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Polymerization of aniline on bacterial cellulose and characterization of bacterial cellulose/polyaniline nanocomposite films

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ABSTRACT

Bacterial cellulose/polyaniline nanocomposite film was prepared by the chemical oxidative polymerization of aniline with bacterial cellulose. Polyaniline conducting polymer nanocomposite films with bacterial cellulose fibers was prepared and characterized. In nanocomposite film, the bacterial cellulose was fully encapsulated with polyaniline by direct polymerization of the respective monomers using the oxidant and dopant. These bacterial cellulose/polyaniline nanocomposite films materials exhibited the inherent properties of both components. The deposition of a polyaniline on the bacterial cellulose surface was characterized by SEM. XPS revealed a higher doping level of the nanocomposite films doped with p-TSA dopant. From the cyclic voltammetry results, the polyaniline polymer was thermodynamically stable because redox peaks of electrochemical transitions in the voltagrams were maintained in bacterial cellulose/polyaniline nanocomposite films.

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1. Introduction

Cellulose fibers are secreted extracellularly by certain bacteria belonging to the genera Acetobacter, Agrobacterium, Alcaligenes, Pseudomonas, Rhizobium, or Sarcina [1]. The most efficient producer of bacterial cellulose (BC) is Acetobacter xylinum (or Gluconacetobacter xylinus), a gram-negative strain of acetic-acid-producing bacteria [2,3]. There are important structural differences between bacterial cellulose and, for example, wood cellulose. Bacterial cellulose is secreted as a ribbon-shaped fibril, less than 100 nm wide, which is composed of much finer 2–4 nm nanofibrils [4,5]. In contrast to the existing methods for obtaining nanocellulose through mechanical or chemo-mechanical processes, bacterial cellulose is produced by bacteria by cellulose biosynthesis and the building up of microfibril bundles [6]. These microfibril bundles have excellent intrinsic properties owing to their high crystallinity (up to 84-89%; [7]), including a reported elastic modulus of 78 GPa [8], which is higher than that generally recorded for macro-scale natural fibers [9] and in the same order as the elastic modulus of glass fibers (70 GPa;

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[10,11]). In addition, bacterial cellulose is produced as a highly hydrated and relatively pure cellulose membrane. Hence, no chemical treatments are needed to remove lignin and hemicelluloses, as is the case for plant cellulose [12,13].

Among the family of conjugated polymers, polyaniline is one of the most useful because it is air- and moisture-stable in both its doped, conducting form and de-doped, insulating form. Compared to other conducting polymers, polyaniline has the advantages of easy synthesis, low-cost, structure complex and special proton doping mechanism, as well as physical properties controlled by both the oxidation and protonation state. These unique properties give polyaniline an important position in the field of conducting polymers. polyaniline has a wide variety of potential applications including anticorrosion coatings, batteries, sensors, separation membranes and antistatic coatings.

Chemical polymerization of conducting polymer on cellulose fiber has attracted attention recently for the manufacturing of conducting composite films and applications based on such materials. However, there are few reports on nanocomposite films composed of bacterial cellulose and conducting polymers.

This study focuses on manufacturing nanocomposite films with bacterial cellulose and conducting polymers, such as polyaniline. The morphological changes occurring during the polymerization process were monitored by field emission-scanning electron microscopy (FE-SEM). In addition, fourier transform infrared (FTIR)

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spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) measurement were used for characterization. Electrically conductivity and cyclic voltammetry were used to examine the electrically properties and electrochemical performance of BC/polyaniline nanocomposite films.

2. Experimental

2.1. Materials

Bacterial cellulose was cultivated using the cultivation method reported below. Aniline monomer was purchased from Sigma Aldrich. Ammonium persulfate (APS) as the oxidant were purchased from Duksan Pure Chemical Co., LTD. p-Toluenesolfonic acid as the dopant was purchased from Sigma Aldrich. All chemical reagents were used as received.

2.2. Bacterial cellulose cultivation

Glucoacetobacter xylinum BRC-5 used to produce the bacterial cellulose pellicles. The bacteria were cultured in Hestrin and Schramm (HS) medium. The medium was sterilized by heating to 120 °C for 15 min in an autoclave. The active bacteria were injected into a 1000 mL Erlenmeyer flask containing 300 mL of the HS medium. The flasks were incubated statically at 30 °C for 10 days. The cellulose pellicle produced in the Erlenmeyer flask was immersed repeatedly in a 0.25 M aqueous NaOH solution for 24 h at room temperature to remove of the residual bacteria and culture medium in the cellulose. The pH was then decreased to 7.0 by repeated washing with distilled water. The purified cellulose pellicles were stored in distilled water at 4 °C to prevent drying.

2.3. Polymerization of polyaniline polymer on the bacterial cellulose surface

Bacterial cellulose with HCl aqueous solution was used as a source for the BC/polyaniline nanocomposite films. Aniline was added to distilled water containing bacterial cellulose. An aqueous HCl solution (35 wt%) was added dropwise to the above-prepared solution until the pH of the solution was 3, and stirred for 1 h under vigorous stirring. APS as an oxidant and p-TSA as a dopant dissolved in distilled water was added to the aniline/bacterial cellulose solution. The monomer: oxidant: dopant molar ratio was kept at 4:1:2. The polymerization of aniline was carried out at room temperature for 2 h. After polymerization, the BC/polyaniline nanocomposite films were obtained. BC/PANi1 was composed of bacterial cellulose and polyaniline with p-TSA (dopant). BC/PANi2 was made up of bacterial cellulose and polyaniline without p-TSA.

2.4. Polyaniline powder polymerization

Polyaniline in the emeraldine salt (ES) form was chemically synthesized according to the method described by MacDiarmid and Epstein [14]. In a typical procedure, 10 mL of aniline was dissolved in 150 mL of a 1 mol/L HCl solution below 5 °C. The oxidant, ammonium persulfate, which had been previously dissolved in 100 mL of an HCl solution (1 mol/L), was cooled and dropped into the reaction medium over 20 min. After 2 h, the resulting dark green solid was filtered several times with a HCl solution. The abbreviation name for the conducting polymer powder with the same nanocomposite films composition except for bacterial cellulose is (PANi1 and PANi2).

2.5. Characterizations

2.5.1. Fourier transform infrared-attenuated total reflectance (FTIR-ATR) measurements

The FTIR-ATR spectra of the polyaniline sepcimens were obtained using a JASCO 6100 FTIR spectrophotometer from Japan. The specimens were analyzed over the range, $650-4000 \text{ cm}^{-1}$, with a spectrum resolution of 4 cm⁻¹. All spectra were averaged over 30 scans. This analysis was performed at the point-to-point contact with a pressure device.

2.5.2. Thermal analysis

Thermogravimetric analysis (TGA) measurements of the polyaniline and BC/polyaniline sepcimens were carried out using a TGA (TA Instruments, TGA Q5000) on about approximately 2–4 mg samples over the temperature range, 25 °C–600 °C at a heating rate of 10 °C/min under a nitrogen flow of 20 ml/min. TGA was measured with the nanocomposite films placed in a high quality nitrogen (99.5% nitrogen, 0.5% oxygen content) atmosphere to prevent unwanted oxidation.

Differential scanning calorimetry (DSC) was used to analyze the conducting polymer at temperatures ranging from -80 to 450 °C at a heating rate of 10 °C/min using a TA Instruments (DSC Q 1000).

2.5.3. Field emission-scanning electron microscopy (FE-SEM)

FE-SEM (SUPRA 55VP, Carl Zeiss, Germany) was used to characterize the polymerization surface of polyaniline and BC/polyaniline. The acceleration voltage was 2 kV. Prior to analysis, the specimens were coated with platinum (purity, 99.99%) to eliminate electron charging.

2.5.4. X-ray diffraction (XRD)

Wide-angle X-ray scattering (WAXS) analysis of the polyaniline and BC/polyaniline were conducted with a D8-Advance (Bruker Miller Co) apparatus. CuK α radiation with a wavelength of $\lambda = 1.54$ Å was used with a nickel filter in 0.02° (2 θ) steps.

2.5.5. Electrical conductivity

All specimens (at least 5 mm in diameter) used for the conductivity measurements were obtained by the polymerized nanocomposite films as described in an earlier section. A four-probe conductivity apparatus (SYD-2, Guangdong, China) was used for the conductivity tests. The conductivity was calculated using the following equation:

$\sigma = LR_VS$

where σ , L, R_V, and S are the conductivity, thickness, volume resistivity and the surface area of the sample, respectively.

2.5.6. X-ray photoelectron spectroscopy (XPS)

XPS of the BC/polyaniline nanocomposite films specimens was obtained with a Sigma Probe (Thermo VG, U.K.) analyzer. The spectra were recorded using a monochromatic Al-Ka radiation X-ray source with 50 W operating at 10 kV voltage and a base pressure of 4×10^{-8} torr in the sample chamber. The XPS spectra were collected in the range, 0–1200 eV, with a resolution of 1.0 eV and a pass energy of 30 eV. The XPS spectra are analyzed using commercial, curve fitting software. The binding energy scale was calibrated with reference to the C1s line at 285.0 eV.

2.5.7. Cyclic voltammetry

Cyclic voltagrams were recorded on aqueous solutions and performed in a standard three-electrode cell setup utilizing an Autolab (PGSTAT 302N) with the nanocomposite films as the



Fig. 1. FTIR-ATR spectra of polyaniline with different oxidant and dopant.

working electrode. A platinum plate and Ag/AgCl were used as a counter and reference electrodes, respectively. The measurements were carried out in a 2.0 M sodium chloride solution at potentials ranging from -0.8 to 0.0 V for BC/polyaniline with different scan rates.

3. Results and discussion

3.1. Polymerization of conducting polymer

3.1.1. Chemical structure of polyaniline powder

The chemical structure of the polyaniline powder oxidized by APS with or without p-TSA as the dopant was examined by FTIR-ATR spectroscopy. Fig. 1 shows the spectra of the polyaniline powder. The FTIR spectra of these two polyanilines were similar. The main peaks in the spectrum at 1560 cm⁻¹ and 1480 cm⁻¹ corresponded to the C=C stretching deformation of the quinoid and benzenoid rings, respectively. The absorption peaks at 1292 cm⁻¹ and 1240 cm⁻¹ were assigned to the C-H stretching vibration with aromatic conjugation [15].



Fig. 2. XRD spectra of polyaniline with different oxidant and dopant.



Fig. 3. TGA curves of polyaniline with different oxidant and dopant.

3.1.2. Crystalline structure of polyaniline powder

Fig. 2 shows X-ray scattering patterns of p-TSA doped polyaniline oxidized by APS. The degree of crystallinity of the polyaniline powders was relatively low. Two broad peaks at $20.4^{\circ} 2\theta$, which might be due to the periodicity parallel to the polymer chain, and $25.2^{\circ} 2\theta$, which may be caused by the periodicity perpendicular to the polymer chain, were observed [16,17]. Other broad peaks centered at 9.0° and $14.9^{\circ} 2\theta$ were indicative of the monoclinic space group P2₁ [18]. However, the crystallinity of PANi1 and PANi2 was very low. This means that the resulting polyaniline powder is amorphous. In addition, p-TSA dopant does not affect the crystallinity of the polyaniline powder, probably because p-TSA is not bulky enough.

3.1.3. Thermal degradation stability of polyaniline powder

Fig. 3 shows TGA thermograms of the polyaniline powders. In the TGA profile, there were two main stages of weight losses for polyaniline. The first weight loss at approximately 160 °C was attributed to the removal of dopant molecules, HCl and the loss of impurities, such as remaining monomers. The second weight loss at approximately 400 °C indicated structural decomposition of the polyaniline polymer. The gradual weight loss over the wide temperature range was attributed to the good thermal stability of the polyaniline main chain [19,20].



Fig. 4. DSC thermograms of polyaniline with different oxidant and dopant.



Fig. 5. FE-SEM images of PANi1 (a) and PANi2 (b) powders.

3.1.4. Thermal properties of polyaniline powder

Fig. 4 shows DSC thermograms of un-doped polyaniline and polyaniline doped with p-TSA. The thermograms of both PANi1 and PANi2 revealed an endotherm peaks from 0 °C to 150 °C. This was attributed to the removal of the loosely bound water molecules present in the polymer matrix [21]. The second endothermic peak at approximately 230 °C was due to thermal dedoping of the p-TSA from the polymer chains. The small broad exothermic peak at approximately 380 °C was attributed to interchain crosslinking and thermally effected morphological changes [21,22]. The thermogram also confirms the absence of any glass transition (T_g) and melting temperature (T_m) for the both polyaniline systems [23].

3.1.5. Surface morphology of polyaniline powder

Fig. 5 shows the typical morphology of PANi1 and PANi2. Aniline was polymerized into spherical nanoparticles, 100–200 nm in diameter. The particles were spherical with a comparatively smoother particle surface in PANi1 and PANi2. The particles were highly aggregated.

3.2. Characterization of bacterial cellulose/polyaniline nanocomposite films

3.2.1. Surface morphology of BC/polyaniline nanocomposite films

SEM was used to evaluate the nanostructure of BC/polyaniline nanocomposite films. As shown in Fig. 6 (a) and (b), the surfaces of the nanocomposite films were covered completely with polyaniline on the surface of bacterial cellulose. The polyaniline on the sample doped with p-TSA had a similar nano -granular morphology to the un-doped polyaniline sample. In addition, the grain size was estimated to be ~ 100 nm.

3.2.2. Thermal degradation stability of BC/polyaniline nanocomposite films

The TGA curve of the BC/polyaniline composites was determined at a heating rate of 10 °C/min, as shown in Fig. 7. The TGA curves of bacterial cellulose are also shown for comparison. The TGA curve of the BC/polyaniline nanocomposite films showed the main weight loss in two stages. The weight loss observed within 100 °C was assigned to the removal of moisture present in the nanocomposite films. The first stage in weight reduction at approximately 200 °C was due to the combination result from bacterial cellulose and the side chain or impurities of polyaniline. The onset temperature of thermal degradation was similar in all samples. However, the main weight loss range was different in the pure bacterial cellulose and polyaniline based nanocomposite films. These results are related to the absence of intermolecular hydrogen bonds of cellulose. This suggests that the cellulose macromolecule changed into a smaller one. Therefore, a main weight reduction will occur at lower temperatures [24]. The second stage in weight loss occurred from approximately 300 °C due to thermal-oxidative degradation of the main polyaniline chain.

3.2.3. Surface chemical structure of BC/polyaniline

The N1s binding energy peak was studied by XPS to characterize the degree of protonation of polyaniline in the nanocomposite films. Table 1 lists the XPS results of the surface chemical composition of BC/polyaniline conducting nanocomposite films. Normally, the N1s core-level spectra of polyaniline could be composed of three distinct components, which exhibit the quinoid imine (-N=), benzenoid amine (-NH-) and positively charged nitrogen $(-NH^+-)$ [25,26]. The N1s envelope was deconvoluted into three components (Table 2). The main peak at 399.6 eV was attributed to



Fig. 6. FE-SEM images of (a) BC/PANi1 and (b) BC/PANi2.



Fig. 7. TGA curves of BC/polyaniline nanocomposite films.

the contribution of the benzenoid amine (-NH-) and the component at (400.6 and 400.7) and (401.5 and 401.8) correspond to two positively charged nitrogen atoms, respectively. The existence of these two N ⁺ was assigned to the existence of different protonation environments, which leaded to the formation of a polaron (at lower energy) and bipolaron (at higher energy) [25,27]. There were no quinoid imine (-N=) species. This indicates the high doping level of the polyaniline nanocomposite films. Table 2 lists the results of XPS elemental quantitative analysis. The doping level was confirmed by the S/N ratio, which showed that more doping anions were incorporated into the polyaniline structure. This showed that the BC/PANi1 nanocomposite film has a higher doping level than BC/PANi2.

3.2.4. Electrical conductivity of BC/polyaniline nanocomposite films

Electrical conductivity measurements were carried out on BC/ polyaniline nanocomposite films using a four-probe method. The calculated electrical conductivities were 1.3 S/cm (BC/PANi1) and 0.8 S/cm (BC/PANi2), respectively, whereas the bacterial cellulose film was insulating. This considerable increase in electrical conductivity from insulating to semiconducting is significant. It was reported that the electrical conductivity of polyaniline depends on the degree of doping, oxidation state, particle morphology, crystallinity, interior intrachain interactions, molecular weight, etc [15,16,28]. The conductivity of the BC/PANi1 nanocomposite film was higher than that of BC/PANi2, which was not doped with p-TSA. Therefore, the doping level affects the electrical conductivity.

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Results of XPS quantitative analysis of polyaniline based nanocomposite films.

	C1s (at.%)	N1s (at.%)	01s (at.%)	S2p (at.%)	S/N ratio
BC/PANi1	71.29	11.85	12.38	4.48	0.378
BC/PANi2	72.82	8.90	15.49	2.80	0.315

Tab	le	2
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N1s peak distribution	(%)	in po	lyaniline	based	l nanocomposite	films.
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Samples	-NH-		$-N^+-$		-N ⁺ -		
	Peak center (eV)	Composition (%)	Peak center (eV)	Composition (%)	Peak center (eV)	Composition (%)	
BC/PANi1 BC/PANi2	399.6 399.6	60.6 52.6	400.6 400.7	23.3 27.8	401.5 401.8	16.1 19.6	



Fig. 8. Cyclic voltagram recorded at the displayed different voltage scan rates 20, 50, 100 mV/s of BC/PANi1 (a) and BC/PANi2 (b) nanocomposite films.

3.2.5. Electrochemical stability of BC/polyaniline nanocomposite films

Cyclic voltammetry was used to measure the electrochemical redox properties of the nanocomposite films and to determine their thermodynamic stability. Fig. 8 shows the cyclic voltagrams of the BC/polvaniline nanocomposite films on Pt in 2 M NaCl. In these voltagrams, the current was normalized to the mass of the nanocomposite films used as the working electrode in the cyclic voltammetry experiments. When the scan rate of the cyclic voltagrams for the nanocomposite films was changed from 20 to 100 mV/s, the redox peaks of electrochemical transitions in the voltagrams were maintained in both the BC/PANi1 and BC/PANi2 nanocomposite films. These results indicated that the polyaniline polymer is thermodynamically stable [29]. The reduction and oxidation peak potential of the PANi1 and PANi2-based nanocomposite films were (-0.53 V, 0.08 V) and (-0.52 V, 0.05 V), respectively. However, as shown in Fig. 8, no more redox peaks were observed in the cyclic voltagrams, which is related to the emeraldine and pernigranile transition peaks. This suggests that a specific transition that yields the redox peak in the particular voltagram is either not thermodynamically stable or the kinetics of the redox transition are slower than the scan rates [29,30].

4. Conclusions

BC/polyaniline nanocomposite films were prepared by chemical oxidative polymerization. New hybrid materials of bacterial cellulose fiber with polyaniline were produced, in which the individual bacterial cellulose fibers were fully encapsulated by polyaniline spherical spheres. The conducting composites were characterized by FE-SEM, TGA, XPS, electrical conductivity and cyclic voltammetry analysis. The oxidant and dopant had a significant effect on the electrical conductivity and thermal stability of the nanocomposite films. FE-SEM revealed the fine globular structure of the polyaniline on the nanocomposite films with average grain sizes ranging from 100 to 200 nm. XPS revealed a higher doping level of the nanocomposite films doped with p-TSA dopant. Cyclic voltammetry was used to measure the electrochemical redox properties of the nanocomposite films and to determine their thermodynamic stability. From the results, the polyaniline polymer is thermodynamically stable because of redox peaks of electrochemical transitions in the voltagrams were maintained in both the BC/polyaniline nanocomposite films.

References

- [1] H. El-Saied, A.H. Basta, R.H. Gobran, Polym. Plastic Technol. Eng. 43 (2004) 797-820.
- [2] R.M. Brown, Abstr. Pap. Am. Chem. Soc. 227 (2004) 154 (CELL).
- [3] D. Klemm, D. Schumann, F. Kramer, N. Hessler, M. Hornung, H.P. Schmauder, S. Marsch, Polysaccharides II 205 (2006) 49–96.
- [4] M. Iguchi, S. Yamanaka, A. Budhiono, J. Mater. Sci. 35 (2000) 261-270.
- [5] E.E. Brown, M.P.G. Laborie, Biomacromolecules 8 (2007) 3074-3081.

- [6] A. Nakagaito, H. Yano, Appl. Phys. A 80 (2005) 155-159.
- [7] W. Czaja, D. Romanovicz, R. Brown, Cellulose 11 (2004) 403-411.
- [8] G. Guhados, W. Wan, J. Hutter, Langmuir 21 (2005) 6642.
- [9] A. Mohanty, M. Misra, G. Hinrichsen, Macromol. Mater. Eng. 276 (2000) 1-24.
- [10] D. Saheb, J. Jog, Adv. Polym. Tech. 18 (1999) 351-363.
- [11] J. Juntaro, M. Pommet, A. Mantalaris, M. Shaffer, A. Bismarck, Compos Interfac 14 (7) (2007) 753-762.
- [12] K. Oksman, M. Sain, Cellulose Nanocomposites: Processing, Characterization, and Properties. American Chemical Society, 2006.
- [13] H. Barud, C. Barrios, T. Regiani, R. Marques, M. Verelst, J. Dexpert-Ghys, Y. Messaddeq, S. Ribeiro, Mater. Sci. Eng. C 28 (2008) 515-518.
- [14] A.G. Macdiarmid, A.J. Epstein, Faraday Discuss. 88 (1989) 317.
- [15] Z. Zhang, Z. Wei, M. Wan, Macromolecules 35 (2002) 5937-5942.
- [16] T. Abdiryim, R. Jamal, I. Nurulla, J. Appl. Polym. Sci. 105 (2007) 576-584.
- [17] Y. Moon, Y. Cao, P. Smith, A. Heeger, Polymer Commun. 30 (1989) 196–199.
- [18] L. Zhang, M. Wan, Y. Wei, Macromol. Rapid Commun. 27 (2006) 366-371.
- [19] L. Ding, X. Wang, R. Gregory, Synth. Met. 104 (1999) 73–78.
- [20] B.-J. Kim, S.-G. Oh, M.-G. Han, S.-S. Im, Synth. Met. 122 (2001) 297-304.
- M. Kulkarni, A. Viswanath, Eur. Polym. J. 40 (2004) 379–384.
 Y. Wei, G. Jang, K. Hsueh, E. Scherr, A. MacDiarmid, A. Epstein, Polymer 33 (1992) 314–322.
- [1352] 914–922.
 [23] Y. Wei, G.W. Jang, K.F. Hsueh, E.M. Scherr, A.G. MacDiarmid, A.J. Epstein, Polymer 33 (1992) 314–322.
- [24] Z. Mo, Z. Zhao, H. Chen, G. Niu, H. Shi, Carbohydr. Polym. 75 (2009) 660-664.
- [25] F. Souza Jr., G. Oliveira, T. Anzai, P. Richa, T. Cosme, M. Nele, C. Rodrigues,
- B. Soares, J. Pinto, Macromol. Mater. Eng. 294 (2009) 739–748. [26] M. Han, S. Cho, S. Oh, S. Im, Synth. Met. 126 (2002) 53–60.
- [27] F. Lux, G. Hinrichsen, V. Krinichnyi, I. Nazarova, S. Cheremisow, M. Pohl, Synth. Met. 55 (1993) 347–352.
- [28] S. Stafström, J.L. Brédas, A.J. Epstein, H.S. Woo, D.B. Tanner, W.S. Huang, A.G. MacDiarmid, Phy. Rev. Lett. 59 (1987) 1464.
- [29] F. Kelly, J. Johnston, T. Borrmann, M. Richardson, Eur. J. Inorg. Chem. 2007 (2007) 5571–5577.
- [30] R.A. Jeong, G.J. Lee, H.S. Kim, K. Ahn, K. Lee, K.H. Kim, Synth. Met. 98 (1998) 9–15.