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Progress in Natural Science: Materials International 24 (2014) 56–60

Progress in Natural Science Materials International

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Original Research

Mechanical properties of carbon fiber/cellulose composite papers modified by hot-melting fibers

Yunzhou Shi, Biao Wang*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai, China

Received 26 September 2013; accepted 14 December 2013
Available online 12 February 2014

Abstract

Carbon fiber (CF)/cellulose (CLS) composite papers were prepared by papermaking techniques and hot-melting fibers were used for modification. The mechanical properties of the obtained composite papers with different CF, CLS and hot-melting fiber ratios were studied and further discussed. It is observed that, for both CF/CLS composite papers and those modified by hot-melting fibers, the normal stress firstly increases and then declines with the addition of carbon fibers. The results also show that with the addition of hot-melting fibers, the modified papers exhibit enhanced mechanical performance compared to CF/CLS composite papers. Through SEM characterization, it is confirmed that the improvement of mechanical properties attributes to the reinforcement of adhesive binding at the fiber overlap nodes. Also, through four-probe method, the resistivity and the electrical performance of the modified and unmodified papers were characterized and the result shows that the hot-melting fiber modification brings no harm to the electrical properties.

Keywords: Carbon fibers; Composite papers; Cellulose fibers; Mechanical properties; Modification

1. Introduction

In the last several years, carbon fiber composite papers have gained growing attention due to the wide application range and low cost of production. Chopped carbon fibers are randomly oriented and distributed in the insulting matrix by papermaking technique. Except for carbon fibers, carbon materials including carbon blacks [1], graphite [2] and CNTs [3] have also been widely used as conductive fillers in composite production. In most occasions, carbon fiber composite papers are used as conductive functional materials. They can be possibly applied in fields like electromagnetic interference (EMI) shielding [4], lightning protection [5] and heating elements [6].

A lot of researches have been done focusing on the electrochemical character of carbon fiber composite papers for the application of gas diffusion layer (GDI) in fuel cells [7,8]. Besides, conductivity and EMI shielding performance are also hot spots in the study of carbon fiber composite papers [9,10].

Due to the rigidity and chemical inertness of carbon fibers, the increase of carbon fiber fraction leads to both conductivity enhancement and mechanical performance reduction. As a result, it is an urgent need to find a balance between the mechanical property and the electrical conductivity. In this paper, by using papermaking process, carbon fiber/cellulose composite papers were successfully prepared. The relationship of the mechanical properties and carbon fiber fraction was studied. Furthermore, hot-melting fibers were used for modification, aiming to improve the mechanical performance of the composite papers.

2. Experimental

2.1. Materials

Chopped carbon fibers (with an average length of 4 mm) were available from Toray Industries. Unbleached softwood

*Corresponding author.
E-mail addresses: iams.y.z@hotmail.com (Y. Shi), wbiao2000@dhu.edu.cn (B. Wang).
Peer review under responsibility of Chinese Materials Research Society.

Production and hosting by Elsevier

1002-0071/$ - see front matter
http://dx.doi.org/10.1016/j.pnsc.2014.01.006

pulp was provided by Weyerhaeuser. Hot-melting fibers (with an average length of 6 mm) provided by Danyang Shuguang fiber Co., Ltd were used for mechanical modification. Anionic polyacrylamide (APAM, Aldrich) was used as fiber dispersant.

2.2. Preparation of CF/CLS composite papers

Unbleached softwood pulp was mechanically beaten for 40 min to acquire cellulose (CLS) aqueous slurries with a concentration of 0.1 wt%. Chopped carbon fiber were dispersed in water (0.1 wt%), adding APAM (0.1 wt%) as dispersant. Both CLS and CF slurries were mechanically stirred for 30 min respectively before mixed together.

The well dispersed CLS and CF slurries were mixed together in different ratios and stirred for another 10 min to ensure both CLS and CF to distribute evenly. The mixed slurries were filtered by using a paper-forming machine (ZT6-00, Zhongtong test equipment Co., Ltd.). After filtration, the obtained samples were dried in an air-circulating oven for 40 min at 70 °C before hot pressed at 105 °C, 10 MPa for 5 min to remove the rest moisture and fixing the shape.

2.3. Modification of CF/CLS composite papers

Hot-melting fibers (HMFs) were dispersed in water with a concentration of 0.1 wt%, adding APAM (0.1 wt%) as dispersant. The obtained HMF slurry was mixed together with the CLS and CF slurries in different ratios as modification component. Then, the mixed slurry was filtered and dried in an air-circulating oven for 40 min at 105 °C before hot pressed at 135 °C, 10 MPa for another 5 min.

The material compositions prepared are presented in Table 1.

2.4. Characterization of the composite papers

The tensile tests of the composite papers were proceeded by using a universal testing machine (WDW3020, Changchun Kexin test equipment Co., Ltd.). For each type of composite paper, 10 rectangular samples (60 × 15 mm) were tested and an average tensile test curve and result were determined. The structure and morphology of the composite papers were characterized by a scanning electron microscope (SEM, JSM-5600LV, JEOL, Japan). The volume resistivity of the prepared composite papers was measured by four-probe method using MCP-T360 ohmmeter available from Mitsubish (Japan).

3. Results and discussion

Fig. 1a shows the morphology of the CF/CLS composite paper. In the CF/CLS composite papers, short carbon fibers form a highly porous rigid network, consolidated by the flexible cellulose entanglement. As is shown in Fig. 1b, the cellular structure of cellulose was squashed after mechanical beaten, providing larger superficial area with abundant hydrogen bonds. Besides, the micro-fibrils generated in the mechanical beating process formed nodes consolidating the fiber network. Moreover,

Table 1
Material compositions (in wt%).

CF/CLS (wt%)		CF/CLS/HMF (wt%)			CF/CLS/HMF (wt%)		
CF	CLS	CF	CLS	HMF	CF	CLS	HMF
0	100	0	80	20	5	76	19
10	90	10	72	18	5	57	38
20	80	20	64	16	5	38	57
30	70	30	56	14	5	19	76
40	60	40	48	12			
50	50	50	40	10			

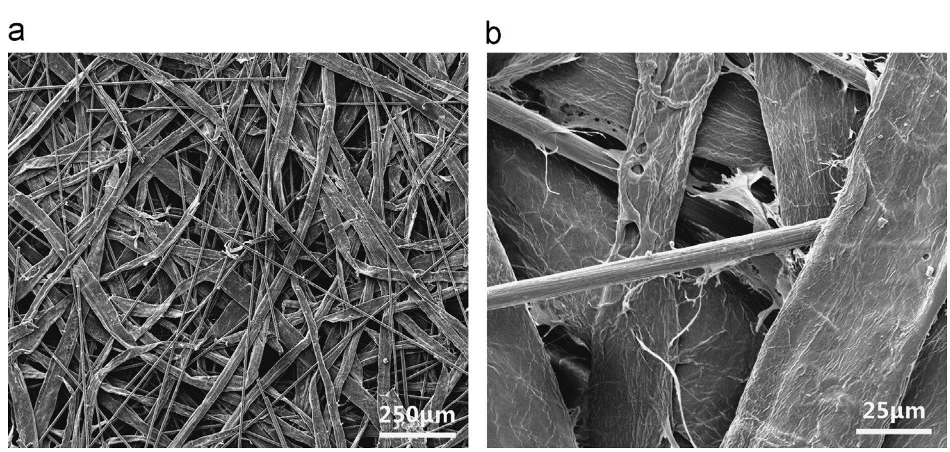

Fig. 1. SEM images of the CF/CLS composite papers (20 wt% of CF).

the flexible cellulose fibers with large superficial area can offer sufficient frictional force and entanglement.

Fig. 2a shows the tensile test average curve of the obtained CF/CLS composite papers. The breaking strength and the elongation rate versus carbon fiber fraction are plotted in Fig. 2b. It is observed that the breaking strength of the composite paper increases with the addition of carbon fibers, reaching the maximum of 5 MPa at 20 wt%.With further increase of CF fraction, the breaking strength declines. In the CF/CLS composite system, the CLS–CLS, CLS–CF and CF–CF inter fiber forces are the three mainly influencing factors deciding the breaking strength of the composite papers. The CLS–CLS inter fiber force includes hydrogen bonds on the cellulose surface, frictional force and entanglement between cellulose fibers. The increase of CF fraction decreases the chance of CLS–CLS interaction because of the decrease of CLS content. CLS–CF inter fiber force is mainly contributed by the entanglement between cellulose and carbon fibers, known as the "anchor effect" [11]. With the addition of carbon fibers, the CLS–CF "anchor effect" first increases with the increase of CF fraction and then declines with the constant decline of CLS content. The CF–CF interaction is much weaker compared to CLS–CLS and CLS–CF forces due to the rigidity and surface inertness of carbon fiber nature. With the CF fraction increases, the chance of CF–CF interaction also increases, reducing the breaking strength of the composite papers. The mechanical performance is a complex integration of the three type of inter fiber interactions discussed above. As a result, the experimental result reveals a nonlinear relationship between breaking strength and CF fraction. The cellulose fiber fraction decrease also leads to the decline of fiber network flexibility. As expected, the breaking elongation declines with the addition of carbon fibers (Fig. 2b).

In this work, hot-melting fibers were used for the modification of the mechanical properties. Fig. 3a shows the tensile test average curve of the modified composite papers. In this series, the matrix of the composite papers consist 80 wt% of cellulose fibers and 20 wt% of hot-melting fibers. The breaking strength and the elongation rate versus carbon fiber fraction are shown in Fig. 3b. Similarly with the unmodified papers, the tensile breaking strength firstly increases and then declines with the addition of carbon fibers, reaching its maximum of 7.5 MPa when CF content is 10 wt%. Compared to the unmodified CF/CLS composite papers, the modified ones show an enhanced overall mechanical performance due to the binding force provided by the added hot-melting fibers, which

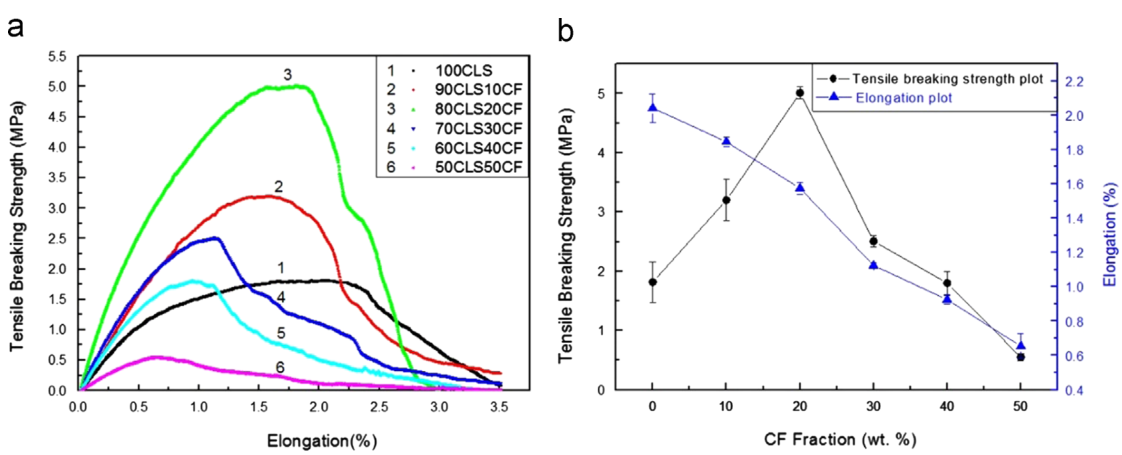

Fig. 2. CF/CLS composite papers of different CF fractions: (a) tensile test average curves and (b) tensile breaking strength and elongation values as a function of CF fraction.

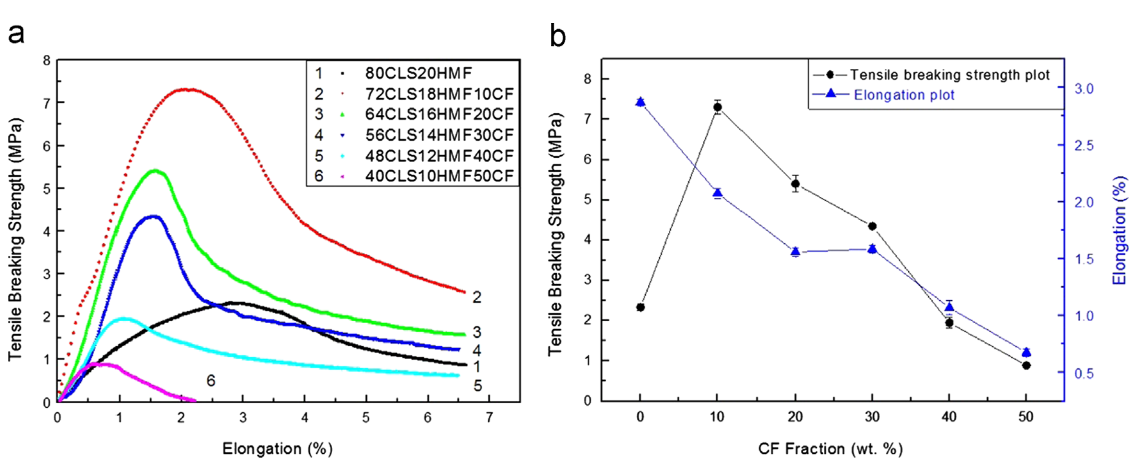

Fig. 3. CF/CLS/HMF composite papers of different CF fractions: (a) tensile test average curves and (b) tensile breaking strength and elongation values as a function of CF fraction.

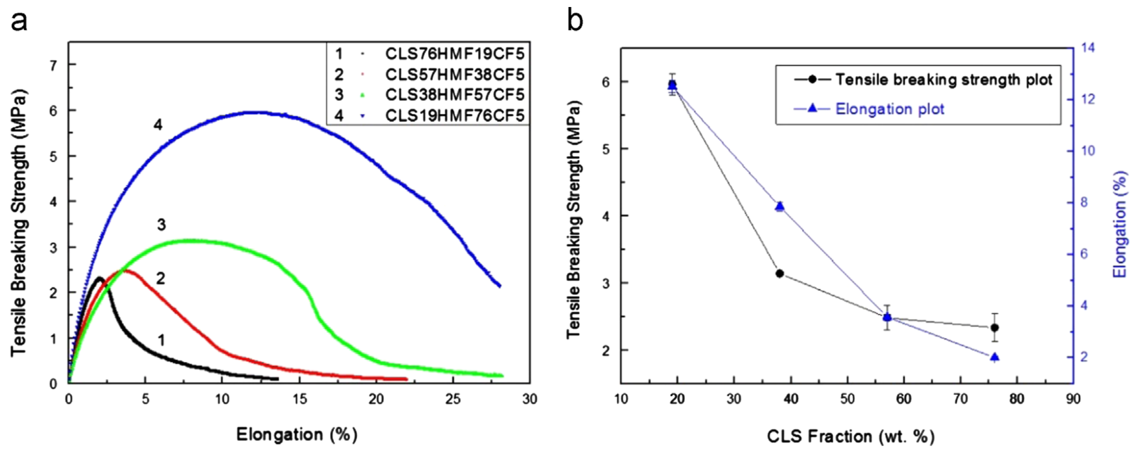

Fig. 4. CF/CLS/HMF composite papers of different matrix compositions: (a) tensile test average curves and (b) tensile breaking strength and elongation values as a function of CLS fraction.

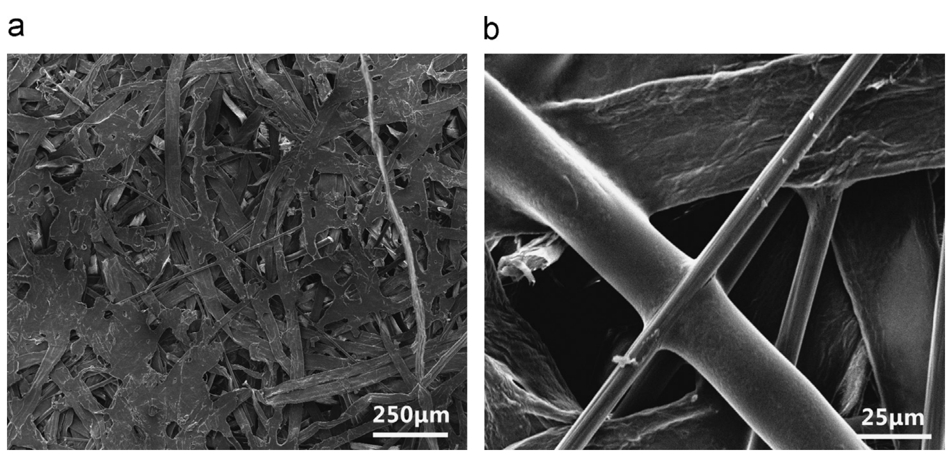

Fig. 5. SEM images of the CF/CLS/HMF composite papers (5 wt% of CF, 57 wt% of CLS and 38 wt% of HMF) at different magnifications: (a) 100 × and (b) 1000 × .

contributes to the stress transfer and dispersion. However, the modified papers show an earlier decline in breaking strength with the addition of carbon fibers. This is mainly caused by the reduction of binding joints formed by hot-melting fibers, as well as the reduction of inter-fiber forces provided by cellulose fibers.

Fig. 4 illustrates the influence of matrix composition on the mechanical performance of composite papers. The CF fraction is held constantly at 5 wt%, while the mass ratio of cellulose and hot-melting fibers ranges from 4:1 to1:4. The result shows that the addition of hot-melting fibers contributes to both tensile breaking strength and breaking elongation rate. As is shown in Fig. 4b, the breaking strength as well as the elongation rate decline with the increase of cellulose fibers in the matrix. This is because the decrease of hot-melting fiber fraction in the matrix reduces the number of binding joints in the fiber network, degrading the perfection of the cross-linking structure.

SEM characterization also confirms that the added hot-melting fibers contribute to the improvement of mechanical properties. Fig. 5 shows the SEM images of the composite papers modified by hot-melting fibers. The hot-melting fibers have a polyethylene (PE) skin and polypropylene (PP) core structure. The PE skin melted during the hot pressing process, forming binding nodes at fiber contacts, strengthening the inter-fiber forces.

As is shown in Fig. 6a, CF/CLS papers exhibit the electrical percolation behavior. There is a sharp decline in volume resistivity with the increase of CF fraction before reaching 5 wt %. With further addition of CF, it shows no significant change in volume resistivity. Fig. 6b shows that the volume resistivity stays steady with the adding of hot-melting fibers in the matrix. And this implies that the electrical performance is mainly determined by the conductive network formed by carbon fibers, irrespective of the material composition of the matrix. Thus the hot-melting fiber modification of carbon fiber reinforced papers brings no harm to the electrical properties and contributes to the mechanical performance in the meantime.

4. Conclusions

Papermaking techniques were used to produce CF/CLS composite papers, and hot-melting fibers were used for mechanical modification. SEM characterization was used to study the structure and morphology of the obtained composite papers. Composite papers modified by hot-melting fibers show

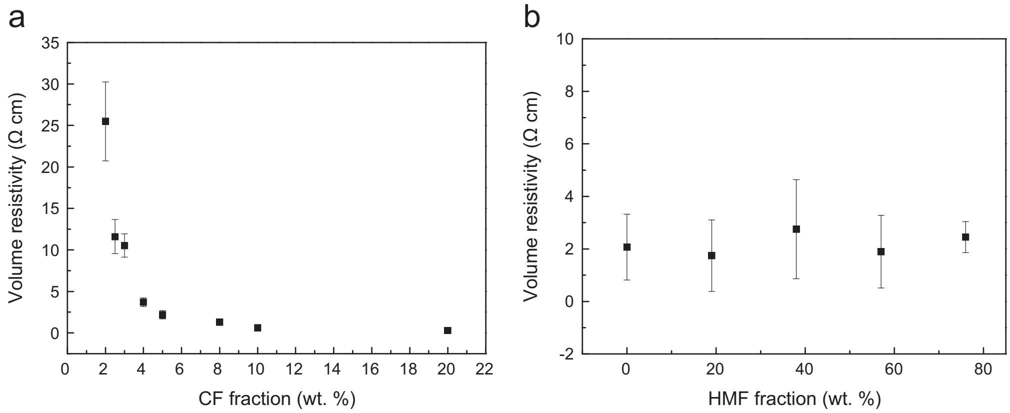

Fig. 6. Electrical property of the obtained composite papers: (a) volume resistivity vs CF fraction curve for CF/CLS papers; (b) volume resistivity of CF/CLS/HMF papers (5 wt% CF) with different HMF fraction in the matrix.

better mechanical performance than the unmodified ones due to the fact that hot-melting fibers can form adhesive binding nodes at fiber contacts. For both modified and unmodified composite papers, the tensile breaking strength firstly increases and then declines with the increase of CF fraction. With the further investigation of the electrical properties of both modified and unmodified papers, a conclusion can be drawn that by increasing hot-melting fiber fraction in the matrix, the mechanical performance can be effectively enhanced with no significant influence on the electrical performance.

Acknowledgments

This work is financially supported Shanghai Leading Academic Discipline Project (No. B603) and the Program of Introducing Talents of Discipline to Universities (No. 111-2-04).

References

[1] Jan C Jason, M.D. Walton, E.P. McConnell, et al., Carbon 44 (10) (2006) 1974–1981.
[2] L. Jabbour, D. Chaussy, B. Eyraud, et al., Compos. Sci. Technol. 72 (5) (2012) 616–623.
[3] Y.I. Song, C.M. Yang, D.Y. Kim, et al., J. Colloid Interface Sci. 318 (2) (2008) 365–371.
[4] M. Imai, K. Akiyama, T. Tanaka, et al., Compos. Sci. Technol. 70 (10) (2010) 1564–1570.
[5] J. Gou, Y. Tang, F. Liang, et al., Composites Part B 41 (2) (2010) 192–198.
[6] D. Sui, Y. Huang, L. Huang, et al., Small 7 (22) (2011) 3186–3192.
[7] R.A. Antunes, M.C.L. De Oliveira, G. Ett, et al., J. Power Sources 196 (6) (2011) 2945–2961.
[8] S. Park, J.W. Lee, B.N. Popov, Int. J. Hydrogen Energy 37 (7) (2012) 5850–5865.
[9] T.A. Ezquerra, M.T. Connor, S. Roy, et al., Compos. Sci. Technol. 61 (6) (2001) 903–909.
[10] D.D.L. Chung, Carbon 39 (8) (2001) 1119–1125.
[11] L.X. Zhong, Shaanxi Univ. Sci. Technol. (2008).