

## Reinforced Conductive Polyaniline-Paper Composites

Jinhua Yan <sup>a,b,\*</sup> and Renmei Xu <sup>c</sup>

A method for direct aniline interfacial polymerization on polyamideamine-epichlorohydrin (PAE)-reinforced paper substrate is introduced in this paper. Cellulose-based papers with and without reinforcement were considered. The polyaniline (PANI)-paper composites had surface resistivity lower than 100  $\Omega$ /sq after more than 3 polymerizations. Their mechanical strength and thermal stability were analyzed by tensile tests and thermogravimetric analysis (TGA). Fourier transform infrared (FTIR) results revealed that there was strong interaction between NH groups in aniline monomers and OH groups in fibers, which did not disappear until after 3 polymerizations. Scanning electron microscopy (SEM) and field emission (FE) SEM images showed morphological differences between composites using reinforced and untreated base papers. Conductive composites made with PAE-reinforced base paper had both good thermal stability and good mechanical strength, with high conductivity and a smaller PANI amount.

*Keywords:* Functional composites; Flexible composites; Electrical properties; Scanning electron microscopy (SEM); Interfacial polymerization

*Contact information:* a: Guangdong Industry Technical College, China; b: Department of Forest Biomaterials, North Carolina State University, Raleigh, NC, USA; c: Department of Technology, College of Applied Sciences and Technology, Ball State University, Muncie, IN, USA;

\* Corresponding author: Jhyan2000@yahoo.com

### INTRODUCTION

Polyaniline (PANI) is considered to have a very high potential for commercial application relative to other conductive polymers (Ding *et al.* 2010) because of its metal-like conductivity, reversible chemical properties, different morphology (Rehim *et al.* 2010), electrochemical properties, physical properties, and relatively cheap monomers. Micro/nanostructured PANI has attracted much interest in recent years due to the additional characteristics of nano-materials in general (Zhu *et al.* 2011). Various methods have been reported to prepare PANI nanofibers using routes based on chemical oxidative polymerization. Examples include uniform porous membranes as templates (Martin 1994; Wu *et al.* 1994), soft templates (*e.g.*, surfactants) (Wei *et al.* 2002; Zhang *et al.* 2004), electrospinning (Reneker and Chun 1996; Norris *et al.* 2000), interfacial polymerization (Huang *et al.* 2004a; 2006), oligomer-assisted polymerization (Li *et al.* 2004), seeding polymerization (Zhang *et al.* 2004), rapid-mixing reactions (Huang *et al.* 2004b; 2006), radiolytic synthesis (Pillalamarri *et al.* 2005), and dilute polymerization (Chiou and Epstein 2005a,b), which have been used to produce PANI nanofibers and/or nanotubes. Since all of these methods depend on either a template or a specific complex chemical reagent, post-synthetic treatments are needed to remove them from the products and to recover the nanostructured PANI. Thus it is important to develop syntheses that do not rely on templates, structural directing molecules, or specific dopants, especially when scaling up to produce large quantities of nanostructured materials and composites.

Paper is a porous sheet made up of cellulose fibers. The sheet usually has many pores generated by the fiber intertexture in both micro and nano sizes, depending on paper grades and manufacturing processes. Cellulose fiber is a classic carbohydrate, consisting of thousands of glucose units linked by linear  $\beta$ -1,4-glycosidic bonds. Each unit has three free hydroxyl groups, except at both ends. As a result, cellulose paper is intrinsically hydrophilic and contains strong hydrogen bonds after being dried. Since the paper substrate has many advantages, such as biological compatibility, being environmentally friendly, light weight, and low cost, it becomes more common to be used as a basis for composites.

Both paper and plastic have large areas and flexibility, so they are inherently suitable for substrates in electric devices and energy storage fabrication by conduction (Hu *et al.* 2009). However, base paper is superior to plastic, due to its adjustable porosity, high productivity, low cost, reproducibility, and non-polluting nature (Nyholm *et al.* 2011). This kind of conductive material will have extensive applications in electromagnetic shielding, anti-static packaging, hot film, proton exchange membrane fuel cells, biological sensors, and actuating (Johnston *et al.* 2006; Agarwal *et al.* 2009).

Nowadays, most research pertaining to conductive paper involves the use of composite fibers. Coating cellulosic fibers with conductive polymers can be accomplished using more than one method, of which the most popular is the *in situ* polymerization of monomers in the presence of pulp fibers (Huang *et al.* 2006; Kelly *et al.* 2007; Youssef *et al.* 2012). It is sometimes presumed that only fibers fully encapsulated with polymer can provide conductivity. However, the strength of papers made with such fibers are dramatically decreased, since the hydrogen bonding between pulp fibers is depressed by the PANI coating layers (Youssef *et al.* 2012; Goto 2011; Youssef *et al.* 2012). In addition, in-site polymerization of aniline monomers in the fiber suspension faces other difficulties. For example, the fiber cell lumen provides a large chamber to polymerize aniline monomers, so the amount of aniline consumed is excessive and inefficiently utilized (Qian *et al.* 2010). Post-treatment with a large water load should also be considered carefully. The use of paper rather than fiber as a composite base provides a means to solve the aforementioned problems. A practical way to transfer conductive PANI into a paper substrate to fabricate conductive paper at low cost, high efficiency, and using a clean process needs to be explored for this metal-like conductive polymer to be applied to paper.

Here we report a novel, simple method to combine paper with PANI. In this method, aniline monomers react with oxidant on porous paper using multiple interfacial polymerizations. The PANI-paper composites obtained from this chemical oxidative polymerization route have the obvious advantages of being simple, water pollution free, sized adjustable, highly efficient, directly useable, and cheap. As such, they may be much more easily applied commercially.

## EXPERIMENTAL

### Methods

Filter paper (quantitative filter paper with a medium filtering speed and a basis weight of 82 gsm; Huangzhou Wohua Filter Paper Ltd., China) was selected as the paper substrate due to its open matrix structure and lack of filler materials or any surface treatment. In addition, filter paper usually has more pores and higher permeability.

The interfacial polymerization was carried out in a watch glass with a large diameter to fully spread the filter paper. Aniline monomers (used as delivered, Chemical Pure (C.P.); Guangzhou Chemical Reagents Co., China) were diluted to 0.365 mol/L in carbon tetrachloride (CCl<sub>4</sub>) (marked as solution A, Analytical Reagent (AR); Tianjing FuYu Finechemical Co., China). Ammonium persulfate (AR; Sinopharm Chemical Reagent Co., Ltd., China) was dissolved into a solution of 0.184 mol/L distilled water (marked as solution B) containing 0.5 mol/L hydrochloric acid (AR; Guangzhou Donghong Chemical Co., China). The filter paper was placed in a clean watch glass and then evenly and thoroughly wetted by several drops of solution A. Excess solution A was squeezed out so that the filter paper was not saturated. The filter paper was quickly transferred to another clean watch glass and evenly set in place. Solution B was added carefully to the glass to soak the filter paper. After several seconds, the filter paper was picked up to be pressed again and allowed to air dry overnight. This ended the first round of aniline polymerization. Before the second round of polymerization, the filter paper was dried by blowing hot air (40 °C) across its surface until the weight reached equilibrium (weight data keeps constant). The above process was repeated, and the third and subsequent cycles were performed as required. The weight of the filter paper was measured after each polymerization.

Reinforced filter paper was treated in a manner similar to the “pond sizing” process, in which a substrate passes through a pond which contains sizing solution and makes the substrate wet, used on certain paper machines. Filter paper was soaked in a polyamideamine-epichlorohydrin (PAE) resin solution (commercial grade, 12.5% solids, used as diluted) for 3 min (PAE aqueous solutions are widely used as a wet strength agent in paper making). Wetted filter paper was pressed, and dried using a hot iron at 105 °C. Reinforced filter paper (88 gsm) was obtained and used for multiple aniline interfacial polymerizations to make the conductive paper composites described above.

The nature of the PANI-paper composite after each polymerization was examined in terms of strength and morphology. Strength was measured using the four probe technique and a nanovoltmeter-current source (Keithley, Model 6221; USA) (Valiavalappil and Harinipriya 2012). Each resistance value was determined from an average of 3 tests. Morphology was obtained using two kinds of scanning electron microscopes (SEM) (ZEISS EVO 18, Germany, for routine SEM and LEO 1530VP, Germany, for field emission SEM (FESEM)). The strength and thermal stability were analyzed, respectively, by a tensile tester and a thermogravimetric analyzer (TGA Q500, TA Instruments, USA) with a heating rate of 10 °C/min and a nitrogen flowing rate of 25 mL/min. The Fourier transform infrared (FTIR) spectra of the samples were recorded on a Perkin-Elmer FT-IR (Model 1000; USA) in the 4,000 to 400 cm<sup>-1</sup> range, at a resolution of 4 cm<sup>-1</sup> and across 16 scans.

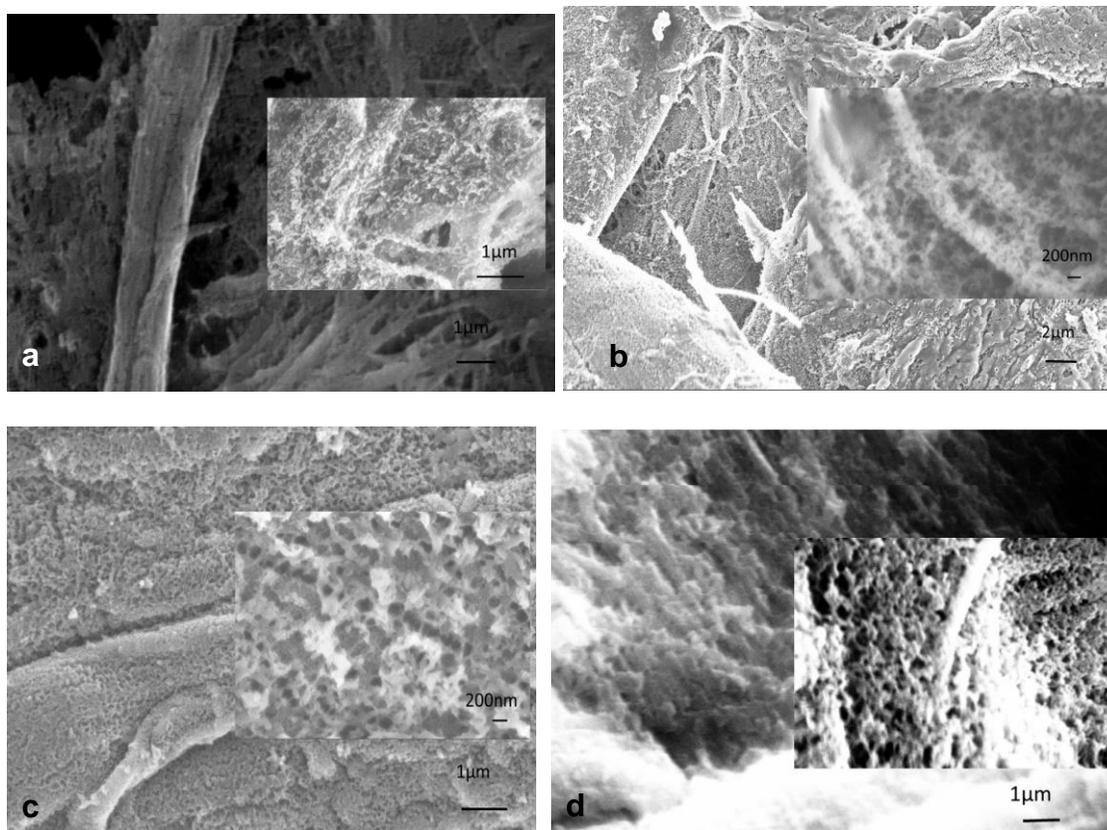
## RESULTS AND DISCUSSION

### Morphology of PANI-Paper Composites

Multiple interfacial polymerizations on paper are different from normal interfacial polymerization in several aspects. During the first round of polymerization, aniline monomers were dispersed in CCl<sub>4</sub> as solution A and the paper substrate was wetted by solution A. Since excess solution A was pressed out after wetting, the paper was unsaturated and the aniline should have been absorbed and well-distributed on the fibers.

When the oxidant solution B was added slowly, interfacial polymerization for aniline monomers and the oxidant took place on the fiber's surface. Aniline fibers very close to the inside surface did not have a chance to react, since the solvent  $\text{CCl}_4$  repelled the oxidant water solution and prevented it from entering. The pressing was not strong enough to squeeze all excess liquid out of the pores of paper. As a result, some of the liquid was left in capillary spaces between fibers. The liquid in the inner capillaries that maintained the aniline solution moisture also participated in the interfacial polymerization once solution B came in contact with it. It is possible to observe the resulting solids that remained on the fiber surface and in the inner holes between fibers in Fig. 1. Since routine SEM images cannot see the particle detail, FESEM was used. After magnifying the picture using FESEM, the initial polymer (aggregates) can be seen on the fiber surface and in the inner holes at around 10 nm. The composite resistivity was in the  $8.9 \times 10^4 \Omega/\text{sq}$  range, which is 10 times lower than that of filter paper. However, the aggregates were not interconnected with each other so that the conductivity was still low.

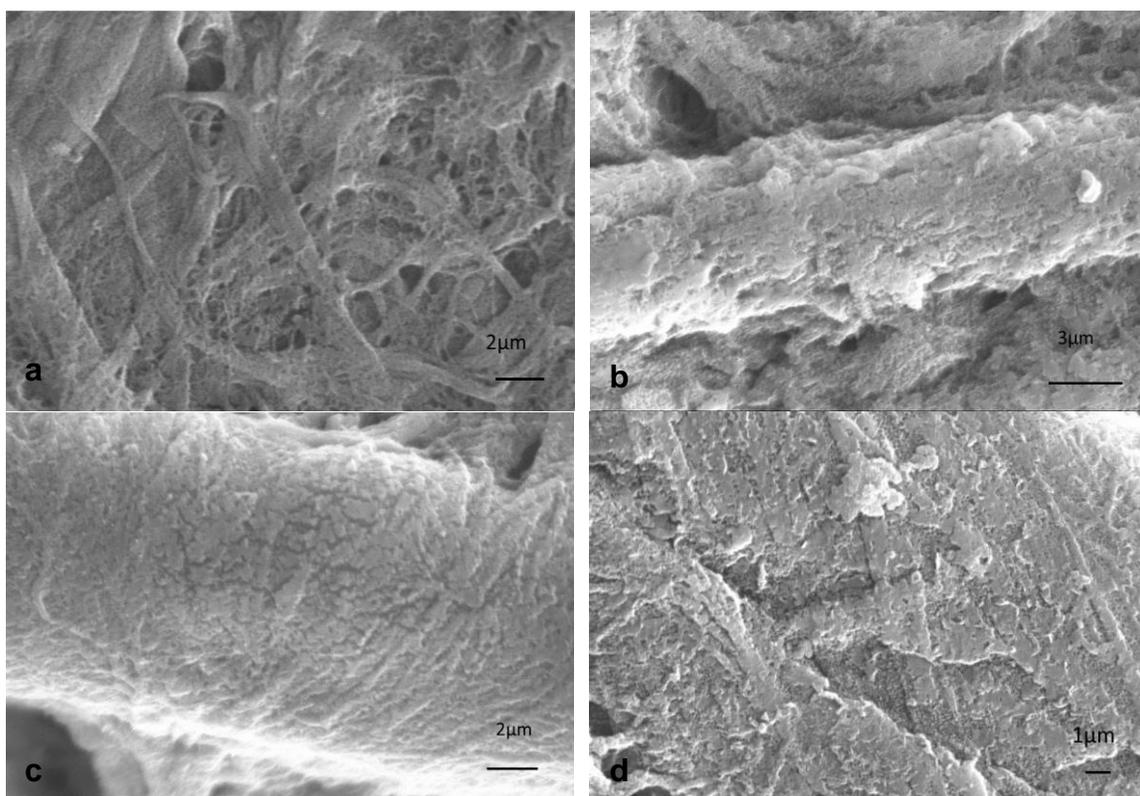
The reinforced filter paper composite had a similar morphology after the 1<sup>st</sup> polymerization in Fig. 2a. There were very small particles attached to the fibers. The resistance was in the  $2 \times 10^5 \Omega/\text{sq}$  range, which is higher than that of the untreated filter paper composite.



**Fig. 1.** Paper-PANI SEM morphology: (a) fiber surface with initial PANI after 1<sup>st</sup> polymerization and its magnification in FESEM; (b) fiber surface with PANI after 2<sup>nd</sup> polymerization and its magnification in FESEM; (c) fiber surface with PANI after 3<sup>rd</sup> polymerization and its magnification in FESEM; and (d) PANI on paper after 4<sup>th</sup> polymerization and 6<sup>th</sup> polymerization on the right corner

After the 2<sup>nd</sup> polymerization, the composite morphology was clearly apparent by SEM (Fig. 1b). The PANI molecules were growing on the fiber surface and in the holes between fibers. The network of PANI had partially formed, yielding a resistivity of 2620  $\Omega$ /sq, which had decreased by a large scale. After the 3<sup>rd</sup> polymerization, the network of PANI had accumulated on the paper substrate (Fig. 1c). The PANI in the holes was linked to the fibers, paving an electrical path. At this time, the measured resistance was 290  $\Omega$ /sq, hundreds of times lower than the composite after the 1<sup>st</sup> polymerization. The 4<sup>th</sup> and 5<sup>th</sup> cycles of polymerization of the composites further lowered their resistivity to 152  $\Omega$ /sq and 72  $\Omega$ /sq, respectively.

The reinforced filter paper composites exhibited different morphology after the 2<sup>nd</sup> polymerization (Fig. 2b). One can see that the PANI crumbs on fibers were not linearly linked. This crumb shape weakened the conductivity contribution, and made the composite resistivity as high as 7380  $\Omega$ /sq. This kind of PANI shape was retained after further polymerizations (Figs. 2c and 2d) so that the composite resistivity remained as high as 256  $\Omega$ /sq after the 5<sup>th</sup> polymerization.



**Fig. 2.** PAE reinforced Paper-PANI SEM morphology: (a) fiber surface with initial polyaniline after 1<sup>st</sup> polymerization; (b) fiber surface with PANI after 2<sup>nd</sup> polymerization; (c) fiber surface with PANI after 3<sup>rd</sup> polymerization; and (d) PANI on paper after 5<sup>th</sup> polymerization

### FTIR Spectra of PANI-Paper Composites

Aniline monomers have a benzene ring with an amino group. Nitrogen atoms in the amino group can easily link with surrounding H atoms in the hydroxyl groups of fibers to form hydrogen bonds. Oxygen atoms in hydroxyl groups also form hydrogen bonds with H atoms in amino groups. Initial aggregates of PANI should be strongly absorbed on the fiber surface.

To confirm the formation of PANI on the cellulose fibers, FTIR spectra of the PANI-incorporated substrate in the transmission mode were recorded. The FTIR spectroscopic evidence confirmed that PANI synthesized on the fiber surface had different characteristic vibrational transitions than those in emeraldine salt, under identical experimental conditions. In other words, the bands around 1590 and 1499  $\text{cm}^{-1}$  that correspond to PANI in the emeraldine base (EB) (Zhang *et al.* 2001) were not present in the composite after the 1<sup>st</sup> polymerization. Doped PANI bands of 1562  $\text{cm}^{-1}$  and 1478  $\text{cm}^{-1}$  did not appear until the 2<sup>nd</sup> polymerization (Fig. 3). This is probably because the PANI aggregates were still in an initial phase. In other words, the polymer molecules might be too small to be monitored because the polymerization was forced to stop too soon. Since PANI could be structured as benzenoid and quinoid moieties with different ratios showed different corresponding conductivity, the FTIR bands were observed to change as the polymerization was changed. For example, 1560 and 1473  $\text{cm}^{-1}$  bands shown after the 3<sup>rd</sup> polymerization moved to 1544 and 1471  $\text{cm}^{-1}$  after the 4<sup>th</sup> polymerization and then to 1545 and 1450  $\text{cm}^{-1}$  after the 5<sup>th</sup> polymerization (Fig. 4). A shift in the band around 1305  $\text{cm}^{-1}$  was readily observed due to the interaction between PANI, and OH groups in the cellulosic fibers (Fig. 3) after the 1<sup>st</sup> and 2<sup>nd</sup> polymerizations; but these became weak following the 3<sup>rd</sup> polymerization (Fig. 4). This interaction confirmed that the PANI was strongly absorbed into the paper substrate at the beginning of polymerization, as no PANI powder was discovered that needed to be wiped off, following composite drying within three polymerizations.

The pretreated paper composites showed similar spectra profiles after the 1<sup>st</sup> and 2<sup>nd</sup> polymerizations (Fig. 2). A shift in the band around 1305  $\text{cm}^{-1}$ , observed due to the interaction of PANI and fibers (Fig. 3), did not become much weaker after the 3<sup>rd</sup> polymerization (Fig. 4), unlike the untreated paper composites. Doped PANI peaks of 1562  $\text{cm}^{-1}$  and 1478  $\text{cm}^{-1}$  became sharper than those of untreated paper composites. This was probably due to the rich amide and amine groups from PAE, which strengthen the interaction between PANI and fibers, although some hydroxyl groups in fibers may be covalently bonded to PAE. It was found that PAE had a positive effect on PANI attachment to the substrate. The PAE molecules have unique four-membered 3-hydroxy-azetidinium groups (AZR) in 70 to 80% of the polyamideamine repeating units (Kricheldorf 1981). Wet-strength development of PAE-containing cellulose sheets is primarily ascribed to the ester bond formation between azetidinium groups of PAE, and carboxyl groups of cellulose fibers (Obokata and Isogai 2007). No powder was observed upon wiping off the treated paper, even after the 10<sup>th</sup> polymerization.

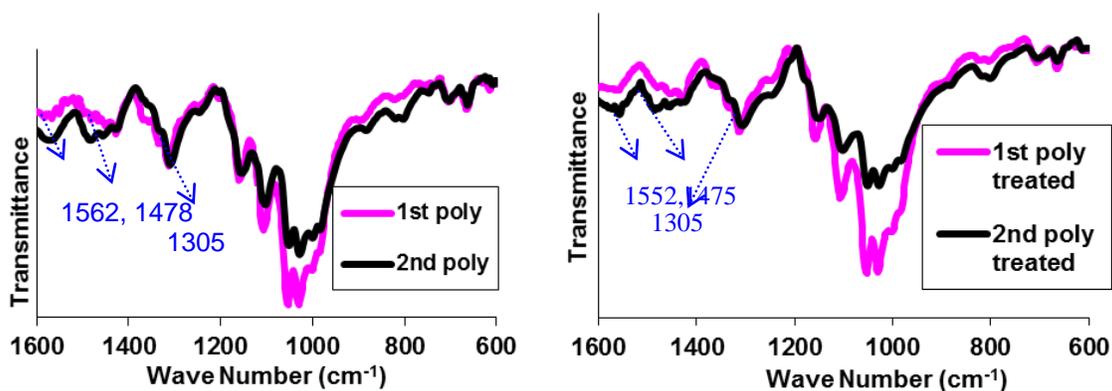


Fig. 3. Fourier transform infrared spectroscopy of composite after 1<sup>st</sup> and 2<sup>nd</sup> polymerization

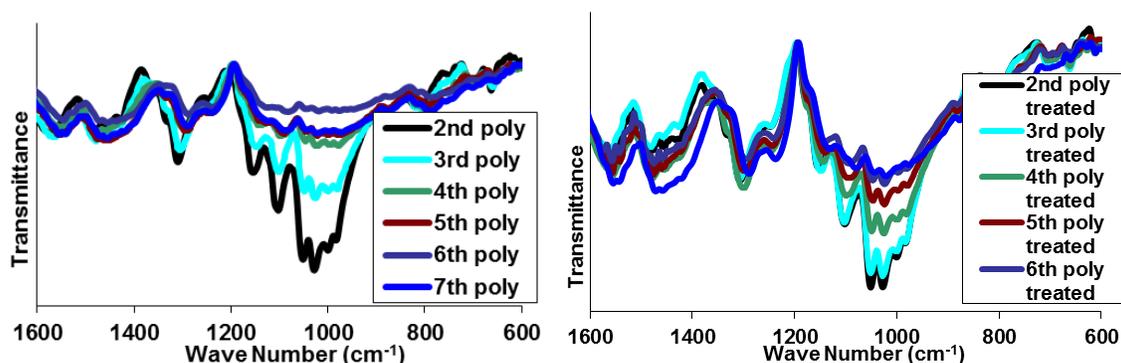


Fig. 4. Fourier transform infrared spectroscopy of composite from 2<sup>nd</sup> to 7<sup>th</sup> polymerization

It is interesting to note in Fig. 5 that the characteristic broad band for the O-H group of cellulosic fibers around  $3300\text{ cm}^{-1}$  and the band around  $2880\text{ cm}^{-1}$  due to C-H present in the  $\text{CH}_2\text{OH}$  group became gradually shortened with further polymerization until they totally disappeared after the 4<sup>th</sup> polymerization. The major cause is the full coverage of cellulose paper surface with PANI. This is further evidence of decreased interaction between fibers and external PANI in multi-layered PANI after the 3<sup>rd</sup> polymerization.

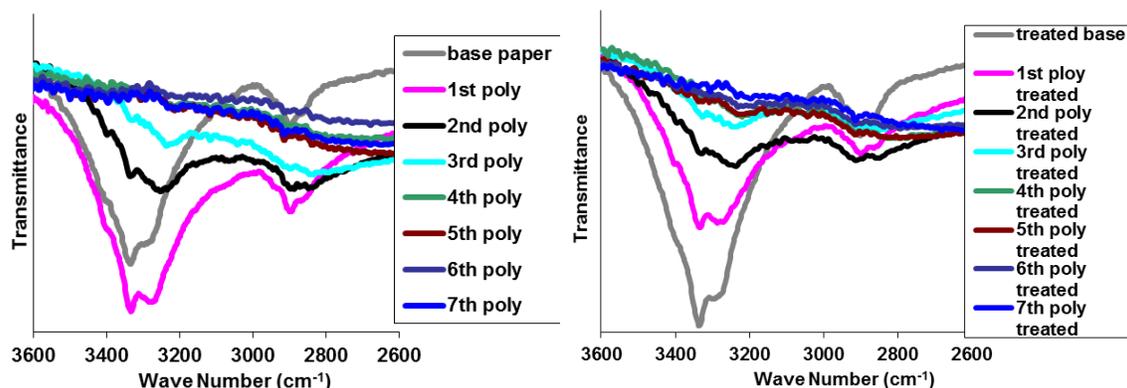


Fig. 5. Fourier transform infrared spectroscopy of composite from 1<sup>st</sup> to 7<sup>th</sup> polymerization at a higher wave number

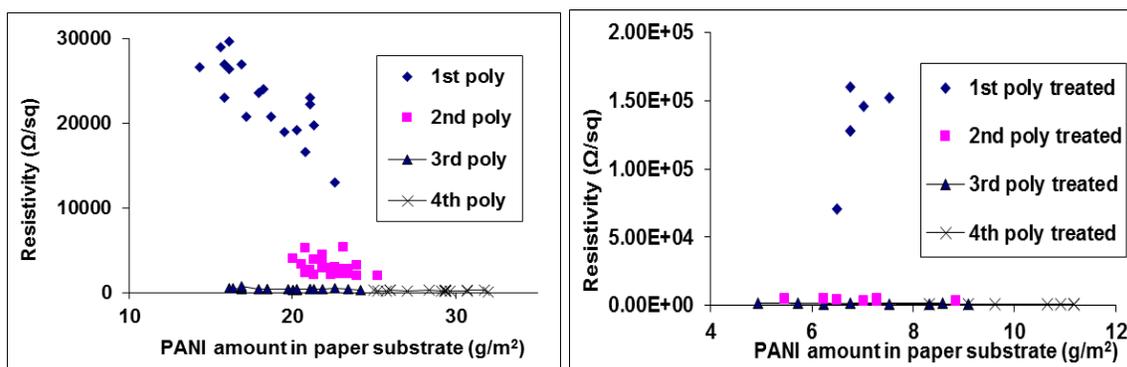


Fig. 6. Resistivity and PANI amount in paper substrate with 1-4 cycles of polymerization

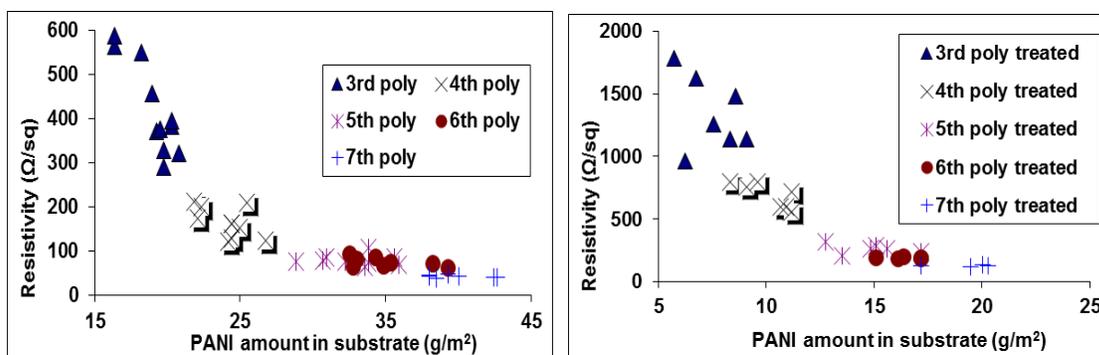


Fig. 7. Resistivity and PANI amount in paper substrate with 3-7 cycles of polymerization

### Electrical Resistance of PANI-Paper Composites

The composite conductivity greatly depended on the number of polymerization treatments and the PANI amount in the substrate. After 7 rounds of polymerization, the electrical resistance and PANI amounts in the paper substrate were measured. The composite resistivity dropped tremendously from the 1<sup>st</sup> polymerization to the 2<sup>nd</sup> polymerization (Fig. 6), and it decreased continuously after further polymerizations (Fig. 7). After the 4<sup>th</sup> polymerization, resistivity approached a steady level. In other words, the 4<sup>th</sup> polymerization was enough to build a PANI network necessary for an electrical path, and further polymerization merely consumed more aniline monomers on the multi layers of PANI networks. Reinforced paper composites performed differently, as shown in Fig. 6 and Fig. 7. They held higher resistivity but retained much lower PANI amounts. Untreated paper composites had an average resistivity of 164 Ω/sq, and 24.1 gsm PANI after the 4<sup>th</sup> polymerization and 78.7 Ω/sq with 32.8 gsm PANI after the 5<sup>th</sup> polymerization. However, PAE-reinforced paper composites had an average resistivity of 748 Ω/sq with 10.9 gsm PANI after the 4<sup>th</sup> polymerization, 256 Ω/sq with 12.7 gsm PANI after the 5<sup>th</sup> polymerization, and 79 Ω/sq with 24.2 gsm PANI after the 8<sup>th</sup> polymerization. The reinforced paper composites presented better conductivity than untreated base composites with the same PANI amount. It is believed that PAE-treated paper-PANI composites achieved advantages in lowering functional material consumption with higher conductivity.

The oxidation conditions were varied with different concentrations of ammonium persulfate, hydrochloride acid, and aniline. The composite resistivity showed a big difference after the 1<sup>st</sup> polymerization under different oxidation conditions, but little difference after the 3<sup>rd</sup> polymerization. In other words, the number of reaction cycles is the key factor in controlling the composite resistivity, no matter the polymerization conditions. It was the same for different polymerizing times and temperatures. After 3 polymerizations, the reacting time and temperature showed little effect on composite conductivity.

### Thermal Stability of PANI-Paper Composites

Figure 8 shows the TGA profiles of PANI composites with reinforced base paper. The weight loss of the reinforced base paper occurred in the 250 to 350 °C range, 30% weight remained at 350 °C, and 21.79% remained at 500 °C. All composites had similar profiles, showing fast weight loss in the 200 to 300 °C range. However, at 350 °C the composites still retained around 50% of their weight and retained 33.57% at 500 °C. Both were higher weight ratios than the base paper. The PANI played a protective role in

resisting heat damage, and showed more PANI with less weight loss. The PANI-paper composites presented good thermal stability.

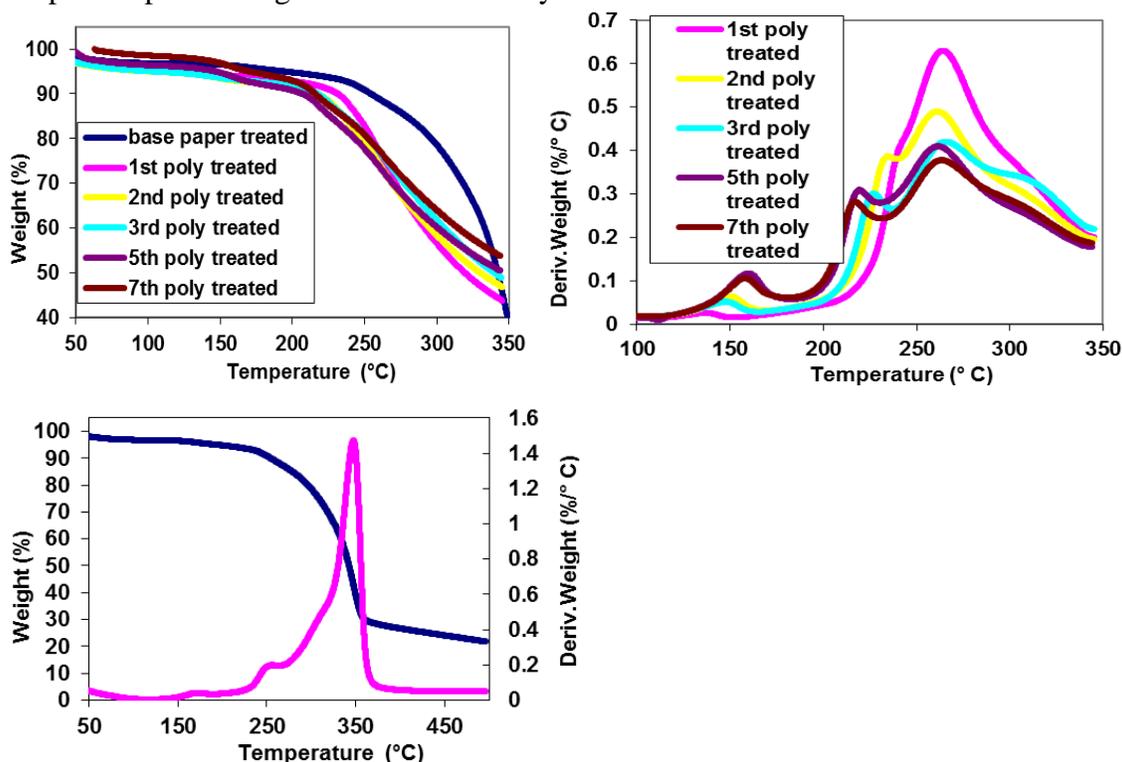


Fig. 8. TGA profile of polyaniline paper composites with different polymerizations

### Mechanical Strength of PANI-Paper Composites

Paper strength is commonly an issue of concern. Strong protonic acid is often utilized during preparation of conductive PANI. The acid liquid system would definitely damage the cellulose fibers from which the base paper is made. An increased fiber surface area exposed to acid, more time spent exposed, and the stronger the acid used are all factors expected to seriously decrease the fiber strength. Here the interfacial aniline polymerization on paper can protect fiber strength to some degree. The polymerizing reaction time is short (20 s), the reaction takes place at the interface and not across the whole paper, and multi-polymerization provides a chance to wash the paper using an organic solvent. The final result is that the PANI-paper composites remained in a good state for two months, but were still weak. A washing process after squeezing out the oxidant solution may be useful for retaining strength. Dust did not appear on composites until the 4<sup>th</sup> polymerization.

Reinforced paper-PANI composites solved the poor strength problem. They performed very well in strength tests, and were kept for one month before tensile tests. The tensile strength index remained almost the same from the 3<sup>rd</sup> to the 6<sup>th</sup> polymerization, ranging from 14.02 to 14.70 Nm/g, although this was lower than the base paper's tensile strength of 17.64 Nm/g. The acids and oxidants remained on the paper composite could decrease the strength durability. Moreover, there was no dust that appeared when wiping the composites, even after 10 polymerizations. In summary, the PAE treated paper-PANI composites possessed good mechanical strength.

## CONCLUSIONS

1. Novel PANI-paper composites have been produced through aniline multi-polymerization on paper substrate using multi interfacial polymerization.
2. The test results of the composites showed that composites using more than three polymerizations could afford low electrical resistivity (below 100  $\Omega$ /sq), with a PANI content of 30 gsm or more. The polymerizing cycle number was the most critical factor influencing the resistivity of all oxidation conditions. The FTIR results indicated that the first round of polymerization only produced PANI aggregates with small molecule sizes, but there was strong interaction between NH groups in aniline and OH groups in fibers, which disappeared after 3 rounds of polymerization. The bands of EB and DP were shifted upon further polymerization. The SEM and FESEM provided clear evidence that PANI networks were not being formed until the 3<sup>rd</sup> polymerization.
3. The PAE-treated base paper substrate solved the problem of poor strength for the PANI-paper composite. The SEM morphology of the composite was different from that of untreated base paper composites according to PANI crumb shape and nonlinear structure.
4. The test results of the PAE-treated PANI-paper composites showed that the composites had good conductivity with lower PANI amounts. The electrical resistivity was 256  $\Omega$ /sq with 12.7 gsm PANI after the 5<sup>th</sup> polymerization. The composites presented better conductivity than untreated base composites with the same PANI amount. The FTIR analysis disclosed that PAE played a positive role in PANI attachment. The TGA analysis and tensile tests revealed that the composites held both good thermal stability and good mechanical strength.
5. This novel conductive paper making process provides a method with the potential to be easily applied commercially for manufacturing composites in the electro-static shielding field.

## ACKNOWLEDGMENTS

The authors are grateful for the support of the Gangdong NSF 2013 and High Level Scholar Seeds Research Grant 2013.

## REFERENCES CITED

- Agarwal, M., Xing, A., Shim, B. S., Kotov, N., Varahramyan, K., and Lvov, L. (2009). "Conductive paper from lignocellulose wood microfibers coated with a nanocomposite of carbon nanotubes and conductive polymers," *Nanotech.* 20(21), 215602. DOI: 10.1088/0957-4484/20/21/215602
- Chiou, N.-R., and Epstein, A. J. (2005a). "A simple approach to control the growth of polyaniline nanofibers," *Synth. Met.* 153(1-3), 69-72. DOI: 10.1016/j.synthmet.2005.07.145

- Chiou, N.-R., and Epstein, A. J. (2005b). "Polyaniline nanofibers prepared by dilute polymerization," *Adv. Mater.* 17(13), 1679-1683. DOI: 10.1002/adma.200401000
- Ding, C., Qian, X., Shen, J., and An, X. (2010). "Preparation and characterization of conductive paper via in situ polymerization of pyrrole," *BioResources* 5(1), 303-315. DOI: 10.15376/biores.5.1.303-315
- Goto, H. (2011). "Electrically conducting paper from a polyaniline/pulp composite and paper folding art work for a 3D object," *Textile Research Journal* 81(2), 122-127. DOI: 10.1177/00405175110377827
- Hu, L., Choi, J. W., Yang, Y., Jeong, S., La Mantia, F., Cui, L.-F., and Cui, Y. (2009). "Highly conductive paper for energy-storage devices," *PNAS* 106(51), 21490-21494. DOI: 10.1073/pnas.0908858106
- Huang, B., Kang, G., and Ni, Y. (2006). "Electrically conductive fiber composites prepared from polypyrrole-engineered pulp fiber," *Canadian Journal of Chemical Engineering* 83(5), 896-903. DOI: 10.1002/cjce.5450830512
- Huang, J., and Kaner, R. B. (2004a). "A general chemical route to polyaniline nanofibers," *J. Am. Chem. Soc.* 126(3), 851-855. DOI: 10.1021/ja0371754
- Huang, J., and Kaner, R. B. (2004b). "Nanofiber formation in the chemical polymerization of aniline: A mechanistic study," *Angew. Chem. Int. Ed.* 43(43), 5817-5821. DOI: 10.1002/anie.200460616
- Huang, J., and Kaner, R. B. (2006). "The intrinsic nanofibrillar morphology of polyaniline," *Chem. Commun.* 367(4), 367-376. DOI: 10.1039/b510956f
- Johnston, J. H., Kelly, F. M., Moraes, J., Bommann, T., and Flynn, D. (2006). "Conductive polymer composites with cellulose and protein fibers," *Current Applied Physics* 6(3), 587-590. DOI: 10.1016/j.cap.2005.11.067
- Kelly, F. M., Johnston, J. H., Bommann, T., and Richardson, M. J. (2007). "Functionalized hybrid materials of conducting polymers with individual fibers of cellulose," *European Journal of Inorganic Chemistry* 2007(35), 5571-5577. DOI: 10.1002/ejic.200700608
- Kricheldorf, H. R. (1981). "15N-NMR spectroscopy 32. Synthesis and characterization of polyelectrolytes based on polyaminamides," *J. Polym Sci: Polym Chem Edition* 19(9), 2195-2214. DOI: 10.1002/pol.1981.170190907
- Li, W., and Wang, H. L. (2004). "Oligomer-assisted synthesis of chiral polyaniline nanofibers," *J. Am. Chem. Soc.* 126(8), 2278-2279. DOI: 10.1021/ja039672q
- Martin, C. R. (1994). "Nanomaterials: A Membrane-Based Synthetic Approach," *Science* 266(5193), 1961-1966. DOI: 10.1126/science.266.5193.1961
- Norris, I. D., Shaker, M. M., Ko, F. K., and MacDiarmid, A. G. (2000). "Electrostatic fabrication of ultrafine conducting fibers: Polyaniline/polyethylene oxide blends," *Synth. Met.* 114(2), 109-114. DOI: 10.1016/S0379-6779(00)00217-4
- Nyholm, L., Nystroem, G., Mihranyan, A., and Stromme, M. (2011). "Toward flexible polymer and paper - based energy storage devices," *Advanced Materials* 23(33), 3751-3769.
- Obokata, T., and Isogai, A. (2007). "The mechanism of wet-strength development of cellulose sheets prepared with polyamideamine-epichlorohydrin (PAE) resin," *Colloids and Surfaces A: Physicochem. Eng. Aspects* 302(1), 525-531. DOI: 10.1016/j.colsurfa.2007.03.025
- Pillalamarri, S. K., Blum, F. D., Tokuhira, A. T., Story, J. G., and Bertino, M. F. (2005). "Radiolytic synthesis of polyaniline nanofibers: A new templateless pathway," *Chem. Mater.* 17(2), 227-229. DOI: 10.1021/cm0488478

- Qian, X., Chen, J., and An, X. (2010). "Polypyrrole-coated conductive paper prepared by vapor-phase deposition method," *Appita Journal* 63(2), 102-107.
- Rehim, M. A., Youssef, A., Hassan, E., Khatab, N., and Turkey, G. (2010). "Morphology and electrical properties of hybrid and sulphonated oxalic acid-doped PANI," *Synthetic Metals* 160(15-16), 1774-1779. DOI: 10.1016/j.synthmet.2010.06.019
- Reneker, D. H., and Chun, I. (1996). "Nanometre diameter fibres of polymer produced by electrospinning," *Nanotechnology* 7(3), 216-223. DOI: 10.1088/0957-4484/7/3/009
- Valiavalappil, S., and Harinipriya S. (2012). "Electrically conducting nylon 6,6-polyaniline short composite fibres synthesized by the solvent coagulation method," *Synthetic Metals* 162(23), 2027-2032. DOI: 10.1016/j.synthmet.2012.10.008
- Wei, Z., Zhang, Z., and Wan, M. (2002). "Formation mechanism of self-assembled polyaniline micro/nanotubes," *Langmuir* 18(3), 917-921. DOI: 10.1021/la0155799
- Wu, C. G., and Bein, T. (1994). "Conducting polyaniline filaments in a mesoporous channel host," *Science* 264(5166), 1757-1759. DOI: 10.1126/science.264.5166.1757
- Youssef, A. M., El-Samahy, M. A., and Rehim, M. H. A. (2012). "Preparation of conductive paper composites based on natural cellulosic fibers for packaging applications," *Carbohydrate Polymers* 89(4), 1027-1032. DOI: 10.1016/j.carbpol.2012.03.044
- Youssef, A. M., Kamel, S., El-Sakhawy, M., and El Samahy, M. A. (2012). "Structural and electrical properties of paper-polyaniline composite," *Carbohydrate Polymers* 90(2), 1003-1007. DOI:10.1016/j.carbpol.2012.06.034
- Zhang, Q.-h., Wang, X.-h., and Jing, X.-b. (2001). "Synthesis of polyaniline and its spectra properties," *Chemistry World* 5, 242-244 (in Chinese).
- Zhang, X., Goux, W. J., and Manohar, S. K. (2004). "Synthesis of polyaniline nanofibers by nanofiber seeding," *J. Am. Chem. Soc.* 126(14), 4502-4503. DOI: 10.1021/ja031867a
- Zhang, X., and Manohar, S. K. (2004). "Polyaniline nanofibers: Chemical synthesis using surfactants," *Chem. Commun.* 20, 2360-2361. DOI: 10.1039/b409309g
- Zhu, Y., Wan, M., and Jiang, L. (2011). "Self-assembled polyaniline micro/nanostructures and their applications," *Polymer Bulletin* 10, 15-32 (in Chinese).

Article submitted: November 26, 2014; Peer review completed: February 16, 2015;  
Revised version received: April 23, 2015; Accepted: May 10, 2015; Published: May 18, 2015.

DOI: 10.15376/biores.10.3.4065-4076