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Heterogeneous preparation of cellulose–polyaniline conductive composites with cellulose activated by acids and its electrical properties

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ABSTRACT

A series of conductive composites cellulose–polyaniline (PANI) were heterogeneously synthesized by chemical oxidative polymerization of aniline with native cellulose activated by various acids. The chemical structure and morphology of the composites were examined by FT-IR analysis and TEM. TGA was used to study their thermal properties. The composites prepared using the di-basic acids exhibited more favorable conductivity than the composites prepared using the monobasic acids. The content of PANI increased with increasing of activation time, and while the conductivity decreased because of the aggregation of PANI particles at the activation time range from 50 to 120 min. Both the PANI content and the electrical conductivity increased with an increase of the amount of aniline, and reached the maximum values at the 0.5 g aniline, respectively. The acids were able to successfully activate cellulose and lead to the improvement of the accessibility and reactivity of the O–H groups. The composites were highly stable compared to pure cellulose due to the safeguard from PANI slices. This work provided a facile method for the synthesis of cellulose–polyaniline conductive composites with excellent conductivity.

1. Introduction

In recent years, polymer–polyaniline (PANI) conductive polymeric composites have received considerable attention because of their potential applications in electrodes, biosensors, batteries, antistatic coatings, gas sensors, membranes and light emitting diodes (Amrithesh, Aravind, Jayalekshmi, & Jayasree, 2008; Bai, Chen, Li, Lu, & Shi, 2007; Chatzidaki, Favvas, Papageorgiou, Kanellopoulos, & Theophilou, 2007; Mi, Zhang, Ye, & Yang, 2008; Shan, Shi, Zhu, & Xue, 2007; Zou, Sun, & Xu, 2007). The majority of polymers selected to prepare PANI composites are insulating polymeric materials with excellent physical properties, such as rubber, plastic and textile. Many papers dealing with the preparation of the rubber–PANI, plastic–PANI, and others have been published (Mitzakoff & Paoli, 1999; Schmidt, Domenech, Soldi, Pinheiro, & Soldi, 2004). Generally, a large number of rubber and plastics are synthesized by using petroleum feedstock as raw materials. As we known, however, the much limited petroleum resource has been exhausting, and the most of nonbiodegradable plastics have become serious threat to environment (Gindla & Keckesb, 2005; Petersson & Oksman, 2006). As a consequence, people are increasingly paying more attention to look for natural eco-friendliness materials as a substitute for petroleum feedstock in recent decades. Cellulose fiber is one of promising natural polymeric materials.

Cellulose fiber derives from wood, annual plants, and agricultural by-products, is an abundant renewable resource (Hinterstoisser, kerholm, & Salmén, 2003; Jaeh, Sungryul, & Zoubeida, 2006; Zhang, Vill, & Heck, 2004). Cellulose is a straight carbohydrate polymer chain consisting of several 1000 β 1–4 glucopyranose units, and the chains link with each other via a mass of intermolecular and intramolecular hydrogen bonds. This structure gives cellulose unique properties like chemical stability, mechanical strength, biocompatibility and biodegradation (Zhao et al., 2007a; Gurjanov, Ibragimova, Gnezdilov, & Gorshkova, 2008). Cellulose is modified to form various cellulose esters, cellulose ether and other cellulose derivatives. These cellulose derivatives exhibit as excellent physical properties as the petroleum products. For instance, cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) have already taken place of petroleum feedstock in making plastic in the commercial market. Among these cellulose esters, cellulose acetate (CA) has been long used in preparation of PANI composites (Ahmeda, Mohammada, & Rahman, 2004; Proń, Zagorska, Nicolauc, Genoud, & Nechtschein, 1997; Walter, Banka, Genoud, Proń, & Nechtschein, 1997). Additionally, the use of viscose and lyocell (regenerated cellulose) in combination with conductive polymers for the preparation of conductive materials has been reported previously (Acqua, Tonina, Peilaa, Ferrerob, & Catellanic, 2004). Either cellulose acetate or viscose (lyocell) is obtained by mean of preparing with homogeneous procedure. In case of homogeneous procedure, the effective synthesis of cellulose products with desired degree of reaction, reproducible substitution patterns and

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the targeted properties both in laboratory or industry scale are permitted. To the best of our knowledge, however, the disadvantage of their stiff molecules and close chains packing via numerous intermolecular and intramolecular hydrogen bonds is the extreme difficulty to dissolve cellulose in water and most common organic solvents. Although *N*-methyl-morpholine-*N*-oxide (NMMO), DMAc/LiCl, 1-butyl-3-methylimidazolium (BMIMCl) and 1-allyl-3-methylimidazolium chloride (AMIMCl) ionic liquids, NaOH/urea aqueous solution etc., (Zhang, Wu, Zhang, & He, 2005; Zhao et al., 2007b; Song, Zhou, Zhang, & Wu, 2008) have been developed as novel and effective solvents for cellulose in more recent decades, there are still some problems associated with its use, such as relatively low dissolution ability and its high cost as well. In this sense, cellulose–PANI conductive composites (CPcc) have been prepared in heterogeneous reaction. In view of heterogeneous reactions, the accessibility and reactivity of the OH groups are clearly determined by hydrogen bond-breaking activation steps through various acids, alkaline compounds, steam explosion process, radiation technology, ultrasound wave and microwave treatment, and biological method (Bolaños et al., 2001; Gedanken, 2004; Lara, Vázquez, Galán, & Benavente, 2006; Song et al., 2008). In this article, kinds of acids would be used as activation regents to break intermolecular hydrogen bands and improve the accessibility and reactivity of cellulose. On the other hand, various acids can also be served as dopants to react with PANI and enhance the conductivity of the composites. The structure and morphology of cellulose–PANI composites were characterized by FT-IR, SEM and TGA. The types of acids, the activation time and the amount of aniline play a major role on the properties of the composites. As a result, the effects of these factors on the content of PANI and the electrical conductivity (EC) of the composites were studied at length.

2. Experimental

2.1. Materials and preparation of cellulose

Cellulose was extracted from raw materials. Aniline monomer was purchased from Sinopharm Group Chemical Reagents Company (Shanghai, China), and doubly distilled prior to use. Ammonium persulphate (APS) was obtained from Xi′an Chemical Reagents Industries (Xi′an, China). Chloride acid (HCl), sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4), nitric acid (HNO_3), *para*-toluenesulfonic acid (*p*-TSA), sodium hydroxide (NaOH) and anhydrous ethanol (C_2H_6O) at analytical reagent grade were obtained from commercial suppliers and used as received. 100 ml of 7 wt.% HNO_3 solution was added to three-neck flask containing 7.0 g 92 corn straw powder. The resulting mixture was refluxed at 11 °C for 2.5 h, and continued for 1.5 h after adding 50 ml of 3 wt.% NaOH aqueous solution. After cooling to ambient temperature, the mixture was washed with distilled water until the filtrate become colorless, and then with anhydrous ethanol several times to remove residual organic impurities, finally dried in an air oven at 50 °C for 10 h, stored in desiccators for experiment.

2.2. Synthesis of cellulose–PANI composites (take HCl for example)

In a typical procedure, 0.5 g cellulose mentioned previously was added to 1.0 mol/L HCl solution dissolving aniline monomer (10:1 by molar ratio). After the cellulose was activated for a period of time, 1.0 mol/L APS aqueous solution was added dropwise to oxidatively polymerize aniline. The mixture was stirred for 20 h at ice temperature. The reaction product was filtrated and washed with doubly distilled water until the filtrate become neutral, and then with anhydrous ethanol till the filtrate become colorless. The composites were dried at 40 °C in an air oven for 5 h. The content of PANI was calculated on the basis of the weight increment of fiber. The preparation of cellulose–PANI composites could be described more clearly by a schematic illustration in Fig. 1.

2.3. Characterization

Fourier transform infrared spectra (FT-IR) of the samples were obtained by using EQUINOX-55 FT-IR spectrometer (Bruker). Spectra were recorded in the range 4000–400 cm^{-1}, KBr pellets, with a resolution of 4 cm^{-1}. Scanning electron microscopes (SEM) were performed by JSM-6330F model to observe the surface morphologies of the composites. Prior to investigate, the composites were frozen in liquid nitrogen, fractured, mounted and coated with a very thin film of gold. Simultaneous thermo gravimetric analysis (TGA) was performed by using SSC-5200 Perkin–Elmer thermo gravimetric analyzer from 25 to 800 °C under nitrogen atmosphere at the heating rate of 10 °C/min. The electrical conductivity (EC) of the composites was measured at room temperature by the standard four-probe method. The samples were compressed to 13 mm diameter and 0.08–0.2 mm thickness pellets for the measurements.

3. Results and discussion

3.1. Structure and morphology analysis

The FTIR spectra of cellulose–PANI composites (a), PANI (b) and pure cellulose (c) are shown in Fig. 2. The characteristic broad band for O–H group (being in presence of H-band) of cellulose appears at 3422 cm^{-1}, a peak around 2917 cm^{-1} due to asymmetrically stretching vibration of C–H in pyranoid ring. The broad absorption band between 1200–935 cm^{-1} is attributed to the contribution of various functional groups, such as C–O, C–O–C. The typical feature of pure PANI is also well known in literature. The peak corresponding to out of bending vibration of C–H band of *p*-disubstituted benzene ring appears at 809 cm^{-1}. The peaks around 1485 and 1570 cm^{-1} result from stretching vibration of N–A–N and N=B=N structures, respectively (where –A–, =B= stand for benzenoid and quinoid moieties in the PANI chains). The peaks at 1125 and 1294 cm^{-1} because of vibration of C–H in benzene ring and stretching of C–N band have been observed. The characteristic absorptions of pure cellulose (3431 cm^{-1}) and PANI (1575, 1486, 1296 and 809 cm^{-1}) have been both present in the spectrum of the composite. Comparing the relative intensity around 3431 cm^{-1}, however, it is also found that the band of the composite is apparently weaker than the band of the stretching vibration of –OH group in pure cellulose. Furthermore, the absorption peak at

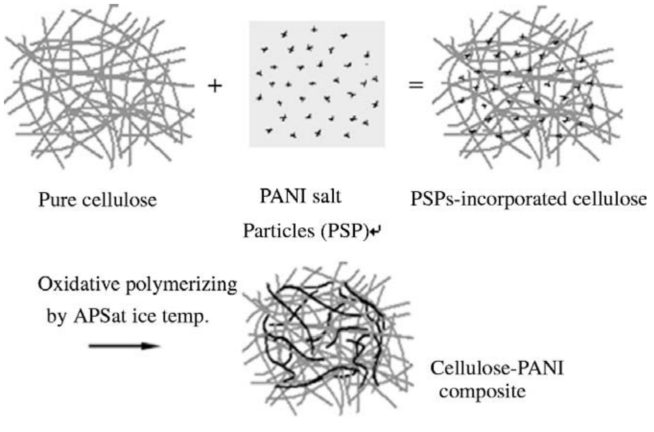

Fig. 1. Schematic diagram of the process of preparing cellulose–PANI composite.

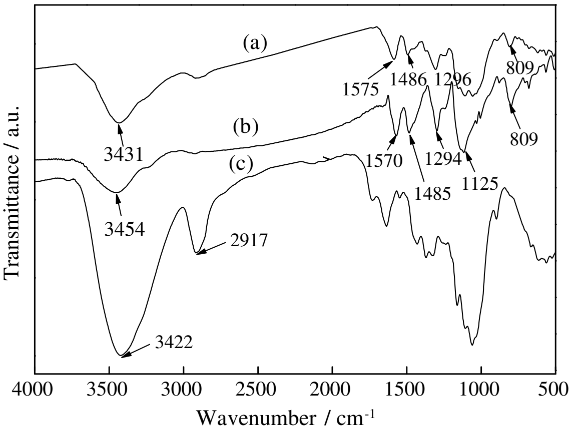

Fig. 2. FT-IR spectra of (a) cellulose–PANI composites (HCl as dopant, activation time 60 min, 0.2 g aniline), (b) PANI (doped by HCl), (c) pure cellulose.

3422 cm^{-1} in the spectrum of pure cellulose is blue-shifted to 3431 cm^{-1} in the spectrum of the composite. These phenomena confirm that native cellulose is successfully activated by superfluous acids. The intermolecular hydrogen bands are broken and the more hydrogen groups become accessible.

The microphotographs of cellulose–PANI composites at different magnifications monitored by SEM, are present in Fig. 3. It is verified that PANI are mostly localized 146 at the intersection of neighboring fibers thus bounding them and reinforcing the composite structures (Fig. 3a and b). It is also found that PANI loaded on the surface and the top of cellulose are present predominantly in the form of slices, but the others exhibit various shapes (cluster, flower, etc.) at the same time (Fig. 3b and c). The phenomenon could be interpreted that the excessive acids was also found to have an effect on the difference of the PANI shapes (Moraes, Vilca, & Motheo, 2004). Additionally, this behavior is also ascribed to cellulose matrix. Cellulose with relative flat surface acts as templates during the growth of PANI. Exactly, PANI deposited on the surface of cellulose grows fast with formation of the larger slices by taking along cellulose templates. However, PANI without cellulose templates grows 156 with other kinds of shapes. Unlike the cellulose–polypyrrole textiles obtained by Acqua et al. (2004), polypyrrole layers on the fiber surface were some polymer islands. In addition, hydrogen bands between aniline cations and hydroxyl in cellulose might serve as traction force to assist the stretching of PANI slices.

3.2. Thermal stability studies

The TG curve of cellulose–PANI composite (a) was measured at heating rate of 10 °C/min, and is shown in Fig. 4. For comparison, the TG curves of pure cellulose (b) and PANI (c) are also shown in Fig. 4. The TG curve of cellulose–PANI composite indicates that weight loss occurred in three steps. A reduction of sample weight observed within 100 °C is attributed to the removal of moisture present in the composite. Additional step in weight loss is recorded in the region 210–425 °C. This weight loss is due to the burning of cellulose in composite. Simultaneously, the onset temperature of thermo-oxidative degradation of pure cellulose is observed at 152 °C, which is lower 58 °C than the composite. In this sense, it indicates that the thermal stability of cellulose–PANI composite is increased than pure cellulose. It is because there are safeguards for cellulose from PANI slices deposited on its surface. However, a massive weight loss of cellulose–PANI composite is observed at 238 °C, but the pure cellulose is at 290 °C. Moreover, a small weight change is observed even at temperature exceeding 482 °C for pure cellulose. These results are related to the absence of intermolecular hydrogen bands of cellulose. It leads to the occurrence that cellulose macromolecules changed into smaller ones. Therefore, a massive weight loss will happen at lower temperature. The final step in weight loss is observed from 425 to 715 °C. This reduction of composite weight results from the thermal-oxidative degradation of PANI. In word, the thermal stability of cellulose is markedly increased by incorporating of PANI. This behavior is consistent with the result obtained by Stejskal, Trchova, and Sapurina (2005).

3.3. Effects of synthesis conditions on the PNAI content and the electrical conductivity of the composites

3.3.1. Effect of the types of acids

It is generally accepted that PANI doped by protonic acids displays more excellent conductivity than the ones undoped. The

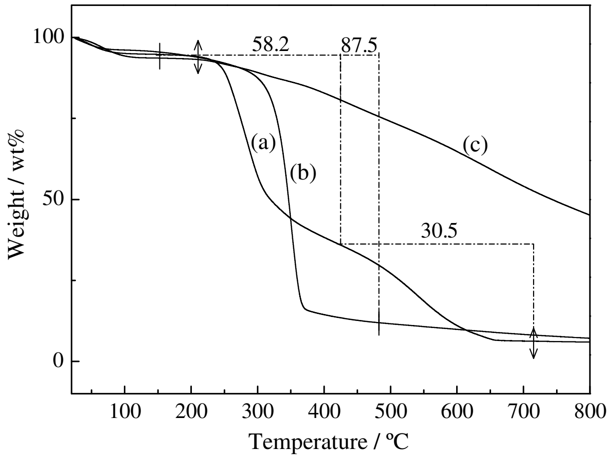

Fig. 4. TG curves of (a) cellulose–PANI composites (0.5 g aniline, activation time 60 min, doped by HCl), (b) pure cellulose, (c) PANI (doped by HCl).

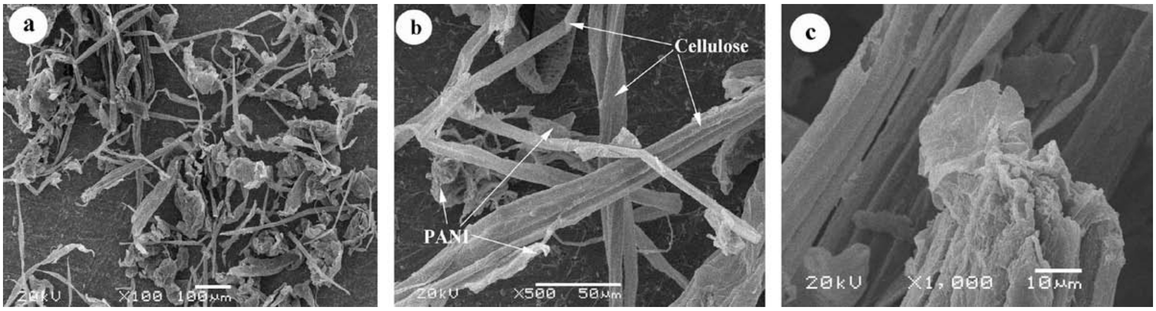

Fig. 3. SEM micrographs of cellulose–PANI composites at different magnifications.

electrical conductivity (EC) of PANI highly depended on the types of acids used. HCl, H_2SO_4, H_3PO_4 and *p*-TSA were provided by our laboratory and chose in this article. The influence of the types of acids on the content of PANI and the EC of the cellulose–PANI composites is shown in Table 1. It can be seen that the EC of the prepared composites is: HCl > H_2SO_4 > *p*-TSA > H_3PO_4, in spite of PANI/HCl/cellulose with fewer PANI content 192 (7.8% < 9.2, 11.6%). It could be concluded that the EC of the composites does not mainly rely on the PANI content. The order could be attributed to the following: (1) the concentration of hydrogen cations. Because hydrogen sulfate anions (HSO_4^-) is exclusively present in PANI/H_2SO_4 (Gemeay, Mansour, El-Sharkawy, & Zaki, 2005). In other word, H_2SO_4 did not completely ionize to produce two hydrogen cations (H^+) and sulfate anion (SO_4^{2-}). Therefore, the concentration of hydrogen cations is different with the value, 2.0×10^{-2} mol/L, 1.0×10^{-2} mol/L for PANI/HCl and PANI/H_2SO_4, respectively. This behavior also confirms that the composites prepared using the dibasic acids are more protonated than the composites prepared using monobasic acids. (2) The acidity of these acids, which is remarkably different. With the same concentration, HCl is markedly stronger than *p*-TSA. Similarly, H_2SO_4 is stronger than H_3PO_4. The weaker acids do not offer enough protonic hydrogen, so by which the PANI doped appear unfavorable EC when the concentration of oxidant is constant. It is also found that, the EC of PANI/H_2SO_4/cellulose is slightly lower than that of PANI/HCl/cellulose, even there is a great difference in their concentration of hydrogen cations. It is because hydrogen bands interaction between HSO_4^- and PANI chains may be present (Gemeay et al., 2005).

3.3.2. Effect of activation time

Table 2 lists the effects of the activation time on the content of PANI and the EC of cellulose–PANI composites. The percolation threshold for EC is observed when the PANI content in the composites increases from 2.2% to 11.0%. The EC increases from 1.0×10^{-5} to 6.0×10^{-3} S/cm with the activation time increasing from 30 to 50 min. It could be explained that in the excessive acids region, a large number of aniline monomers were loaded on the cellulose surface because of the strong hydrogen band interaction between aniline and hydrogen groups of cellulose, which results in the improvement of the yield of PANI. When the activation time increases from 50 to 120 min, slight gradual increase in the PANI content and small gradual decrease in electrical conductivity can be seen in Table 2. This is to some extent related to the aggregation of PANI particles. This behavior is in agreement with the results obtained by Yin, Li, Li, Wu, and Gu (1997).

3.3.3. Effect of the amount of aniline

Table 3 shows the effects of the amount of aniline monomer on the PANI content and the EC of cellulose–PANI composites. The molar ratio between aniline and HCl keeps constant (1:10) during the preparing process. The amount of acids increases with the increase of aniline used. Consequently, the amount of aniline deposited on the surface of cellulose also increase. As shown in Table 3, both the PANI content and the EC of the composites increase with the amount of aniline increasing from 0.18 to 0.5 g. Nevertheless, it is too tiny for the EC of the composites to be examined when the aniline used are 0.08, 0.1 and 0.15 g, as well as the PANI content when aniline is 0.08 g. It indicates that the composites approach to insulator under the above reaction conditions. When the aniline used is up to 0.5 g, the highest PANI content and the EC of the composites can be observed and the values are 21.2% and 3.0×10^{-2} S/cm, respectively. The EC of pure PANI (100% PANI content) is 0.142 S/cm, which is not reported for sake of brevity. It is apparent that the cellulose–PANI composites are present with favorable conductivity. It would be a promising material in the application of electrode, gas sensor and membrane fields.

Table 1
Effects of the types of acids on the PANI content and the electrical conductivity of cellulose–PANI composites

Dopant	Content of PANI (wt.%)	Electrical conductivity (S/cm)
HCl[a]	7.8	2.0×10^{-3}
H_2SO_4[b]	11.6	9.7×10^{-4}
H_3PO_4[b]	9.2	1.18×10^{-5}
p-TSA[a]	3.4	1.97×10^{-4}

The conductive composites were prepared under the conditions: 0.5 g cellulose, 0.2 g aniline, 0.23 g APS, activation time 60 min.

[a] 20 ml of 1.0 mol/L.

[b] 10 ml of 1.0 mol/L.

Table 2
Effects of activation time on the PANI content and the electrical conductivity of cellulose–PANI composites

Activation time (min)	Content of PANI (wt.%)	Electrical conductivity (S/cm)
30	2.2	1.0×10^{-5}
50	11.0	6.0×10^{-3}
60	11.5	4.71×10^{-3}
90	12.4	3.67×10^{-3}
120	13.0	1.18×10^{-3}

The conductive composites were prepared under the conditions: 0.5 g cellulose, 0.2 g aniline, 20 ml 1.0 mol/L HCl and 0.23 g APS.

Table 3
Effects of the amount of aniline on the PANI content and the electrical conductivity of cellulose–PANI composites

Amount of aniline (g)	Content of PANI (wt.%)	Electrical conductivity (S/cm)
0.08	–	–
0.1	1.8	–
0.15	2.0	–
0.18	4.0	2.43×10^{-4}
0.2	7.8	1.84×10^{-3}
0.3	9.6	2.71×10^{-3}
0.5	21.2	3.0×10^{-2}

The conductive composites were prepared under the conditions: 0.5 g cellulose, aniline/APS (concentration ratio) = 1:1, aniline/HCl (molar ratio) = 1:10, activation time 60 min.

4. Conclusions

In the present paper, cellulose–PANI conductive composites were prepared by chemical oxidative polymerization of aniline with natural cellulose activated by various acids. The conductive composites were characterized by FT-IR, TEM and TG analysis. The absence of intermolecular hydrogen bands interaction of cellulose macromolecules were confirmed by FT-IR. This result affects the thermo-stability of the composites to some degree. It is suggested that PANI was loaded on the surface of cellulose in the form of slices by TEM analysis. The thermal analysis by TGA indicates that the composites are more thermo stable than pure cellulose due to the safeguard from PANI slices. The composites prepared using the di-basic acids exhibit more excellent conductivity than the composites prepared using the monobasic acids. The content of PANI increases with increasing of activation time, and while the conductivity decreases because of the aggregation of PANI particles at the activation time range from 50 to 120 min. Both the PANI content and the electrical conductivity increase with an increase of the amount of aniline, and reached the maximum values at the 0.5 g aniline, respectively. The cellulose–PANI conductive composite would be a promising material in application in electrode, gas sensor and membrane fields.

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