol–gel test. The results of this test confirm that the cross-linking reaction using the GA–acetone solution occurred mostly on the surfaces of the PVA and the BC–PVA composites. This was mainly because the GA–acetone solution could not penetrate into the PVA with a sufficient quantity to trigger the cross-linking reaction inside the PVA. The results also indicate that the gel (cross-linked) percentage of the highly cross-linked PVA could be over 90 %. The levels of cross-linking were also close in both the highly cross-linked PVA and the resin in the highly cross-linked BC–PVA composites. While both resin and composite specimens were swollen after being exposed to water, they remained intact. The results of this test further demonstrate that the cross-linking reaction with the GA–water solution occurred on the surface as well as inside of the specimens as a result of easy penetration of the GA–water solution into the PVA.

WXR D of BC, PVA and their highly cross-linked specimens

WXR D was used to evaluate the crystallinity and the crystal sizes of the BC, the PVA, and their corresponding highly cross-linked specimens. The crystallinity (%) values for individual specimens were calculated using a ratio of crystalline area to the combined crystalline and amorphous areas in the WXR D patterns [43]. The crystal sizes (d -spacing) were calculated by means of the WXR D patterns by analysis software (Scintag, Inc., Cupertino, CA) based on Scherrer Equation.

Figure 3A(a, b) illustrate WXR D patterns obtained for BC and highly cross-linked BC, respectively. Both WXR D patterns showed distinct peaks at 2θ values of 5.5° , 14.5° , and 22.5° . Figure 3A also shows that the crystallinity of the

BC decreased from 62.5 (Fig. 3A(a)) to 12.7 % (Fig. 3A(b)) after the cross-linking reaction. The reduction in the crystallinity is mainly because the cross-linking within the BC that changes the morphology and destroys the crystallites.

Figure 3B shows WXR D patterns of the control PVA (a) and highly cross-linked PVA (b). Both the WXR D patterns show a distinct peak at 2θ values of 20° . Figure 3B indicates that the crystallinity of the PVA decreased from 61.7 (Fig. 3B(a)) to 4.9 % (Fig. 3B(b)) after cross-linking and the average crystal size of the PVA at 20° decreased from 45 (Fig. 3B(a)) to 14 Å (Fig. 3B(b)). It should be noted that the transparency of highly cross-linked PVA was slightly higher than the noncross-linked PVA further confirming the reduction in crystallinity after cross-linking. The lower crystallinity is largely because of the cross-links formed in the PVA that restrict crystallization. The cross-links are also known to play the role of defect centers impeding the folding of the macromolecular chains, and thus decrease the size of the crystals [44, 45].

Tensile properties of BC, PVA, BC–PVA composites, and their corresponding cross-linked specimens

Table 3 presents the tensile test results for BC, PVA, and BC–PVA composites with varying BC contents (25, 50 and 75 %). For comparison, theoretical values calculated, using the rule of mixture, for Young's modulus and fracture stress are also presented in Table 3. The Young's modulus of the BC membrane was 3424 MPa, while the Young's modulus of the PVA was 12.8 MPa. The Young's modulus values of the BC–PVA composites were between those obtained for BC and PVA as expected. With the increase in BC content (or decrease in PVA content), the Young's modulus of the BC–PVA composites increased as well. For composites with BC content of 25 %, the Young's modulus was only around 731.6 MPa, and when the BC content

Table 3 Tensile properties for BC, PVA, and BC–PVA composites with varying BC content

Specimens	Young's modulus (MPa)	Rule of mixture (MPa)	Fracture stress (MPa)	Rule of mixture (MPa)	Fracture strain (%)
BC	3424 (8.2)		63.7 (50.4)		5.8 (44.7)
PVA	12.8 (36.3)		5.4 (3.4)		234.3 (14.4)
BC–PVA composites (25 % BC)	731.6 (1.1)	754.8	22.9 (6.5)	18.1	3.7 (1.6)
BC–PVA composites (50 % BC)	1590 (12.0)	1565	32.6 (10.9)	31.9	2.4 (26.1)
BC–PVA composites (75 % BC)	2473 (5.2)	2449	44.6 (13.3)	47.0	2.0 (18.9)

Values in the parentheses are % coefficient of variation values

increased to 50 and 75 % the Young's modulus values increased to 1590 and 2473 MPa, respectively. The fracture stress values for BC and PVA were 63.7 and 5.4 MPa, respectively. It is clear that BC–PVA composite fracture stress values are between those of BC and PVA and increase as the BC content in the composites increases. This is again as expected. While the fracture stress values for composites increased with the BC content, they did not show a direct correlation with BC content as the modulus values did. This is due to the decreased fracture strain of the composites with increase in BC content. The fracture stress values ranged from 22.9 MPa for composites with BC content of 25 % to 44.6 MPa when the BC content was 75 %. For the fracture strain, the value of the PVA was 234.3 %, which was much higher than BC's fracture strain of 5.8 %. However, most fracture strain values of the BC–PVA composites were close to or even lower than that obtained for BC. This is likely due to the two components in composites having extremely good bonding resulting in a brittle composite [46, 47].

Table 4 presents tensile test results for BC, PVA, BC–PVA composites (50 % BC), and their corresponding cross-linked specimens at different cross-linking levels. The Young's modulus values of partially cross-linked BC and highly cross-linked BC increased to 4243 and 5107 MPa, respectively, from 3424 MPa obtained for BC. The Young's modulus values of partially cross-linked and highly cross-linked PVA increased to 54.1 and 270.1 MPa, respectively, from 12.8 MPa obtained for the control (noncross-linked) PVA. The Young's modulus values of the partially cross-linked and highly cross-linked BC–PVA composites increased to 1875 and 2429 MPa, respectively, from 1590 MPa obtained for the BC–PVA composites. While the increase in Young's modulus values is due to the cross-linked structure and increased molecular weight in the case of PVA, the cross-linking of BC makes the structure rigid when cross-linked [48]. The reduction in moisture content from 9.1 % of the PVA to a lower range

Table 4 Tensile properties for BC, PVA, and BC–PVA composites at different levels of cross-linking

Specimens	Young's modulus (MPa)	Rule of mixture (MPa)	Fracture stress (MPa)	Rule of mixture (MPa)	Fracture strain (%)
BC	3424 (8.2)		63.7 (50.4)		5.8 (44.7)
Partially cross-linked BC	4243 (14.6)		61.6 (17.5)		1.9 (27.9)
Highly cross-linked BC	5107 (11.2)		43.8 (37.6)		1.0 (41.1)
PVA	12.8 (36.3)		5.4 (3.4)		234.3 (14.4)
Partially cross-linked PVA	54.1 (15.8)		7.9 (9.2)		59.6 (11.1)
Highly cross-linked PVA	270.1 (19.6)		19.2 (5.1)		19.9 (22.9)
BC–PVA composites (50% BC)	1590 (12.0)	1565	32.6 (10.9)	31.9	2.4 (26.1)
Partially cross-linked BC–PVA composites (50% BC)	1875 (15.2)	1938	31.9 (30.4)	32.3	2.0 (34.2)
Highly cross-linked BC–PVA composites (50% BC)	2429 (4.7)	2471	31.6 (14.3)	30.4	1.5 (39.3)

Values in the parentheses are % coefficient of variation values

of 3.8–6.0 % for the cross-linked specimens may also partially contribute to the increased Young's modulus. As is expected, higher cross-linking level leads to higher modulus. From data presented in Table 4, it is clear that with increased cross-linking, all three specimens, PVA, BC, and the composites, become brittle with lower fracture strain values. This affects their fracture stress values which

do not show a correlation seen for Young's modulus. For example, cross-linking reduces the fracture stress of BC, whereas cross-linking increases the fracture stress of PVA and for the BC–PVA composites, there is almost no effect.

Tables 3 and 4 also present theoretical values for Young's modulus and fracture stress values calculated using the rule of mixtures [49]. The densities of cellulose and PVA used were 1.52 and 1.27 g/cc, respectively [50], and the BC content in the BC–PVA composites varied from 25 to 75 % by weight. It is clear that the theoretical values and the experimentally obtained values for both Young's modulus and fracture stress are very close to each other.

Figure 4 shows typical stress versus strain plots of BC–PVA composites (a) and partially (b), and highly cross-linked (c) BC–PVA composites. The BC content in all the three specimens is around 50 % by weight. Figure 4a for BC–PVA composite shows an initial elastic behavior followed by a plastic yielding. The yielding may be due to PVA's high ductility and breaking of some BC nanofibers that are in the stress direction and possible alignment of the remaining nanofibers. Once that process was over, BC–PVA composites showed elastic behavior until the fracture point. Figure 4b, c indicate no obvious yielding for partially or highly cross-linked BC–PVA composites. Once the PVA becomes cross-linked it loses its ductility. As can be expected, Fig. 4 also indicates that higher cross-linking level leads to higher modulus and lower fracture strain values.

It is interesting to note that both Young's modulus and fracture stress values for the BC–PVA composites and the cross-linked BC–PVA composites are close or higher than many traditional plastic materials, including polyethylene (Young's modulus: 800 MPa; fracture stress: 15 MPa), polypropylene (Young's modulus: 1900 MPa; fracture stress: 40 MPa), and nylon 6 (Young's modulus: 1800 MPa; fracture stress: 70 MPa) [51]. As a result, the BC–PVA composites, both cross-linked and noncross-linked, have the

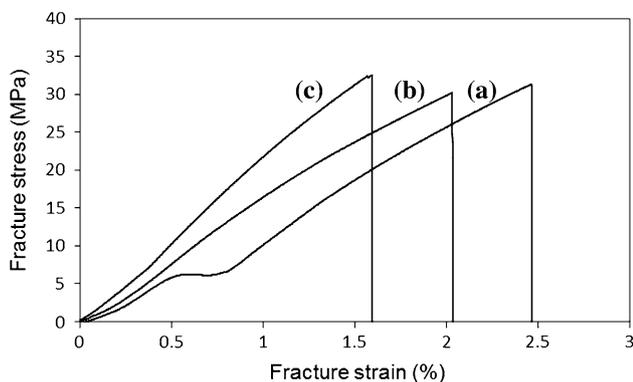


Fig. 4 Stress versus Strain plots for BC–PVA composites (a), partially cross-linked BC–PVA composites (b), and highly cross-linked BC–PVA composites (c)

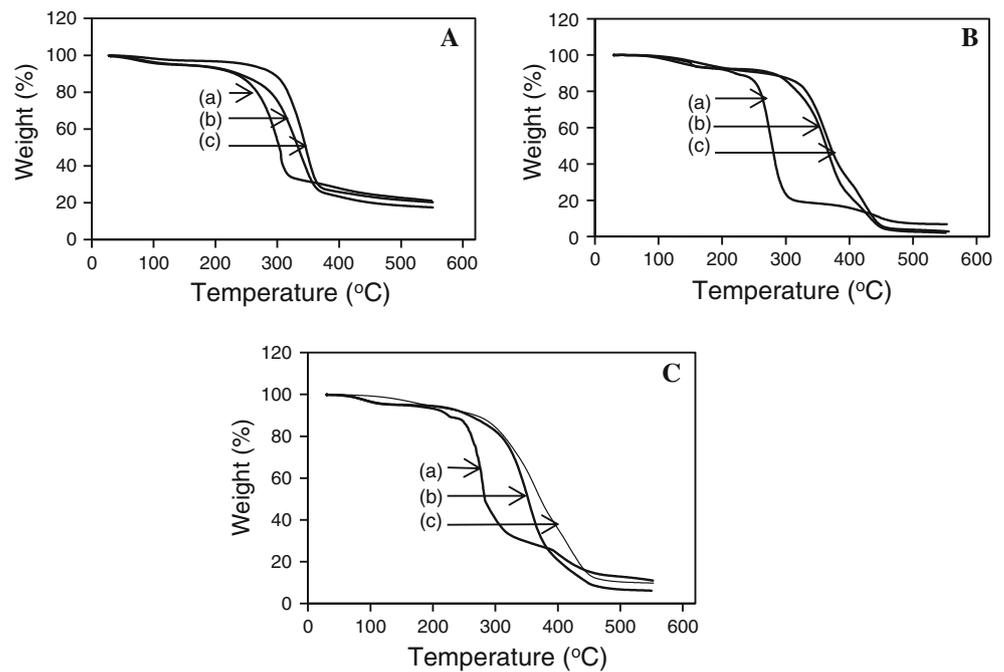
potential to replace these traditional non-biodegradable plastic materials in many applications, including racket frame, ski pole, circuit board, automobile inside, etc. These degradable composites may be easily protected from water by applying varnish or other water-resistant coatings to increase their durability.

TGA of BC, PVA, BC–PVA composites, and their corresponding cross-linked specimens

Figure 5A presents typical TGA thermograms of BC, partially cross-linked BC, and highly cross-linked BC specimens. Figure 5A(a), the TGA thermogram for BC, shows the onset decomposition temperature (T_d) at 260 °C. Weight losses for BC were 30 % at 284 °C, 50 % at 303 °C, and 80 % at 600 °C. It has been reported that two competing reaction pathways, low-temperature pathway and high-temperature pathway (>300 °C), occur simultaneously during the thermal degradation of cellulose [52]. The low-temperature pathway is mainly responsible for the water loss. The primary reaction in the high-temperature pathway is depolymerization, as the cellulose structure can absorb enough energy to activate the cleavage of the glycosidic linkages to produce glucose, which is dehydrated to levoglucosan and oligosaccharides. The production of volatile compounds is complete when the temperature reaches around 450 °C. The continuing weight loss is due to degradation when all other elements are driven off and the char (carbon) remains [52]. The thermogram for the BC indicates that the weight loss of cellulose is the result of a combination of both low-temperature and high-temperature pathways. Thermogram 5A(b), for partially cross-linked BC, showed a T_d at 285 °C. Weight losses for the partially cross-linked BC were 30 % at 309 °C, 50 % at 334 °C, and about 83 % at 600 °C. Thermogram 5A(c) for highly cross-linked BC showed a T_d at 315 °C with weight losses of 30 % at 329 °C, 50 % at 346 °C, and about 80 % at 600 °C. These results indicate that the cross-linking makes the BC thermally more stable.

Figure 5B presents typical TGA thermograms for PVA and partially and highly cross-linked PVA. Thermogram 5B(a) for the PVA shows two decomposition onset temperatures, T_{d1} and T_{d2} , at 255 and 400 °C, respectively. Weight loss for the PVA was 30 % at 267 °C, 50 % at 279 °C, and up to 93 % at 600 °C. Two-step degradation of PVA has been reported earlier [50]. A likely explanation for this is that PVA first degrades into small molecular weight polymer at approximately 250 °C, and then further degrades into carbon char at temperatures above 350 °C. These results confirm the earlier findings of Peng and Kong [53]. Thermogram 5B(b) for partially cross-linked PVA shows a single T_d at 325 °C. Weight losses observed were 30 % at 340 °C, 50 % at 364 °C, and about 97 % at

Fig. 5 TGA thermograms **A** BC (a), partially cross-linked BC (b), and highly cross-linked BC (c); **B** PVA (a), partially cross-linked PVA (b), and highly cross-linked PVA (c); **C** BC–PVA composite (a), partially cross-linked BC–PVA composite (b), and highly cross-linked BC–PVA composite (c)



600 °C. Thermogram 5B(c), for highly cross-linked PVA, shows T_d at 330 °C. Weight losses observed for highly cross-linked PVA were 30 % at 348 °C, 50 % at 370 °C, and about 97 % at 600 °C. The two-step degradation pattern was not so obvious in the thermograms for partially and highly cross-linked PVA.

Figure 5C presents typical TGA thermograms for BC–PVA composites and partially cross-linked and highly cross-linked BC–PVA composites. As mentioned earlier, BC content in all the BC–PVA composites was around 50 %. Thermogram 5C(a) for BC–PVA composites shows two decomposition temperatures, T_{d1} and T_{d2} at 257 and 380 °C, respectively. Weight losses observed were 30 % at 273 °C, 50 % at 283 °C, and about 90 % at 600 °C. When thermograms for BC and BC–PVA composites are compared, it is clear that BC reinforcement is able to increase the thermal stability of the PVA. Two distinct and well-separated degradation onsets can be seen in thermogram 5C(a) for BC–PVA composites. As a result, this degradation can also be regarded as a two-step-degradation and could be a result of the PVA. Thermogram for partially cross-linked BC–PVA composites presented in 5C(b) shows much better thermal stability than the BC–PVA composites. The T_d for the partially cross-linked BC–PVA composites was at 307 °C and the weight losses were 30 % at 331 °C, 50 % at 352 °C, and about 94 % at 600 °C. Thermogram 5C(c) obtained for highly cross-linked BC–PVA composites showed the highest thermal stability among the three BC–PVA composites, as expected. The T_d for the highly cross-linked BC–PVA composites was 313 °C and weight losses were 30 % at 337 °C, 50 % at 372 °C, and about 90 % at 600 °C. The two-step

degradation pattern was not obvious in the thermograms for partially and highly cross-linked BC–PVA composites.

These results clearly indicate that cross-linking can increase the thermal stability of BC, PVA, and BC–PVA composites. Other researchers have obtained similar results for soy flour, collagen, and chitosan after cross-linking [54–56]. These results also confirm that the BC–PVA composites and their cross-linked specimens, particularly the highly cross-linked ones, can exhibit excellent thermal stability in addition to their high tensile properties. The final char weights of the cross-linked specimens in TGA tests were slightly less than those of the specimens without cross-linking treatments. The lower char weight of the cross-linked specimens is probably due to volatilization of the residual GA trapped in the cross-linked specimens during the TGA test.

Conclusions

The biodegradable membrane-like BC–PVA composites with differing BC contents were produced by simple immersion methods. The SEM images indicated that the PVA not only penetrated into the BC network, but also filled in the pores present within the BC nanofiber membrane. The ATR-FTIR results showed that acetal linkages were formed in the BC–PVA composites after a cross-linking reaction. The sol–gel results showed cross-linked PVA to be water-insoluble, and a good correlation between cross-linking level and insolubility was observed. The WXR D results indicated a reduction in crystallinity as a result of cross-linking for BC and PVA as well as a

reduction in the crystal size of the PVA. The tensile test results showed good mechanical properties for BC–PVA composites indicating the ability of the BC to reinforce the PVA. The TGA showed higher thermal stability for the BC–PVA composites than the PVA. This was because the BC itself is thermally more stable. Cross-linking of PVA was shown to increase the Young's modulus and thermal stability of the BC–PVA composites. At the same time, the fracture strain decreased significantly with cross-linking. The methods developed in this study make it possible to control the PVA content in the composites as well as the cross-linking level of PVA.

Acknowledgements This work was partly supported by the National Textile Center (NTC) and the Wallace Foundation. The authors would like to thank Profs. Dan Luo, John March, and Antje Baeumner of the Cornell University for allowing the use of their laboratory facilities. The authors also thank the Cornell Center for Materials Research (CCMR) for the use of their facilities.

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