

# Polyaniline (PANI) Composites – Preparation in Carbonated Water, PANI/Pulp Paper Sheet, and PANI/Surfactant

## Abstract

*The polymerisation of aniline in the presence of pulp was carried out in saturated carbonated water in the place of sulfuric acid for the preparation of a PANI/pulp composite, and a conductive paper sheet was prepared from the composite using the papermaking technique. The surface structure and conductivity were examined. Furthermore, micro-fibre of PANI was prepared using a surfactant.*

**Key words:** carbon dioxide, electrical conductivity, pulp, polyaniline, micro-fibre.

## Introduction

Generally the synthesis of polyaniline (PANI) as an electrical conductive polymer can be carried out with chemical or electrochemical polymerisation. Recently the polymerisation of aniline monomer in carbonated water was performed to obtain polyaniline [1]. Moreover the preparation of a PANI/pulp composite with sulfuric acid has also been performed, and a conducting paper was prepared from the PANI/pulp composite by a papermaking technique [2]. The combination of textile and conducting polymer can open a new avenue for textile materials science [3 - 7]. In the present research, a PANI/pulp composite material was synthesised in carbonated water with a view to conductive textile applications. Here, carbonated water was employed for the acid conditioning of aniline polymerisation instead of sulfuric acid, which was possibly the first attempt at the preparation of a PANI based composite in carbonated water. After the reaction the polymerisation water contained no sulphuric acid, which can be an advantage for industry with respect to the environment.

The PANI/pulp composite was fabricated by a papermaking method for the preparation of a conductive paper sheet. Furthermore, polyaniline micro-fibre was prepared using a surfactant by means of the bottom up method. The materials processing techniques used in this study

may contribute to the production of new conductive materials.

## Experimental

### Materials

Aniline (Tokyo Kasei, TCI), and water were distilled prior to use. Ammonium persulphate (APS; Kanto Chemicals, Japan) was used as received. For the present research saturated carbonated water was prepared by the injection of high pressure CO<sub>2</sub> gas into the distilled water in a small stainless steel jar prior to the polymerisation of aniline. A membrane filter (Toyo filter paper) was homogenised in an appropriate amount of carbonated water to prepare dispersed pulp fibres. Furthermore sodium dodecylbenzene sulphonate (SDBS) was obtained from TCI.

### Synthesis

The PANI/pulp composite was prepared by the following method: Aniline (3.0 g) and pulp (3.0 g) were added to 240 mL of saturated carbonated water in an Erlenmeyer flask at room temperature. The mixture was stirred for 30 min at 0 °C. APS (9.0 g) was then slowly added to the mixture at 0 °C. After 24 h, the mixture was filtered, washed with a large volume of water for 12 h, filtered again, and the resultant material was then washed with a large volume of methanol for 12 h. After filtration, the PANI/pulp mixture was dried. Next a PANI/pulp composite paper sheet was prepared using a papermaking technique [2]. The composite fibres were dispersed in a large volume of water, and the suspension was then filtered using a large Büchner funnel. A wet dark-coloured PANI/pulp paper layer appeared on the filter paper of the Büchner funnel. The wet PANI/pulp layer was sandwiched between a thin aluminium plates

and several pieces of dry paper, pressed to remove moisture, and then the PANI/pulp composite sheet was dried.

The composite sheet was immersed in ammonia/water to neutralise the PANI component in the paper sheet, during which the colour of the surface changed from dark emerald green to dark blue, and was then dried at room temperature. The reduction treatment in ammonia produces a composite paper sheet with insulating properties.

The preparation of PANI/SDBS was carried out as follows: SDBS (25 mg), water (0.5 g), and *N*-methyl-2-pyrrolidone (0.2 g) were added to a suspension (10 mg, conc. < 2.5%) of polyaniline (as polymerisation solution) in CO<sub>2</sub>, and the mixture was ultrasonicated for 30 min. The solvents in the solution were then evaporated using a hot stage at ca. 100 °C to yield a dark emerald green material. Visual inspection of the dark emerald green colour indicated that the resultant material consists of PANI.

### Technique

IR absorption spectra for the polymers were obtained using a Jasco IR 550 spectrometer with the KBr method. SEM observation was performed with a JEOL JSM-521. At room temperature, the electrical conductivity of the polymers was measured by using a Mitsubishi Lowrester-GP MCTP-T610 with MCP-TP06P probe and a Hioki SM-8213. Circular differential interference contrast optical microscopy (C-DIM) observations were carried out using a Nikon ECLIPS LV 100 high-resolution microscope with circular polariser and Nikon CFIUW lenses. The composition of the PANI/pulp composite paper was evaluated by X-ray photoelectron spectroscopy (XPS, JPS-9010TR, JEOL).

## Results and discussion

### IR

The IR spectra of the pulp and PANI/pulp composite paper in both forms the pristine and deprotonated using ammonia are shown in **Figure 1**. The pulp exhibits absorption bands in the high energy region due to  $\nu_{OH}$  stretching vibration at  $3378\text{ cm}^{-1}$  and  $\nu_{CH}$  at  $2897\text{ cm}^{-1}$ . In contrast, the polymer composite paper (pristine) displays no clear absorption bands related to  $\nu_{CH}$  and  $\nu_{OH}$  stretching, due to overlapping with the polymer absorptions in the same infrared region. The pristine PANI sample has an intense absorption band at  $1580\text{ cm}^{-1}$  derived from the quinoid (Q) structure, as compared with that due to the benzenoid (B) structure at  $1510\text{ cm}^{-1}$ . This is characteristic of IR absorptions of emeraldine salt, while the deprotonated PANI/pulp (treated with ammonia) displays relatively weak Q structure absorption, indicative of the emeraldine base.

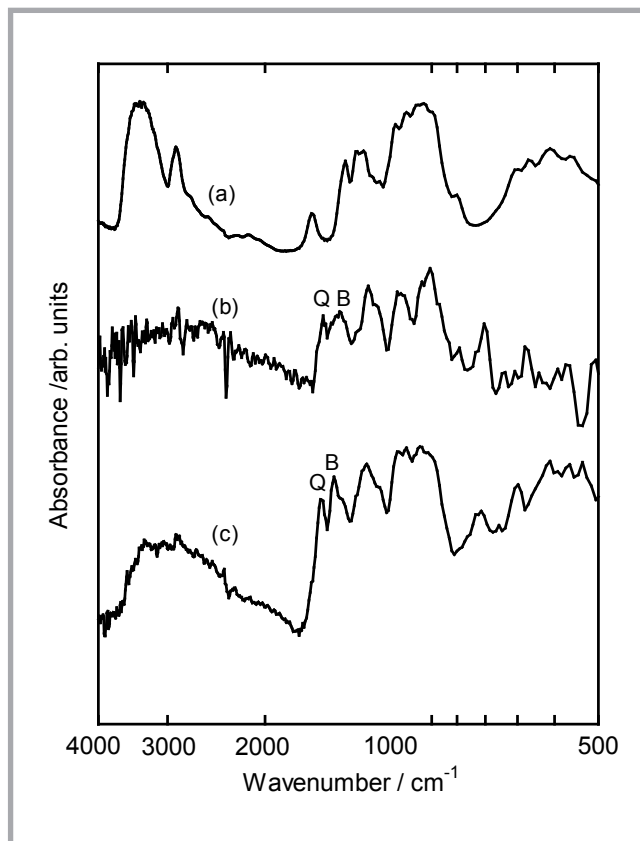
### Electrical conductivity

The pristine PANI/pulp composite paper sheet displays a rapid decrease ( $<5\text{ s}$ ) in resistance from  $>10\text{ M}\Omega$  to ca.  $1.35\text{ k}\Omega$  upon *in situ* vapour phase doping with hydrochloric acid. In this case, hydrochloric acid functions as an agent for further protonation, and a salt form (conductive state) is produced from the emeraldine base of PANI in the composite, as indicated by the quick decrease in resistance (increase in conductivity).

### Surface image

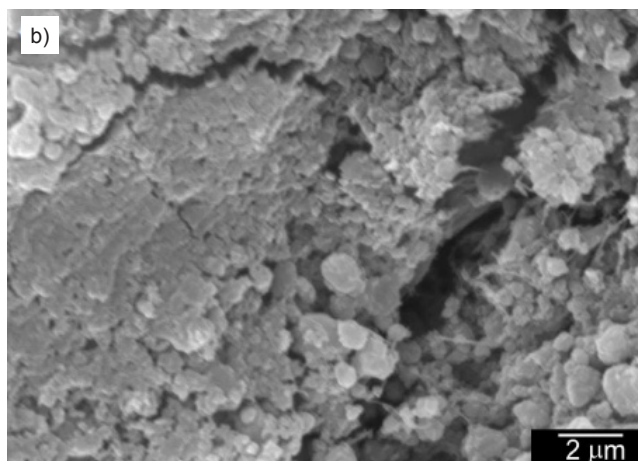
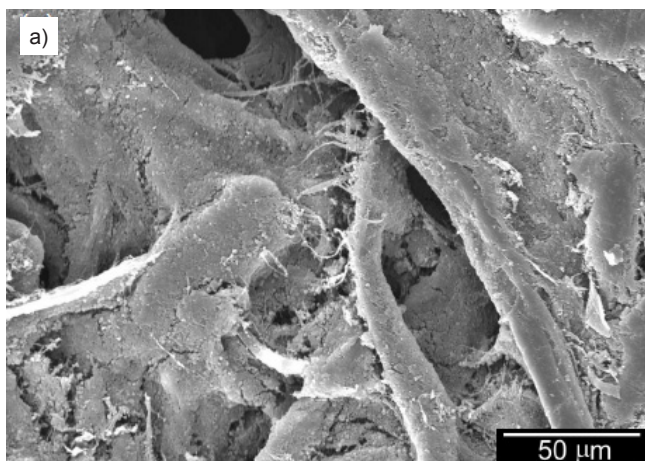
The pristine PANI/pulp composite paper sheet has a smooth surface of dark emerald green colour. Although a PANI/pulp composite sheet was obtained with sul-

**Figure 1.** IR absorption spectra of (a) the pulp, (b) pristine PANI/pulp (emeraldine salt), and (c) PANI/pulp treated with ammonia (emeraldine base).

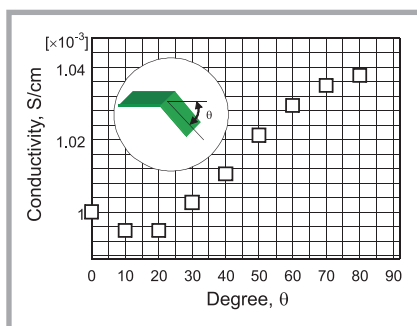


furic acid in a previous study [2], this result demonstrates that a conductive sheet can be prepared by using carbon dioxide instead of acid reagents. The low magnification SEM image of the PANI/paper composite paper sheet in **Figure 2.a** indicates that the PANI coated the entire sheet. The higher magnification SEM image in **Figure 2.b** shows fine particle agglomerates distributed over the individual fibres. The SEM images visually demonstrate that the polymerisation of the aniline monomer on the pulp surface is achieved in the presence of APS in saturated carbonated water. **Figure 3**

shows the change in conductivity with the bend angle. The sample was doped with vapour phase of HCl before the conductivity measurements. The conductivity measurements were carried out by the two-probe method along the sample length. The inset of **Figure 3** shows an illustration of the bend degree. An increase in the bend degree allows an increase in electrical conductivity. This can be due to the fact that the bending process made the paper dense, which partly improves the conduction pass, resulting in an increase in electrical conductivity.



**Figure 2.** SEM image of the composite paper sheet surface at (a)  $500\times$  and (b)  $6,000\times$  magnification.



**Figure 3.** Conductivities of the PANI/pulp paper as a function of the bend degree ( $\theta$ ). The inset shows the bend degree. The conductivities were obtained by the two-probe method.

### Composition

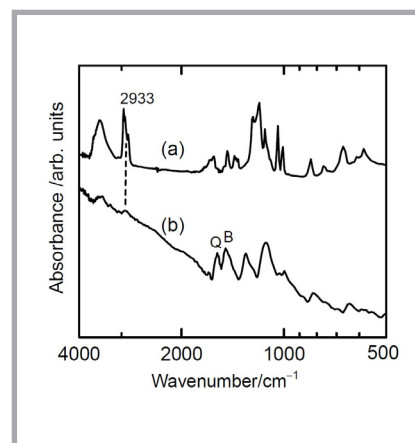
**Figure 4.a** shows the X-ray photoelectron spectroscopy (XPS) measurement result of the PANI/pulp. The PANI/pulp was treated with hydrazine for the preparation of a completely reduced (dedoped) state of the PANI in the composite, and the sample was washed with ethanol and dried in a vacuum before the XPS measurement. XPS signals of nitrogen and oxygen appear at 399 eV (abundance =

= 24.36%) and 533 eV (abundance = = 75.64%), respectively. Magnification of the XPS result clearly indicates these signals, as shown in **Figures 4.b, 4.c**. The composition of MRU<sub>PANI</sub>/MRU<sub>CELLULOSE</sub> (MRU = monomer repeat unit, MRU<sub>PANI</sub> = C<sub>6</sub>H<sub>5</sub>N, MRU<sub>CELLULOSE</sub> = C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>) of the composite is calculated to be ca. 15.5, obtained from the XPS data. However, this composition value was estimated for only the skin of the PANI/pulp because XPS analysis was carried out for the surface of the sample.

### PANI and surfactant

The treatment of polymers with surfactant can produce a characteristic structure, such as a sphere. In this study, the treatment of PANI with a surfactant (SDBS) was conducted to explore the preparation of an ordered structure.

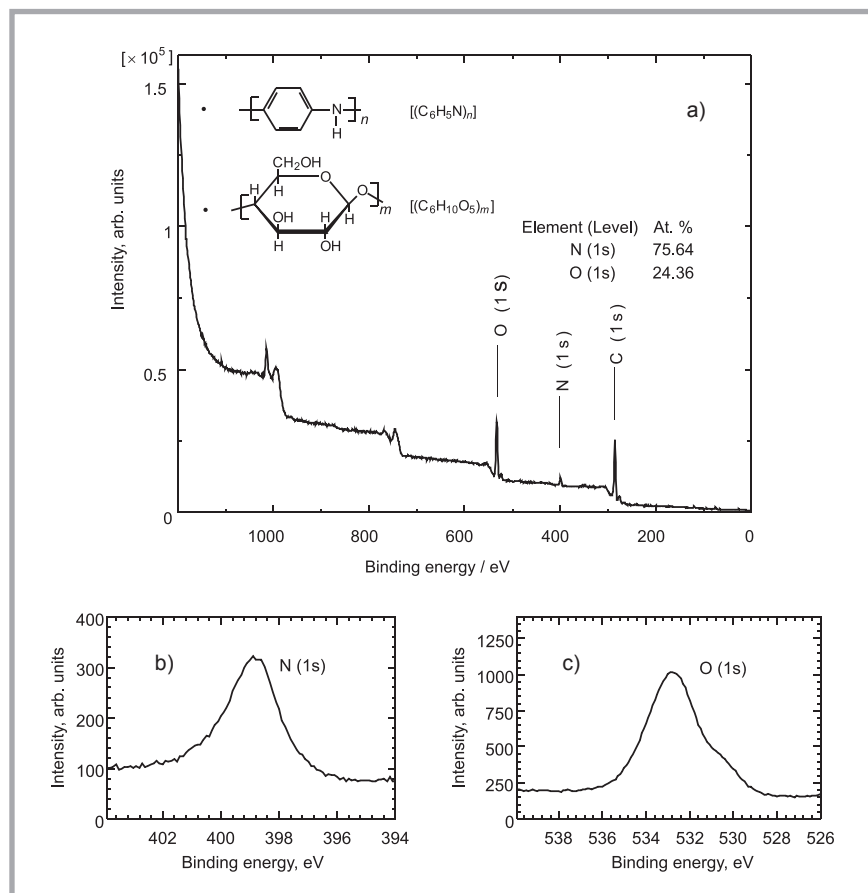
**Figure 5** shows the IR absorption spectra of SDBS and the resultant material. The absorption band of SDBS at 2933 cm<sup>-1</sup> is due to the stretching vibrations of alkyl groups (CH<sub>2</sub>, and CH<sub>3</sub>) (**Figure 5.a**). The surfactant treated compound shows



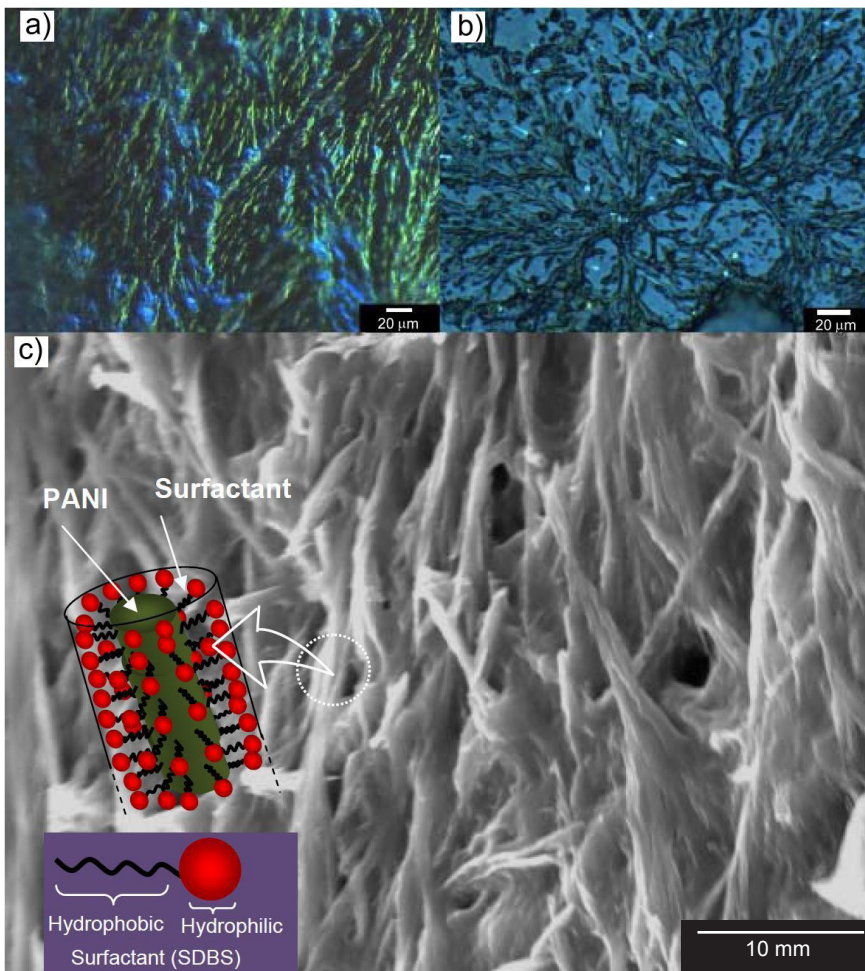
**Figure 5.** IR absorption spectra of (a) sodium dodecylbenzene sulphonate (SDBS) and (b) PANI/SDBS composite.

a weak absorption signal due to these alkyl groups at 2933 cm<sup>-1</sup> and absorption bands at 1570 cm<sup>-1</sup> and 1484 cm<sup>-1</sup> due to the Q and B structures, respectively (**Figure 5.b**). Other absorption bands, such as 1293 cm<sup>-1</sup> (C-N stretching of the ternary aromatic amine), 1128 cm<sup>-1</sup> (in-plane C-H vibration of the benzene ring) and 823 cm<sup>-1</sup> (out-of-plane C-H vibration of the benzene ring) are characteristic of PANI [9]. These results suggest that the material obtained is a PANI/SDBS composite. Circular differential interference contrast optical microscope images of the PANI/SDBS indicate microfibril structures with colour at low magnification, as shown in **Figure 6.a**. The PANI/SDBS composite exhibits a radial structure, like a dendrite in the neuron system, revealed at higher magnification (500 ×), as shown in **Figure 6.b**. The SEM image (2000 ×) of the PANI/SDBS composite confirms the formation of a microfibril structure, as shown in **Figure 6.c**. An ordered structure is derived from the self-assembly process due to the aggregation properties of the surfactant [10 – 12]. This experiment demonstrates that the treatment of PANI with a surfactant enables the formation of an ordered microstructure. The electrical conductivity of the PANI/SDBS composite is 2.3 × 10<sup>-5</sup> S/cm, evaluated by the four-probe method.

A proposed schematic illustration of the PANI/SDBS composite structure is given in **Figure 6** (c, inset). The hydrophilic moiety of SDBS (anion part) and the hydrophobic alkyl group located in the outer layer and core, respectively, form the micro-fibril structure.



**Figure 4.** X-ray photoelectron spectroscopy (XPS) measurement result of the PANI/pulp sheet. Wide scan measurement (a) (At = atomic%), narrow scan measurement at nitrogen region (b), and narrow scan measurement at oxygen region (c). Inset (a) shows the molecular structure of PANI and cellulose, and chemical formulas.



**Figure 6.** Circular differential interference contrast optical microscopy (C-DIM) images at (a) 200 $\times$  and (b) 500 $\times$ , and (c) SEM image of the PANI/SDBS composite at 2000 $\times$ . (Inset (c)) plausible structure of PANI/SDBS micro-fibres. SDBS = sodium dodecylbenzene sulphonate (surfactant).

## Conclusions

A PANI/pulp paper was prepared by the polymerisation of aniline in CO<sub>2</sub> water in the presence of pulp, followed by a papermaking procedure. Generally, the employment of a high boiling point solvent, such as *N*-methyl-2-pyrrolidone, and evaporation processes is required for the

preparation of conductive polymer films using the casting method. On the other hand, the conductive paper sheet has advantage of processability.

In this study, the surface structure, electrical conductivity and sensor function were examined. Furthermore a PANI/surfactant composite with an or-

dered structure was prepared in a mixed solution of water. These simple and convenient methods for the preparation of a conductive organic composite may enable to produce low-cost conductive polymer materials, which may extend to industrial applications.

## Acknowledgment

The author would like to thank the Glass workshop of the Central Workshop of the University of Tsukuba for the fine glass work. H. Kawashima measured the XPS for the sample.

## References

- Goto, H. *Fibres & Textiles in Eastern Europe*, **2011**, 19, 15–17.
- Goto, H. *Text. Res. J.*, **2011**, 81, 122–127.
- Śniechowski, M.; Łuźny, W.; Djurado, D.; Dufour, B.; Rannou, P.; Proń, A.; Bee, M.; Johnson, M.; Gonzales, M. *Fibres & Textiles in Eastern Europe*, **2005**, 13, 96–99.
- Fryczkowski, M.; Rom, M.; Fryczkowska, B. *Fibres & Textiles in Eastern Europe*, **2005**, 13, 141–143.
- Połowiński, S.; Szumilewicz, J.; Stawski, D. *Fibres & Textiles in Eastern Europe*, **2011**, 19, 119–123.
- Krucińska, I.; Urbaniak–Domagała, W.; Skoneczna, M.; Cosseddu, P.; Bonfiglio, A. *Fibres & Textiles in Eastern Europe*, **2011**, 19, 78–83.
- Rahman, N. A.; Gizdavic-Nikolaidis, M.; Ray S.; Eastal A.J.; Travas-Sejdic J. *Synth. Met.*, **2010**, 160, 2015–2022.
- Tang, J.; Jing, X.; Wang, B.; Wang, F. *Synth. Met.*, **1988**, 24 231–238.
- Landfester, K.; Montenegro, R.; Scherf, U.; Gunter, R.; Asawapirom, U.; Patil, S.; Neher, D. Kietzke, T. *Adv. Mater.*, **2002**, 14, 651–654.
- Li, Y.; Wang, Y.; Wu, D.; Jing, X. *J. Appl. Polym. Sci.* **2009**, 113 868–875.
- Tada, K.; Onoda, M. *Thin Solid Films*, **2006**, 499, 19–22.

Received 03.11.2010 Reviewed 20.09.2011



# FIBRES & TEXTILES in Eastern Europe

reaches all corners of the world! It pays to advertise your products and services in our magazine! We'll gladly assist you in placing your ads.