Combination of Nitrogen Plasma Modification and Waterborne Polyurethane Treatment of Carbon Fiber Paper Used for Electric Heating of Wood Floors

Jianbin Song,[a,b,] Quanping Yuan,[a] Xueshen Liu,[b] Dong Wang,[a] Feng Fu [a,*] and Wenbin Yang,[b*]

The aim of this study was to improve the electrical resistivity, mechanical properties, and interfacial properties between the carbon fiber (CF) and cellulose of conductive paper containing 10% CF so as to better meet the demands for electric heating wood floors. With waterborne polyurethane (WPU) treatment and nitrogen plasma modification methods, the interfacial properties between CF and cellulose were improved dramatically. Fourier transform infrared spectrometry (FTIR) revealed that the plasma modification method reduced the C-H contents and introduced numerous polar groups onto the CF surface. Scanning electron microscopy (SEM) showed that the CF modified by WPU and plasma had good adhesion with cellulose. The tensile index, tensile energy absorption index, and burst index of the paper were enhanced because of the plasma and WPU coating. The carbon fiber and WPU method presented good synergistic action with respect to mechanical properties and electrical resistivity, and the lowest electrical resistivity of conductive paper was reduced from 0.68 Ω•cm^2 to 0.44 Ω•cm^2.

Keywords: Carbon fiber; Wood floor; Plasma; Paper

*Contact information: a: Research Institute of Wood Industry, Chinese Academy of Forestry, Beijing, 100091, China; b: College of Materials Engineering, Fujian Agriculture and Forestry University, Fuzhou, 350002, China; *Corresponding authors: feng@caf.ac.cn; fafuywb@163.com*

INTRODUCTION

During winters in non-equatorial latitudes, most people warm their homes using circulating hot water produced through burning traditional energy fuels such as coal, petroleum, and natural gas. Because of the rapid population increase, especially in Asia, the demand for traditional energy sources has increased substantially. Also, during the combustion of fuel, much sulfur dioxide, nitrogen oxides, and soot are emitted, exerting pressure on human development and environmental preservation. Consequently, people have started developing new energy fields and reforming traditional technology to protect the environment and achieve sustainable development.

Electric heating wood floor technology is one of the most promising methods for reducing environment pollution. Endowing the wooden floor with the function of heating not only raises the value of wood floor products, but it also saves energy and reduces environmental pollution (Armstrong 1978; Yuan and Fu 2014). This technology consists of placing a conductive layer embedded between veneers to make the floor conductive. Such technology has developed rapidly in China. Figure 1 shows the construction of electric heating wood floors. Among the components, the key technology is the electric heating layer.

At present, several candidate materials can be used to produce the electric heating layer. For example, in early electric heating materials, conductive ink printed on paper or a polymer resin such as polyethylene terephthalate or epoxy resin was applied to produce a heating wood floor. However, the electrical resistivity of such materials is not stable because low-molecular weight compounds in ink will shift and evaporate upon heating, resulting in structural changes in the electric heating layer. Additionally, the interfacial adhesion properties between veneer and conductive ink materials is relatively poor. Another electric heating material used is conductive fiber mats, including carbon fiber mats and glass fiber mats coated with conductive materials such as carbon black or conductive ink. This class of material usually leads to an increase in the thickness of wood flooring, as well as exhibiting poor interfacial properties.

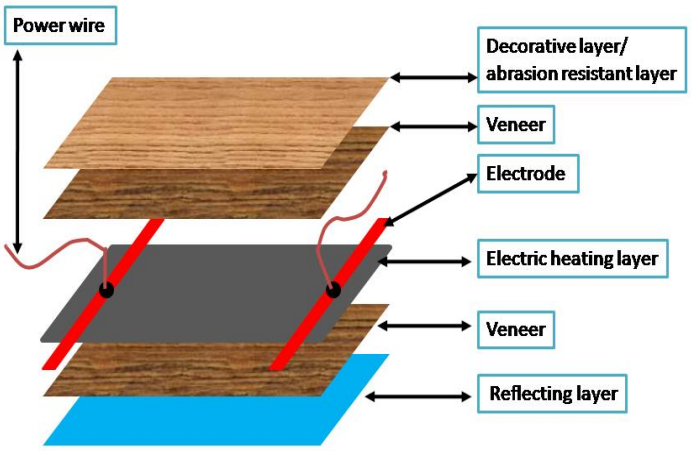

Fig. 1. Sketch of electric heating wooden floor

Carbon fiber (CF)-based paper is regarded as the most promising material for electric heating wood floors. Carbon fibers (CFs) exhibit high tensile strength, good conductivity, excellent thermal and chemical stability, and have been successfully applied in many fields (Wei *et al*. 2013; Yuan *et al*. 2013; Sha *et al*. 2014). CFs are also good heating elements (Pang *et al*. 2013), and the conversion efficiency from electricity into caloric energy of CF-based materials can be as high as 97% (Li 2002). In particular, electrifying carbon fiber can emit a 8- to 20-μm infrared ray, beneficial to human health (Li 2002).

According to the Ohm's law, the electric power of electric heating wood floor could be calculated by the following equation,

$$P = \frac{U^2}{R} \quad (1)$$

where P is the electric power, U is the input voltage, and R is the electrical resistance of the electric heating layers. The higher the conversion efficiency from electricity into caloric energy, the more input electric power will be transformed into caloric energy by and large. The input electric power, in the light of equation 1, was dependent on the resistance to a large extent. The lower the resistance is, the more obvious the heating effect of electric heating layers is. It should be noted that the low resistance would lead to the increase in power consumption, whereas excessively high resistance also would cause

a decline in heating efficiency. A previous report showed that the acceptable electrical resistivity should lie within the range from 0.1 Ω•cm to 10000 Ω•cm (Li 2002).

However, the poor dispersion of CF in pulp, interfacial properties between CF and pulp, and the mechanical properties of the resulting paper have been major issues with the use of carbon fiber-based paper, such that it is necessary to modify the CF. The previous studies have shown that acid oxidation, coupling agents, polymer resin coating, γ-ray irradiation, and plasma treatment can improve the CF surface (Zhou *et al*. 2012; Encinas *et al*. 2014). Acid oxidation (HNO_3, H_2SO_4, *etc*.) usually can graft some polar groups, but it also can seriously destroy the molecules structure and produce toxic waste water. The γ-ray irradiation method needs large space and expensive apparatus. The plasma method has been regarded as a convenient, clean, and pollution-free technology, which is a way to introduce polar groups in the polymer structure (Wang *et al*. 2011).

In the present study, the plasma technology was employed on account of its convenience, efficiency, and low environmental impact. To promote CFs dispersion and improve the mechanical properties of CF-based paper, waterborne polyurethane was used to produce conductive CF-based paper. This is because WPU includes the –NCO groups, which can chemically react with hydroxyl of cellulose and of CF. At the same time, the WPU does not precipitate in bleached softwood kraft pulp and can form a stable emulsion. The mechanical properties, morphology, and electrical resistivity of the paper were studied in detail.

EXPERIMENTAL

Materials and Preparation

Polyacrylonitrile (PAN)-based carbon fibers with diameter of 7 μm and length of 10 mm were purchased from Nanjing Weida Composite Material Co., Ltd., China. During carbon fiber production, the carbon fibers were coated with a proprietary water-based sizing agent. Waterborne polyurethane (WPU) with 30% solid content was purchased from Dongguan Xinghang Coating Technology Co., Ltd., China, and the molecular weight of WPU was about 6000 g/mol. The Bayhydur®XP2487/1 (German Bayer company) was selected as the sizing agent for WPU. Bleached softwood kraft pulp was kindly donated by Fujian Youlanfa Co., Ltd., China.

Prior to experimentation, necessary CF surface modifications were performed using a plasma processor (OSKUN-PR60L, produced by Austrian Xin Kun Technology Company, China) with the power of 100 W. This process was carried out in a nitrogen environment at room temperature. The pressure of the plasma processor was first decreased to 6 Pa for 5 min, followed by treatment with N_2 for 1 min.

The papermaking pulp, carbon fibers, and waterborne polyurethane were mixed at a set mass ratio for 30 min. The mixture was then filtered and rendered into disc paper, followed by drying at 110 °C. The composition of the CF paper is given in Table 1.

Characterization

To study the changes induced by plasma treatment, the CF surfaces were analyzed by FTIR (VERTEX 70) with the transmission method, produced by Bruker Company, Germany. The scanning range was from 400 to 4000 cm^{-1}, and the resolution was 4 cm^{-1}.

The carbon fiber was cut into powder, mixed with dry KBr, and finally pressed into a disc with the pressure of 5 MPa.

The surface of carbon fiber before and after plasma modification was studied by the X-ray photoelectron spectroscopy (XPS, Thermofisher scientific corporation, ESCALAB-250) using an Al Ka radiation source at a power of 150 W.

Table 1. Components and Mechanical Properties of CF Paper

	CF 1	CF2	CF3	CF4
Thickness (mm)	0.08	0.08	0.08	0.08
Bleached softwood kraft pulp (%)	90	66.9	90	66.9
Unmodified carbon fiber CF (%)	10	10	—	—
Modified carbon fiber (CF) (%)	—	—	10	10
Waterborne polyurethane (WPU) (%)	—	23.1	—	23.1
Tensile index (N·m/g)	76.19	85.60	84.14	96.48
Tensile energy absorption index (J/g)	0.82	1.07	1.03	1.29
Burst index (kPa·m²/g)	5.49	6.27	6.15	6.50
Area Specific Resistance (Ω·cm²)	0.68	0.51	0.61	0.44

The surface morphology observation of CF-based paper was carried out using a scanning electron microscope (SEM, Quanta 200, FEI Corporation, USA) with an accelerating voltage of 20 kV.

The tensile index and tensile energy absorption index were measured on a tensile testing machine (DCP-KZ(W)300), produced by Sichuan Changjiang Papermaking Instrument Co., Ltd., China, and the test velocity was 7 mm·min^{-1}. The burst index of the CF-based paper was tested on a paper bursting strength tester (DCP-NPY1200), manufactured by Sichuan Changjiang Papermaking Instrument Co., Ltd., China.

The electrical resistance R (Ω) of the CF-based paper was measured using a milliohmmeter VC480C+, produced by Shenzhen City Vichy Technology Co., Ltd., China. The electrical resistivity, ρ (Ω.cm), was calculated using the following relation,

$$\rho = R \times S \quad (2)$$

where R is the sample electrical resistance; S represents the surface area of the electrodes.

RESULTS AND DISCUSSION

FTIR

Figure 2 shows the FTIR spectra of unmodified and modified CF. There are several distinctive absorption peaks at 721, 1378, 1459, 1626, 2852, 2923, and 3428 cm^{-1}. Of these peaks, the peak at 721 cm^{-1} was ascribed to the bending vibrations of methylene (-CH_2-), the peaks at 1378 and 1459 cm^{-1} were the bending vibrations of the CH_3 groups and CH bonds, respectively, and the peaks at 2852 and 2923 cm^{-1} were the stretching vibrations of the CH bonds. The peaks at 1626 cm^{-1} was attributed to stretching vibrations of the C=C or C=N groups; the peak at 3428 cm^{-1} was ascribed to the stretching vibrations of OH groups. These results indicated that some polar groups were introduced to the CF surfaces and the CF became hydrophilic after treatment with a sizing agent.

To further improve its hydrophilicity, the CF was modified by nitrogen plasma for 1 min. As shown in Fig. 2, the FTIR spectrum of the modified CF underwent substantial changes compared to the unmodified CF. The intensity of the peaks of C-H groups (721, 1378, 1459, 2852, and 2923 cm^{-1}) was substantially reduced, indicating that the amount of CH on the CF was greatly decreased. In addition, the absorption peak at about 3428 cm^{-1} became wider than the unmodified CF because of the NH groups formed by nitrogen plasma. These confirmed that plasma modification reduced the quantity of non-polar groups and increased the amount of polar groups.

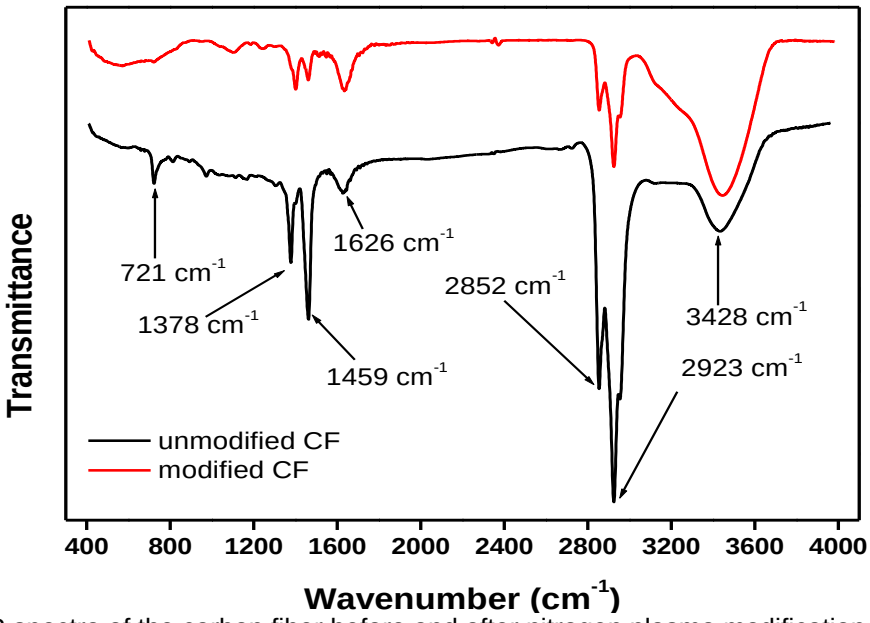

Fig. 2. FTIR spectra of the carbon fiber before and after nitrogen plasma modification

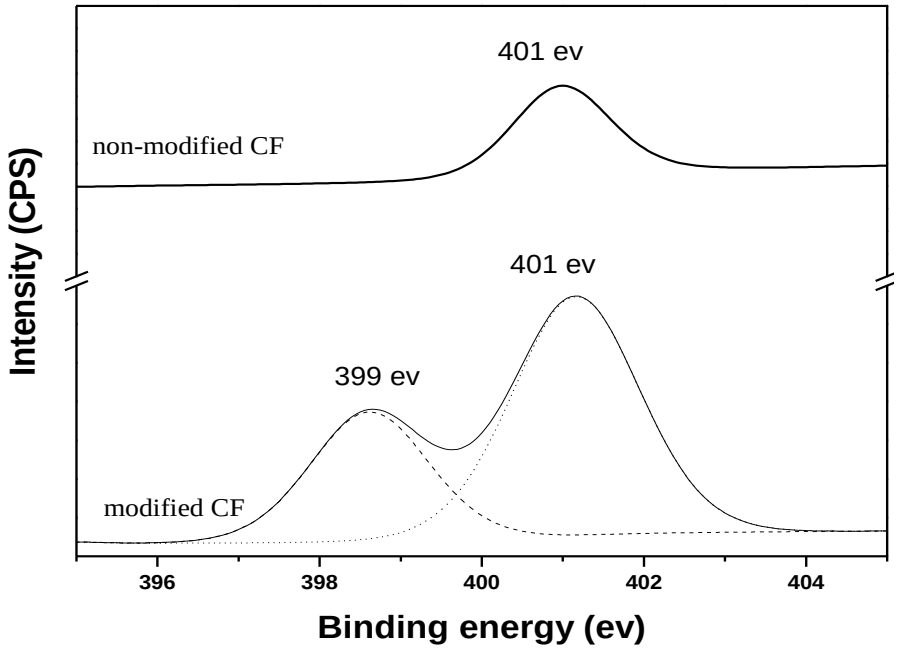

Fig. 3. XPS spectra of N 1s of the carbon fiber before and after nitrogen plasma modification

XPS

Figure 3 displays the XPS curves of carbon fiber before and after plasma treatment. For non-treated CF, there appeared a photoelectron signal at 401 eV, which was attributed to the N1s and originated from the sizing agent coating on the surface of CF. However, after N_2 plasma treatment, the N1s peak had been divided into two peaks: one at 401 eV, and the other at 399 eV, and this indicated that more nitrogen had been introduced on the carbon fiber surface. For the two peaks, the peak at 401 eV was ascribed to the free NH_2 groups, and the lower peak at 399 was ascribed to the NH_2 groups in a single hydrogen bond to an N or O elements on the carbon fiber surface (McLeod *et al.* 2006). These results showed that the N_2 plasma introduced many NH_2 groups in the carbon fiber.

SEM

Carbon fiber, unmodified and modified by plasma, was used to prepare the conductive paper. Figure 4 shows the morphology of these conductive papers. For CF1 paper, the CF surface was smooth and no links connected the CF to cellulose, indicating poor interfacial properties. When waterborne polyurethane was added, some polymers were found to adhere to the CF or cellulose, as shown in Fig. 4 (CF2). This suggested that the interface between the CF and cellulose was relatively improved.

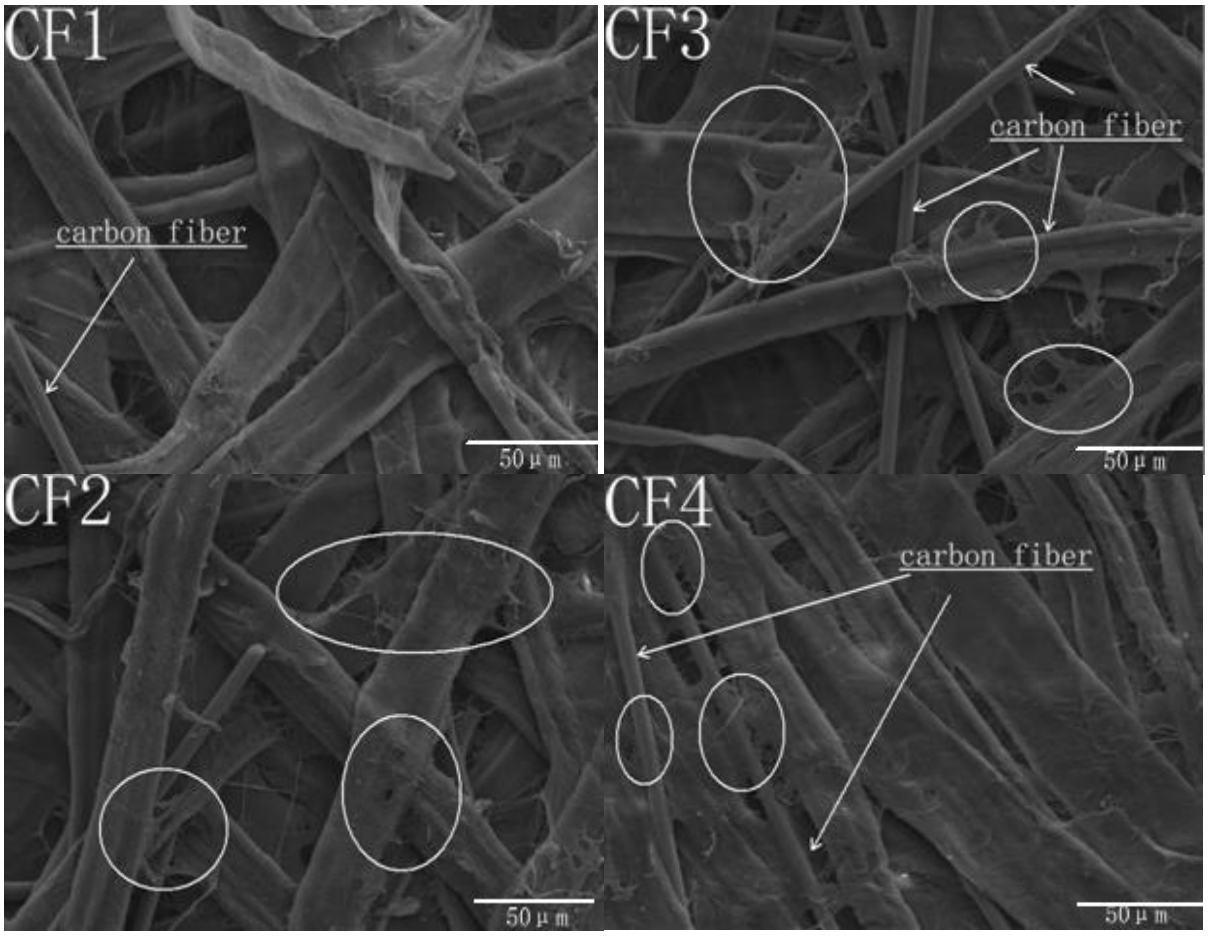

Fig. 4. Morphology of the carbon fiber paper: **a. CF1; b.** CF2 paper (WPU modified CFs); **c.** CF3 paper (plasma modified CFs); **d.** CF4 paper (plasma and WPU modified CFs)

CF3 was the modified CF-based paper. It was observed that there were some polymer fragments on the surface of the CF and cellulose because the plasma modification degraded the sizing agent. These polymer resin fragments linked the CF with cellulose and improved the interface between the CF and cellulose. When the plasma and waterborne polyurethane methods were used together, the CF4 paper showed a more dense structure. CFs that were coated with a layer of resin showed a tight connection with cellulose, exhibiting good synergistic action. This suggests that CF4 had better physical properties than the other samples.

Mechanical Properties

The addition of CFs also improved the mechanical properties of the paper. Table 1 shows the tensile index, tensile energy absorption index, and burst index of the CF-based paper.

In CF1 paper, only small amounts of OH groups appeared on the unmodified CF surface, resulting in weak interaction between the CF and cellulose. The low tensile index of CF1 was shown to be 76.2 N·m/g, and this was due to weak intermolecular force between CF and cellulose. However, after the addition of WPU, the tensile index of CF2 increased to 85.6 N·m/g. This occurred because the –NCO groups of one end of WPU chemically reacted with the –OH groups of CF, and the –NCO groups of other end of WPU could react with the –OH groups of cellulose, forming the –NHCOO groups, as shown in Fig. 5a. This indicated the interface properties between CF and cellulose was improved. When comparing CF1 and CF2, it was observed that the tensile index of CF3 was higher than that of CF1. The reason for this was the increase in polar groups (-NH) in CF3 as a result of the plasma modification, which formed more hydrogen bonds between CF and cellulose (Fig. 5b). Additionally, the tensile index of CF2 was slightly higher than that of CF3, meaning that the WPU method was more effective than the plasma method. By combining these two approaches, the CF4 paper presented the highest tensile index (96.48 N·m/g), increasing 26.6% above CF1, which indicated that the interfacial properties between the CFs and cellulose was enhanced (Fig. 5c).

The tensile energy absorption index (TBA) can be used to evaluate the toughness of paper. The higher the TBA is, the better the toughness of paper is. The TBA of CF1 was determined to 0.82 J/g. After adding some WPU, the TBA of CF2 rose sharply, reaching 1.07 J/g. This indicated that the toughness of the CF paper was improved. The plasma modified CF-based paper (CF3) also showed higher TBA (1.03 J/g) than CF1 because of the enhanced interaction between CF and cellulose. Like the tensile index, the highest TBA also appeared in CF4 and reached 1.29 J/g.

The burst index, similar to the tensile index and TBA, also exhibited the same behaviors. As expected, both the WPU (6.27 kPa·m²/g) and plasma (6.15 kPa·m²/g) methods improved the burst index of CF paper. The WPU and plasma methods showed positive synergistic effects, and the burst index of CF4 was measured at 6.50 kPa·m²/g, higher than that of CF1 (5.49 kPa·m²/g). This can be attributed to the improved interfacial properties between the CFs and cellulose.

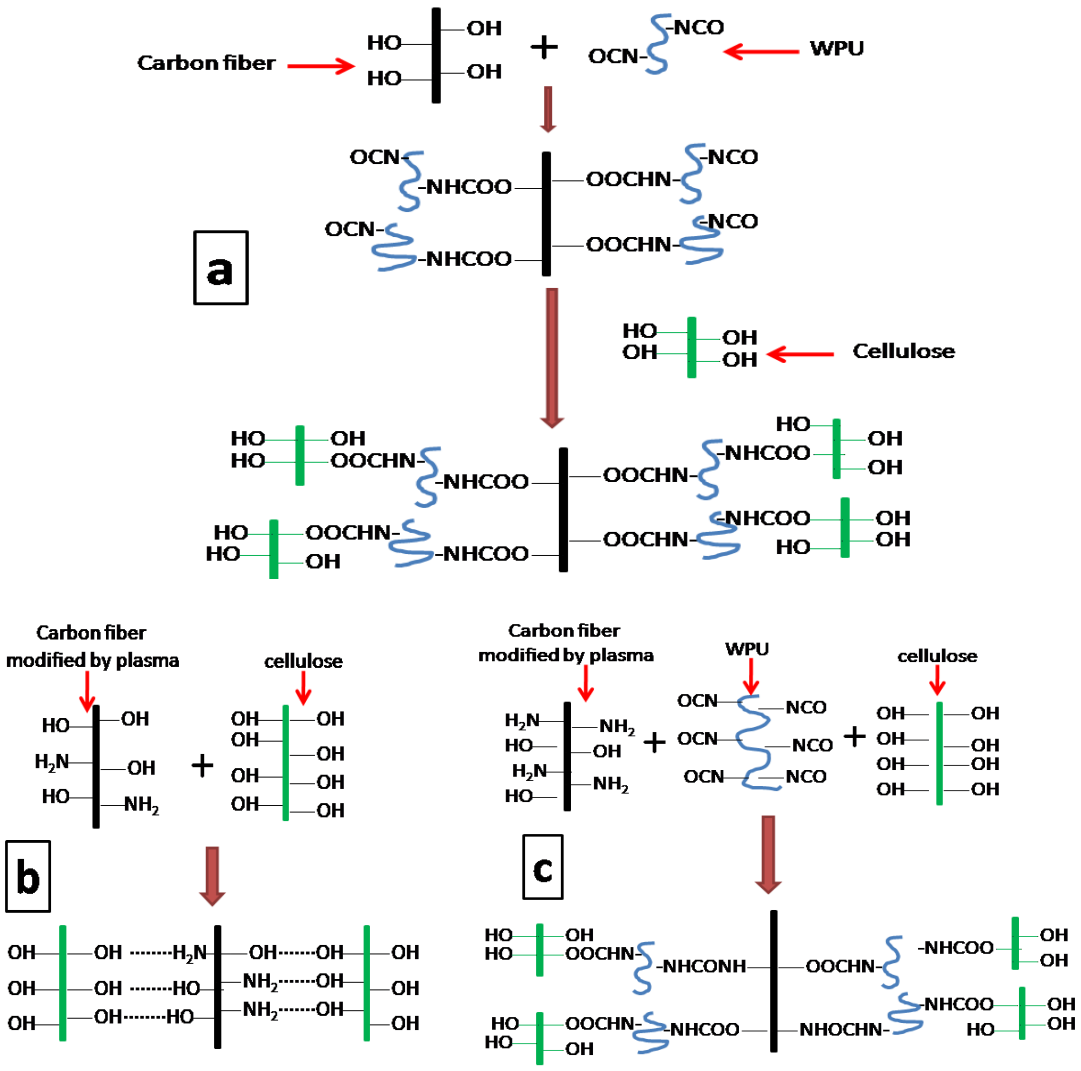

Fig. 5. Schematic of interactions in CF-based paper. **a.** CF2 paper (WPU modified CFs); **b.** CF3 paper (plasma modified CFs); **c.** CF4 paper (plasma and WPU modified CFs)

Area Specific Resistance

Electric heating wood floors require CF-based paper to have good conductivity. Consequently, conductive fillers need to be added to the paper. Research has shown that the electric heating layer materials should exhibit the appropriate electrical resistivity (0.1 to 10,000 Ω·cm). Higher (≥ 10,000 Ω·cm) or lower (≤ 0.1 Ω·cm) ranges are not recommended for use in electric heating wood floors (Li 2002).

Table 1 shows the area specific resistance of CF-based paper prepared with various modifications. It is known that area specific resistance is strongly dependent on the dispersion of the conductive fillers, filler shape, and interfacial properties. Good dispersion and interfacial properties are helpful to the formation of conductive networks in paper, reducing the area specific resistance.

The area specific resistance of the unmodified CF-based paper (CF1) was measured at 0.68 Ω·cm^2. This means that the CF content in paper exceeded the area specific resistance percolation (the percolation level at which electrical resistivity can be expected to reach a stable, relatively low value). However, this value can be further

reduced by modifying the CF surface; the area specific resistance of CF3 was 0.61 $\Omega \cdot cm^2$ because of the increased quantity of polar groups on the CF as a result of plasma modification, and this improved the dispersion of CF in the papermaking pulp. The area specific resistance of CF2 was reduced to 0.51 $\Omega \cdot cm^2$ because of the improved interface between CFs and cellulose. The improvement was attributed to the ability of WPU to chemically react with –OH groups of CFs and cellulose, which improved the dispersion of CFs in matrix, reduced the aggregation of CFs, and formed the stable CFs conductive networks. The SEM results also showed that the interface between CFs and cellulose was greatly improved. When the WPU and plasma method were used together, the lowest area specific resistance obtained was 0.44 $\Omega \cdot cm^2$.

CONCLUSIONS

1. FTIR showed that there were significant changes to the carbon fiber (CF) surface before and after nitrogen plasma modification, resulting in reduced amounts of CH groups and increasing amount of polar groups.
2. The SEM outcomes proved that both waterborne polyurethane (WPU) and plasma modifications can enhance the interfacial properties between CFs and cellulose.
3. Mechanical property improvements were observed as a result of WPU coating and nitrogen plasma modification methods. The tensile index of the papers increased from 76.19 to 96.48 N·m/g, the tensile energy absorption index rose from 0.82 to 1.29 J/g, and the burst index improved from 5.49 to 6.50 kPa·m²/g.
4. The area specific resistance of CF-based paper decreased from 0.68 to 0.51 $\Omega \cdot cm^2$ after WPU modification, further decreased to 0.61 $\Omega \cdot cm^2$ after plasma modification, and decreased to 0.44 $\Omega \cdot cm^2$ after both WPU and plasma modification.

ACKNOWLEDGMENTS

This article was supported by "Twelfth Five-year Plan" of National Science and Technology (No. 2015BAD14B04); the Postdoctoral Science Foundation of China (No.2014M560138), the Scientific Research Foundation for the Returned Overseas Chinese Scholars, the State Education Ministry, the Natural Science Foundation of Fujian Province of China (No. 2014J01068), and the Youth Foundation of Fujian Agriculture and Forestry University (No. 2012XJJ05).

REFERENCES CITED

Armstrong, T. B. (1978). "Wire mesh floor heating systems," *IEEE T. Ind. Appl.* 14(6), 498-505. DOI: 10.1109/TIA.1978.4503581

Encinas, N., Oakley, B. R., Belcher, M. A., Blohowiak, K. Y., Dillingham, R. G., Abenojar, J., and Martínez, M. A. (2014). "Surface modification of aircraft used composites for adhesive bonding," *Int. J. Adhes. Adhes.* 50, 157-163. DOI: 10.1016/j.ijadhadh.2014.01.004

Li, L. X. (2002). "The application of high performance carbon fiber paper," *Hi-Tech Fiber & Application* 27(5), 15-16, 40.

McLeod, K., Kumar, S., Smart, R. St. C., Dutta, N., Voelcker, N. H., Anderson, G. I., and Sekel, R. (2006). "XPS and bioactivity study of the bisphosphonate pamidronate adsorbed onto plasma sprayed hydroxyapatite coatings," *Appl. Surf. Sci.* 253, 2644-2651.

Pang, E. J. X., Pickering, S. J., Chan, A., and Wong, K. H. (2013). "Use of recycled carbon fibre as a heating element," *J. Compos. Mater.* 47(16), 2039-2050. DOI: 10.1177/0021998312454033

Sha, J. J., Dai, J. X., Li, J., Wei, Z. Q., Hausherr, J. M., and Krenkel, W. (2014). "Measurement and analysis of fiber-matrix interface strength of carbon fiber-reinforced phenolic resin matrix composites," *J. Compos. Mater.* 48(11), 1303-1311. DOI: 10.1177/0021998313485264.

Wang, W. H., Huang, B. C., Wang, L. S., and Ye, D. Q. (2011). "Oxidative treatment of multi-wall carbon nanotubes with oxygen dielectric barrier discharge plasma," *Surf. Coat. Tech.* 205(21-22), 4896-4901.

Wei, P., Wang, B. J., Zhou, D. I., Dai, C., Wang, Q., and Huang, S. (2013). "Mechanical properties of poplar laminated veneer lumber modified by carbon fiber reinforced polymer," *BioResources* 8(4), 4883-4898. DOI: 10.15376/biores.8.4.4883-4898

Yuan, Q. P., and Fu, F. (2014). "Application of carbon fiber paper in integrated wooden electric heating composite," *BioResources* 9(3), 5662-5675. DOI: 10.15376/biores.9.3.5662-5675

Yuan, Q. P., Su, C., Huang, J., Gan, W., and Huang, Y. (2013). "Process and analysis of electromagnetic shielding in composite fiberboard laminated with electroless nickel-plated carbon fiber," *BioResources* 8(3), 4633-4646. DOI: 10.15376/biores.8.3.4633-4646

Zhou, J. Y., Wang, Z. W., Zuo, R., Zhou, Y., Cao, X. M., and Cheng, K. (2012). "The surface structure and chemical characters of activated carbon fibers modified by plasma," *Asia-Pac. J. Chem. Eng.* 7, S245-S252. DOI: 10.1002/apj.570

Article submitted: January 20, 2015; Peer review completed: May 15, 2015; Revised version received: July 16, 2015; Accepted: July 18, 2015; Published: July 28, 2015.
DOI: 10.15376/biores.10.3.5820-5829