
11 “Green” Composites Based on Bacterial Cellulose Produced Using Novel Low-Cost Carbon Source and Soy Protein Resin

*Kaiyan Qiu and Anil N. Netravali**

CONTENTS

11.1	Introduction	194
11.2	Materials and Methods	196
11.2.1	Microorganism and Culture Media	196
11.2.2	SF Powder Treatment.....	196
11.2.3	Sugar Consumption of SFE Medium during Culture.....	196
11.2.4	BC Production	197
11.2.5	Preparation of SF and MSF Resin Sheets.....	197
11.2.6	Fabrication of BC-Based “Green” Composites with SF and MSF Resins.....	197
11.2.7	Characterization.....	198
11.3	Results and Discussion	198
11.3.1	Influence of Autoclaving on the SFE Medium.....	198
11.3.2	Sugar Consumption in SFE Medium during the Culture	199
11.3.3	BC Yield in SFE Medium.....	200
11.3.4	Microstructure of BC–Soy Resin Composite and Its Fabrication Mechanism.....	202
11.3.5	Tensile Properties of Resins and Green Composites	203
11.3.6	Thermal Stability of BC–SF and BC–MSF Resin Composites.....	205

* Prof. Anil N. Netravali was the lead author for this chapter and can be contacted at ann2@cornell.edu.

11.4 Conclusions.....	206
Acknowledgments.....	206
References.....	206

A novel low-cost carbon source, soy flour extract (SFE), was developed from defatted soy flour (SF) to produce bacterial cellulose (BC). The enriched protein remaining after extracting sugars was used as a resin to form BC-based thin membrane-like “green” composites. The results of this study showed that SFE consists of five sugars: fructose, glucose, sucrose, raffinose, and stachyose. The study indicated that *Acetobacter xylinum*, the bacterium used in this study, metabolized sugars in the following decreasing order: fructose and glucose, sucrose, raffinose, and stachyose during the culture process. However, the consumption rates of raffinose and stachyose were extremely low. Results also indicated that autoclaving process resulted in hydrolyzing sucrose to fructose and glucose. Based on the same concentration of sugars, BC yield achieved using SFE medium (based only on the concentration of fructose, glucose, and sucrose) was close to or even higher than the yields obtained using expensive conventional carbon sources such as fructose, mannitol, and glucose. Modified soy flour (MSF), the residual protein after removing sugars from SF, was successfully used as a resin to fabricate “green” BC–MSF membrane-like thin composites. These composites had excellent tensile and thermal properties that were better than the BC–SF resin composites. This is primarily due to the higher protein content in MSF compared to SF. The sugars in SF also plasticized the protein, thus reducing its modulus and increasing the fracture strain.

11.1 INTRODUCTION

Bacterial cellulose (BC) produced by *Acetobacter xylinum* is a promising, sustainable, and biodegradable nanofibrous material that has the same chemical structure as the plant-based cellulose. However, BC fibers have diameters in the range of a few nanometers and display many unique characteristics including high purity, high degree of polymerization, high crystallinity, high tensile strength, high modulus, and strong biological adaptability [1–5]. 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, and so forth [5–10]. Many pure sugars, such as glucose, sucrose, fructose, and so forth, and sugar alcohols, such as mannitol, xylitol, sorbitol, and so forth, have been used as carbon sources for BC culture [11–15]. Among them, glucose, fructose, and mannitol are the most common and have shown excellent results in terms of BC production [11–17]. However, the cost of these sugars or sugar alcohols is high, and hence, they are not considered to be ideal for large-scale, inexpensive BC production. As a result, many researchers have attempted to obtain higher BC yields as well as to reduce the cost of the carbon sources. Some of these efforts have been

successful. For example, konjac powder hydrolyzate [11], sugarcane molasses [18], beet molasses [19], and processed rice bark [20] have been found to be useful in BC production. While some of these sources may be used for industrial BC production in the near future, there is significant scope to further reduce the cost of BC production by using inexpensive waste products and expand its use in many mass volume applications. This chapter describes a novel and inexpensive source derived from soybeans for BC production.

Defatted soy flour (SF) is obtained as a by-product after extracting oil from soybeans. It is commercially available and consists mainly of protein (52%–54%), sugars (30%–32%), dietary fiber (2%–3%), minerals and ash (3%–6%), and moisture (6%–8%). SF is also very inexpensive, about \$0.25/lb. The soybean is a legume species native to East Asia and is classified as an oilseed. It is an annual and economic crop and has been abundantly produced and used in many countries for over 5000 years [21]. Currently, it is an important global crop and provides a major amount of edible oil and protein [22]. Soybeans contain decent amounts of sugars, including fructose, glucose, sucrose, raffinose, and stachyose [23]. Fructose, glucose, and sucrose have been used routinely as carbon sources for BC production [24]. It has also been reported that raffinose and stachyose can be metabolized by lactic acid bacteria [25]. To obtain higher protein content from SF, the sugars are removed in the form of soy flour extract (SFE), a by-product. The present research discusses the use of SFE, a mixture of five sugars mentioned earlier, as an inexpensive carbon source to produce BC.

Because of the excellent mechanical properties of BC, some research on fabrication of BC-based composites with petroleum-based resins has already been reported [26,27]. High-strength composites using BC sheets impregnated with phenolic resin or acrylic resin have been developed [24,25]. Although useful, these resins are not biodegradable, and as a result, composites are not biodegradable or environment friendly. It should, however, be possible to fabricate completely degradable BC-based "green" composites using sustainable and biodegradable resins.

As mentioned earlier, SF contains sugars and protein. It is possible to dissolve and extract water-soluble sugars from SF, termed soy flour extract (SFE). After removing SFE, the residual protein product, called modified soy flour (MSF), has a higher protein content of 65%–70%. MSF-based resin has been shown to have better tensile properties than SF resin [28]. MSF resin also has a higher interfacial bonding with ramie fiber compared to SF resin [28]. As a result, composites using MSF resin could be expected to have much better mechanical properties than those using SF resin.

In the present research, the sugar-containing SFE has been successfully developed for BC production as a high-yield and low-cost carbon source [29]. The consumption of different sugars by *A. xylinum* and the compositional changes of sugars in the SFE medium during autoclaving were analyzed as well. The residual insoluble protein, after SFE extraction, called MSF, was successfully used as resin to fabricate BC-based "green" composite. Thus, both fibers and resins were produced from defatted SF as the sole feedstock. The tensile and thermal properties of the composites were characterized and were found to be comparable to or even better than those of traditional plastic materials.

11.2 MATERIALS AND METHODS

11.2.1 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 SFE medium used for BC production consisted of 5 g/L yeast extract, 5 g/L tryptone, and the autoclaved SFE as the sole carbon source [29]. Other culture media used for comparison of BC yields consisted of 25 g/L carbon sources raffinose, glucose, sucrose, fructose, and mannitol, individually, and 5 g/L yeast extract and 5 g/L tryptone, which have a similar function for BC production as Hestrin–Schramm (HS) medium [17].

11.2.2 SF POWDER TREATMENT

The SF (product no. 7B) powder obtained from ADM Co. (Decatur, IL) was mixed with deionized water to obtain SFE. SF powder was initially soaked in deionized water in a ratio of 3:17, and the pH of the mixture was adjusted to 4.5, its isoelectric point, by adding hydrochloric acid. The mixture was kept at 50°C in a water bath for 1 h. After that, the mixture was filtered to remove the solid content (MSF), mostly the insolubilized protein. Part of the filtrate, containing the soluble sugars (SFE), was then allowed to evaporate to obtain the desired sugar concentration for BC culture [29].

11.2.3 SUGAR CONSUMPTION OF SFE MEDIUM DURING CULTURE

The concentrations of sugars in the SFE, including fructose, glucose, sucrose, raffinose, and stachyose, were determined before and after autoclaving using high-performance liquid chromatography (HPLC) (UltiMate 3000 LC system, Dionex, Sunnyvale, CA) equipped with a refractive index (RI) detector (RI-101, Ecom, Purage, Czech Republic). Autoclaving of the SFE was carried out at 121°C and about 0.1 MPa pressure in a sterilizer (Market Forge, Alfa Medical, Westbury, NY) for 25 min. After autoclaving, the SFE was filtered to remove the remaining solid protein deposits and used for BC culture. Sugar concentrations in the SFE during 10 days of culture were determined on a daily basis using HPLC to obtain a quantitative measure of the sugar consumption by the bacteria. After filtering the SFE culture medium samples through a Teflon filter (0.45 µm pore size) and removing tiny BC fibrils and other impurities, concentration for each sugar was analyzed using a SUPELCOSIL LC-NH₂ column (25 cm × 4.6 mm inner diameter (ID) and 5 µm particles, Supelco, Bellefonte, PA) and the RI detector. The HPLC column was used at 30°C. The mobile phase was a mixture of acetonitrile and deionized water (3:1, v/v) and was kept at a flow rate of 1 mL/min. It is important to note that while all sugar concentrations were determined individually, it was not possible to measure the fructose and glucose concentrations separately, and hence, they were measured together and reported as “fructose plus glucose” [29].

11.2.4 BC PRODUCTION

The *Acetobacter* strain was inoculated into a conical flask containing the prepared SFE 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 6 mL of this was inoculated into a 100 mL culture medium in a 600 mL conical flask for production of BC. The cultivation was carried out initially at a pH of 5.0 and 30°C in a static incubator for 10 days. Samples of the culture medium and BC were extracted every day during the 10-day culture period to measure consumption of individual sugars and BC yields. The BC pellicles taken out from the medium were washed successively with water and 1% (w/v), aqueous NaOH at 90°C for 15 min each and then washed with deionized water to remove all microbial product contaminants. The purified cellulose pellicles were finally dried at 105°C on a Teflon plate until constant weight was reached [29].

In another set of experiments, BC pellicles produced using other culture media containing individual sugars (mentioned in Section Microorganism and Culture Media) were harvested every day. The BC pellicles were then washed and dried using the same procedure mentioned earlier. BC pellicles cultured in SFE medium and other culture media (mentioned in Section Microorganism and Culture Media) were compared for their yields. Dried BC specimens were conditioned at American Society for Testing and Materials (ASTM) conditions of 21°C and 65% relative humidity (RH) for 3 days before tensile testing [29].

11.2.5 PREPARATION OF SF AND MSF RESIN SHEETS

The SF powder and MSF obtained during SFE production were individually mixed with deionized water at a weight ratio of 1:15. Glycerol was added (15% by weight) as a plasticizer; the pH value of both solutions were adjusted to 10 by addition of sodium hydroxide [22]. The solutions were maintained at 75°C while stirring continuously for 30 min to obtain precured SF resin and MSF resin. This "precurving" process helps denature the globular protein by opening up the molecules. Precured SF resin and MSF resin were individually cast on a Teflon-coated glass plate and dried in a 35°C air-circulated drying oven for 16 h. A dried SF resin sheet and MSF resin sheet were cured using a Carver hydraulic hot press (model 3981-4PROA00, Wabash, IN) at 120°C for 25 min under a pressure of 7 MPa. The thickness of all resin sheets was in the range of 0.2 mm. The cured SF and MSF resin sheets were conditioned at ASTM conditions for 3 days prior to characterizing their tensile properties.

11.2.6 FABRICATION OF BC-BASED "GREEN" COMPOSITES WITH SF AND MSF RESINS

BC-based membrane-like "green" composites with SF and MSF resins were produced by using BC pellicles impregnated individually with precured SF and MSF resins. Resin impregnation into the BC pellicle was achieved using ultrasonication for 30 min. The wet BC-SF and BC-MSF resin composites were dried in an air-circulating oven at 35°C for 8 h to obtain prepreps. The BC content in the BC-SF

resin composite and BC–MSF resin composite was kept around 50% in order to achieve tensile properties that are comparable to traditional nonbiodegradable plastics. While the BC content in both composites could be easily adjusted by varying the resin concentration, it was difficult to obtain uniform distribution of resin with higher BC concentration. The prepregs were then cured by hot-pressing at 120°C under a pressure of 7 MPa. The thickness of all composites was in the range of 0.2 mm. The cured composites were conditioned at ASTM conditions for 3 days prior to characterizing their tensile properties.

11.2.7 CHARACTERIZATION

Freeze-dried specimens of BC and BC–MSF resin composites were sputter-coated with gold, and their surface topographies were observed with a scanning electron microscope (SEM; LEO 1550 FESEM) at an accelerating voltage of 15 kV.

Tensile testing was performed using an Instron tensile testing machine (Instron, model 5566). The test specimens were prepared by cutting the BC membranes and green composites into 10-mm-wide and 60-mm-long strips using a precise cutter. The Young's moduli of the specimens were determined from the tensile test results conducted according to ASTM D882-02. Two ends of the specimens were fixed between the upper and lower jaws of the Instron, leaving a gauge length of 30 mm. Crosshead speed during the tensile tests was maintained at 0.6 mm/min to obtain a strain rate of 0.02/min.

Thermogravimetric analysis (TGA; TA Instruments, model no. 2050) was carried out to analyze the thermal properties of both BC–SF and BC–MSF resin composites. TGA runs were performed using aluminum pans between 25°C and 600°C under a nitrogen environment. The scan rate was 20°C/min, and the nitrogen purge flow rate was maintained at 10 mL/min.

11.3 RESULTS AND DISCUSSION

11.3.1 INFLUENCE OF AUTOCLAVING ON THE SFE MEDIUM

The HPLC analysis of the as-obtained SFE used in this study showed that it consisted of 1.92 g/L fructose and glucose (combined), 21.21 g/L sucrose, 1.59 g/L raffinose, 11.92 g/L stachyose, water, and other components, including proteins. The concentration of total sugars was over 36 g/L. After autoclaving (sterilizing) at 121°C and pressure of 0.1 MPa for 25 min, however, the HPLC analysis showed a different composition of sugars in the SFE medium. Therefore, the influence of autoclaving on the SFE medium was further explored.

It has been reported that sucrose is prone to partial hydrolysis during autoclaving, and hence, a sucrose-containing sterilization medium will result in a mixture of D-glucose, D-fructose, and sucrose [30]. In another study it was shown that 15%–25% of the sucrose may hydrolyze to glucose and fructose during autoclaving at the elevated temperature [31,32].

Table 11.1 presents the HPLC data of various sugar concentrations in SFE before and after autoclaving. Table 11.1 also gives adjusted values for all sugars after taking

TABLE 11.1
Effect of Autoclaving on the Concentrations of Various Sugars in the SFE Medium

	Concentrations of Sugars in SFE Medium				
	Fructose + Glucose (g/L)	Sucrose (g/L)	Raffinose (g/L)	Stachyose (g/L)	Total Sugars (g/L)
SFE before autoclaving	1.92	21.21	1.59	11.92	36.64
SFE after autoclaving	7.54	17.54	1.58	9.92	36.58
SFE after autoclaving (Adjusted data by considering water evaporation)	7.16	16.66	1.50	9.42	34.74

into consideration the water evaporation during autoclaving. Before autoclaving, the freshly made SFE medium had concentrations of 1.92 g/L for fructose plus glucose, 21.21 g/L for sucrose, 1.59 g/L for raffinose, and 11.92 g/L for stachyose. After autoclaving, the concentrations changed to 7.54 g/L for fructose plus glucose, 17.54 g/L for sucrose, 1.58 g/L for raffinose, and 9.92 g/L for stachyose. The concentration of total sugars was 36.58 g/L, and the concentration of three traditional carbon sources (fructose, glucose, and sucrose) for BC production was approximately 23–25 g/L, which was almost the same as the regular concentration of the carbon source used for BC production by others [11].

The data in Table 11.1 clearly indicate that there was a significant (about 20%) decrease in sucrose concentration and a corresponding increase in the concentration of fructose plus glucose after autoclaving. As a result, there was no significant change in the combined concentration of fructose, glucose, and sucrose, which remained in the range of 23–25 g/L, before and after autoclaving. As discussed earlier, this was mainly due to the degradation of sucrose [30–32]. During the autoclaving process, our data also indicated a small decrease in the concentrations of both stachyose and raffinose (Table 11.1). While the reasons for this are not well understood, this may be either due to hydrolysis of raffinose and stachyose similar to that of sucrose or due to side reactions such as caramelization or the Maillard reaction [33]. The splitting of sucrose into glucose and fructose is, in fact, better as it will be seen later that the *A. xylinum* bacteria metabolize glucose and fructose much more easily than sucrose.

11.3.2 SUGAR CONSUMPTION IN SFE MEDIUM DURING THE CULTURE

Our preliminary study had indicated that all five sugars in SFE, fructose, glucose, sucrose, raffinose, and stachyose, could be used as carbon sources separately for BC culture by *A. xylinum*, and different sugars had different effectiveness for BC yields. A detailed discussion of this is presented later in this chapter. To measure the actual consumption of individual sugars in the SFE culture medium, specimens were analyzed for sugar content every day.

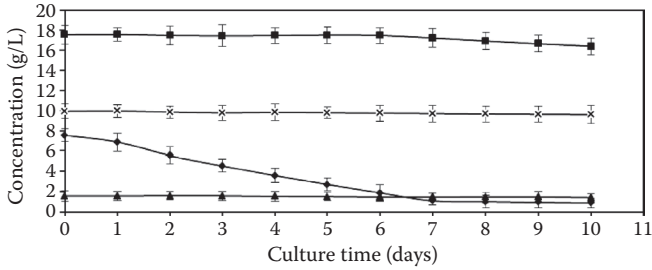


FIGURE 11.1 Consumption of sugars in SFE medium during BC culture by *Acetobacter xylinum* as a function of time in days. Symbols: ◆, fructose plus glucose; ■, sucrose; ▲, raffinose; ×, stachyose.

Figure 11.1 shows plots of changes in the concentrations of all five sugars as a function of culture time in days. As can be seen from the plots, concentration of fructose plus glucose decreased steadily and almost linearly until day 7. During that period, concentrations of the other three sugars remained more or less stable. After the sixth day, the sucrose concentration started to decrease. This suggests that when the concentration of fructose plus glucose decreased to an extremely low value (around 1.09 g/L) from the initial 7.54 g/L, the *A. xylinum* started to consume sucrose. These results indicate that the *A. xylinum* preferred to consume fructose and glucose before the other three sugars present in the SFE medium. During the entire 10-day culture time, very little or no raffinose and stachyose were consumed, and as a result, no significant change was noticed in their concentrations.

11.3.3 BC YIELD IN SFE MEDIUM

It has been reported that BC yield in a fructose or glucose medium was higher than in a sucrose medium [24]. Based on our preliminary experiments, fructose and glucose were better carbon sources for BC production compared to a combination of sucrose, raffinose, and stachyose, if the pH value of the medium was kept constant. As mentioned earlier, after autoclaving, the concentration of fructose plus glucose in the SFE medium reached 7.54 g/L from the initial concentration of 1.92 g/L. This higher concentration of fructose plus glucose was obviously beneficial for the BC culture. It is important to note that the total concentration of the three sugars (fructose, glucose, and sucrose) in the SFE medium that *A. xylinum* mainly consumed during the 10-day culture was around 25 g/L, which was almost the same as the concentration of conventional carbon sources used by other researchers for BC production [11].

Figure 11.2 shows BC yields in SFE (blue), fructose (brown), mannitol (green), glucose (purple), and sucrose (light blue) media as a function of culture time in days. As seen in the blue curve in Figure 11.2, BC yield in SFE medium increased rapidly during the initial 3–4 days. However, after 7 days of culture, the yield growth significantly decreased. The main reason for this was that the preferred carbon sources, fructose and glucose, were used up almost fully at this time. BC yield, however, continued to increase during the period from days 7 to 10 but with a relatively lower

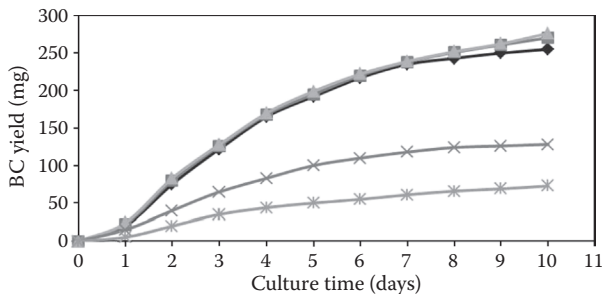


FIGURE 11.2 BC yields in SFE (◆), fructose (■), mannitol (▲), glucose (×), and sucrose (*) media as a function of culture time.

rate partially because *A. xylinum* started to consume sucrose and other sugars, which were not as suitable or metabolizable as fructose and glucose for BC production. The results in Figure 11.2 also indicate that BC yield in an SFE medium can reach 255 mg after 10 days of culture, which is close to or even better than BC yields obtained with other conventional carbon sources under similar culture conditions [11,34]. According to the comparison presented in Figure 11.2, BC yields in mannitol and fructose media have almost the same yield curves as in an SFE medium during the initial 7 days of culture. However, the BC yield rates in mannitol and fructose media were slightly higher than in an SFE medium during the period from days 7 to 10. This further confirms that preferred carbon sources, fructose and glucose, were at low concentrations during this time. BC yields in pure glucose and sucrose media show consistently lower BC yield values during the entire culture period.

Figure 11.3 compares BC yields obtained using different carbon sources individually after 10 days of culture. The BC yield of 255 mg in the SFE medium was almost as high as those using fructose (270.3 mg) and mannitol (276.3 mg) media, which have been regarded as two excellent carbon sources for BC production. Based on these data, it may be concluded that SFE could be used as an excellent carbon source for BC production and one of the least expensive ones. BC yield in the SFE medium was also significantly higher than those obtained individually in raffinose (29.7 mg), sucrose (72.8 mg), and glucose (128.2 mg) media. Glucose has also been reported as an excellent carbon source for BC production [34]. However, in our trial carried out

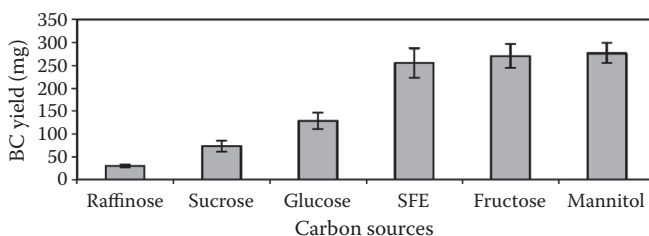


FIGURE 11.3 BC yields obtained for different carbon sources.

with a pure glucose medium, under the same conditions, the yield was lower because the pH value of the medium was not regulated and gluconic acid generated by glucose during the culture caused the pH value to change to less than 3.5, which was not suitable for BC production. However, glucose in an SFE medium still could be used as a good carbon source because the pH value in SFE medium did not change significantly during the culture. The reason might be that the relatively small amount of gluconic acid formed during culture was not able to change the pH of the medium. Also, other sugars present in SFE created a buffer effect in the SFE medium. Since sucrose partially hydrolyzed into glucose and fructose during autoclaving, as seen in our results as well as by others [30–32], the BC yield obtained in a sucrose medium was from the combined presence of sucrose, fructose, and glucose.

The BC yield in the SFE medium (255 mg) was also higher than previously reported BC yields obtained using konjac powder hydrolyzate (212 mg, *A. xylinum* ATCC 23770, 8 days) and processed rice bark (242 mg, *A. xylinum* ATCC 23769, 10 days) [11,20].

In addition, the cost of the carbon source, one of the major expenses for BC cultures, is indeed reduced largely because the SFE is a by-product obtained from the soy protein production process. The cost of SFE is almost nothing. Therefore, based on rough calculation, the cost for BC production can be reduced by more than 30%.

11.3.4 MICROSTRUCTURE OF BC–SOY RESIN COMPOSITE AND ITS FABRICATION MECHANISM

The photographs of BC–SF resin and BC–MSF resin composites are shown in Figure 11.4a(i) and (ii), respectively. Both of these thin membrane-like composites

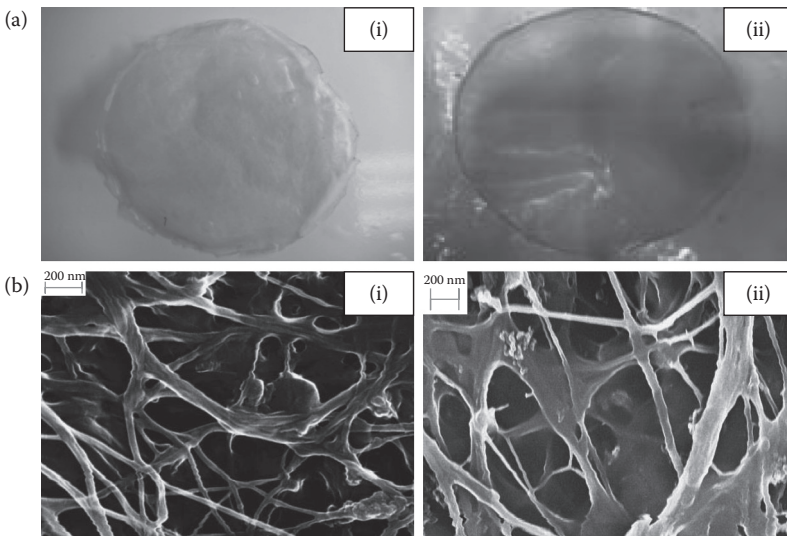


FIGURE 11.4 (a) Images of (i) BC–SF resin composite and (ii) BC–MSF resin composite. (b) SEM micrographs of (i) freeze-dried BC and (ii) freeze-dried BC–MSF resin composite.

had fairly smooth surfaces. This indicates that both SF resin and MSF resin are fully embedded into BC to fabricate corresponding composites.

Figure 11.4b shows SEM images of a freeze-dried BC pellicle and a BC–MSF resin composite. Both specimens were not hot-pressed prior to SEM observations. In Figure 11.4b(i), the BC network and porous structure can be observed clearly at the surface of the membrane. Since these specimens were freeze-dried, the porous structure has been maintained. The mean diameter of BC nanofibers is less than 100 nm, and the pore diameters range from several tens to several hundred nanometers. Figure 11.4b(ii) shows the structure of a BC–MSF resin composite. MSF resin penetrated into the BC network structure and filled in most of the pores of BC. Again, since the specimen was freeze-dried, the porous structure was partially maintained. The spread of the MSF resin in between the BC nanofibers and their embedment in the resin can be clearly seen. If this resin containing membrane is hot-pressed, the gaps are fully filled as a result of the resin flow and consolidation, forming a thin membrane-like composite. The SEM micrographs of freeze-dried BC and BC–MSF resin composite specimens shown in Figure 11.4b(i) and (ii), respectively, look identical.

MSF resin infiltration into the BC pellicle is facilitated by the ultrasonication process. When the wet pellicle is immersed into the resin solution, there exists a big concentration difference between water inside of the BC network structure and MSF resin outside of BC. The mass transfer was driven by the concentration gradient, resulting in MSF resin penetrating into the BC network structure. Since BC is hydrophilic and the resin is water based, the diffusion is easy, though assisted by the ultrasonication. The equilibrium could be achieved until there is no concentration gradient between the resin inside of BC and outside of BC. Once the MSF resin infiltrates the BC pellicle, the wet BC–MSF resin composite is achieved. It is then dried and hot-pressed to form a strong composite. This composite fabrication procedure was also used for SF resin as well.

11.3.5 TENSILE PROPERTIES OF RESINS AND GREEN COMPOSITES

Table 11.2 presents the tensile test results for BC, SF resin, and MSF resin, as well as BC–SF resin composites and BC–MSF resin composites. The soy resin content in both composites was around 50% by weight.

The Young's modulus value for BC with randomly organized and entangled nanofibers (Figure 11.4b(i)) was 2493 MPa, while the value for the MSF resin was 104.3 MPa. The Young's modulus value for the BC–MSF resin composite was 1231 MPa, which was between the modulus values of MSF resin and BC.

The tensile strength at a break of BC was 78.9 MPa, and for MSF resin, it was 8.1 MPa. The tensile strength value for BC–MSF resin composite was around 47.7 MPa, which was between those of BC and MSF resin.

Both the modulus and tensile strength values of the BC–MSF resin composite are close or even higher than those of many traditional plastic materials, including polyethylene (modulus 800 MPa, tensile strength 15 MPa); polypropylene (modulus 1900 MPa, tensile strength 40 MPa); and nylon 6 (modulus 1800 MPa, tensile strength 70 MPa) [35]. The BC–MSF resin composites may be easily protected from water by

TABLE 11.2
Tensile Properties of BC, SF Resin, MSF Resin, and BC–Soy Resin Composites

	Young's Modulus (MPa)	Theoretical Young's Modulus (MPa)	Tensile Strength (MPa)	Theoretical Tensile Strength (MPa)	Tensile Strain (%)
BC	2493 (9.6)*		78.9 (13.7)		5.7 (17.5)
SF resin	62.3 (31.9)		7.5 (4.0)		110.7 (28.4)
MSF resin	104.3 (22.0)		8.1 (11.1)		23.4 (25.2)
BC–SF resin composite (50 wt% BC)	1178 (2.4)	1183	43.3 (5.3)	40.4	3.4 (2.9)
BC–MSF resin composite (50 wt% BC)	1231 (2.6)	1206	47.7 (9.3)	40.8	3.1 (41.9)

*Values in parentheses are % coefficient of variation values.

applying a varnish or other water-resistant coatings to increase their durability. They have the potential to replace traditional nonbiodegradable plastic materials in many applications, including racket frames, ski poles, circuit boards, automobile insides, and so forth.

It should be noted that the BC nanofiber Young's modulus has been estimated to be up to 78 GPa or even up to 114 GPa [36,37]. However, the nanofibers in the pellicles are not unidirectionally oriented but instead are highly entangled as a result of the random path traveled by the *A. xylinum* (Figure 11.4b(i)). Their strength, like the Young's modulus, is reduced significantly. This is reflected in the composite strength as well.

The tensile strain value for MSF resin was 23.4%, which was much higher than the value of 5.7% obtained for BC. The tensile strain of the BC–MSF resin composite, however, was only 3.1%. Although the tensile strain is controlled by the BC, since both BC and resin are hydrophilic in nature, the fiber/resin bonding is expected to be good. Better bonding allows the resin to lock the fibers in place, reducing the tensile strain of the composite.

The SF resin and BC–SF resin composites were fabricated and used for comparison. The results presented in Table 11.2 indicate that MSF resin and BC–MSF resin composites have higher Young's modulus and tensile strength than those of SF resin and BC–SF composites, respectively. The enhanced MSF resin properties are due to high protein content in the MSF resin compared to SF [28]. Also, the SF resin contains low-molecular-weight sugars (up to 35% by weight), which plasticize the resin. As mentioned earlier, these sugars were removed to obtain MSF. This is evident in the higher tensile strain and lower Young's modulus obtained for SF. The enhanced properties of the MSF resin are reflected in the BC–MSF composite properties as

can be expected, though the difference in tensile properties between BC–MSF resin composites and BC–SF resin composites here is not significant, only 5%–10%. This is because the tensile values of MSF and SF resins are an order of magnitude lower than BC and both composites have 50 wt% BC content; the tensile values of the composites are dominated by BC properties. However, both experimental and theoretical values shown in Table 11.2 indicate that BC–MSF resin composites have better tensile properties than BC–SF resin composites. This conclusion was further confirmed by composites with 10 wt% BC content for the two resins in our preliminary experiments.

Table 11.2 also presents theoretically calculated values for Young's modulus and tensile strength values calculated using the rule of mixture [38]. The densities of cellulose and soy resins were 1.52 and 1.30 g/mL, respectively [39], and the weight ratio of BC to resin is 1:1 in the composites. It is clear that the theoretical and experimental Young's modulus values are very close, but the experimental strength values are slightly lower, which is controlled by the defects in the specimens.

11.3.6 THERMAL STABILITY OF BC–SF AND BC–MSF RESIN COMPOSITES

TGA studies were conducted to obtain information on the thermal decomposition behavior of BC–SF and BC–MSF resin composites. Figure 11.5 shows typical TGA thermograms obtained for the two composites. These curves confirm that the BC–MSF resin composite has better thermal stability than the BC–SF resin composite, as can be expected. The degradation temperature, T_d , for BC–SF resin composites was found to be around 205°C, compared to 220°C obtained for BC–MSF composites. This was, again, due to the higher protein content in the MSF resin than that in the SF resin after removing sugars. The sugars start to degrade at much lower temperatures. Our preliminary experiments had shown that fructose, glucose, and sucrose start to degrade at around 160°C, 170°C, and 200°C, respectively, much lower than the degradation temperatures of proteins and cellulose. These results confirm that the BC–MSF resin composite is thermally slightly more stable than the BC–SF resin composite and hence may be used at slightly higher temperatures or would be more durable at the same temperature.

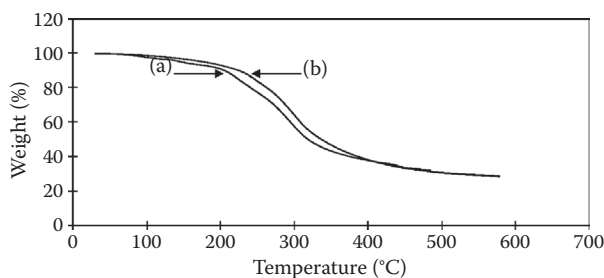


FIGURE 11.5 TGA thermograms of (a) BC–SF resin composite and (b) BC–MSF resin composite.

11.4 CONCLUSIONS

The present study has shown for the first time that SFE can be an excellent carbon source for BC production. The BC yield obtained with the new carbon source (SFE) was high and close to or even better than those obtained with other expensive conventional carbon sources. The cost of the SFE carbon source can be very low because it is a by-product of SF processing and is produced in abundance throughout the world.

The study also showed that SFE contains at least five sugars, and three of them, fructose, glucose and sucrose, can be utilized as an excellent carbon source for BC production. In addition, the study confirmed that the autoclaving process can hydrolyze higher sugars in SFE.

The results further indicated that *A. xylinum* prefers to consume fructose and glucose before sucrose and other higher sugars such as raffinose and stachyose during the culture. Importantly, the results show that the rate of BC production is much higher when the concentration of fructose and glucose combined is high.

The study successfully developed membrane-like “green” composites using BC obtained by SFE and MSF resin produced by residual protein product after SFE extraction. The BC–MSF resin composite showed better tensile and thermal properties than the BC–SF resin composite. These composites could provide a “green” choice to replace many traditional plastic materials.

ACKNOWLEDGMENTS

This work was partly supported by the National Textile Center (NTC) and the Wallace Foundation. The authors would like to thank Profs. Dan Luo, Antje Baeumner, and Jocelyn Rose of Cornell University for allowing the use of their facilities. We would also like to acknowledge Dr. Jun Tae Kim for his help in the SFE process and useful discussions about the HPLC data.

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