

## Preparation and Properties of Thermally Conductive Copper Paper

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A new thermally conductive copper paper was prepared with cellulose pulp and ultrafine copper powder in a traditional paper making process. The thermal conductivity of the copper paper was studied in different weight ratios, and the surface morphology was observed by scanning electron microscopy (SEM). The results showed that the addition of copper powder enhanced the thermal conductivity of copper paper distinctly, with a maximum of up to  $0.560 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  in the weight ratio of pulp/copper of 1:12, which was an increase of 143% compared with the paper without copper. Scanning electron microscopy images showed that copper papers consisted of copper powder particles distributing compactly on the fiber surface. The tensile index of copper paper decreased compared with the paper without filler. A calendaring process was used to improve the combination between copper particles and fibers and to enhance the thermal conductivity of copper paper.

*Keywords:* Copper paper; Thermal conductivity; Ultrafine copper powder

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### INTRODUCTION

Advances in electronic packaging have led to an increasing need for developing highly thermally conductive, low cost, and environmentally friendly thermally conductive materials (Amon *et al.* 2001; Kish 2002; Kong *et al.* 2011). Polymer composites filled with conductive metal particles are of interest for many fields of engineering (Serkan Tekce *et al.* 2007). The thermal characteristics of these composites are similar to the properties of metals, whereas the mechanical properties and the processing methods are typical for the polymer.

Cellulose is the oldest and most abundant natural polymer on the earth, and it is the most valuable natural renewable resource. However, traditional paper made with plant fiber has poor thermal conductivity, which limits its application and development in many areas. Additionally, plant fibers have a high length-diameter ratio, specific strength, and specific surface area (Hui *et al.* 2005). Thus, cellulose has potential to be an excellent material for use as a matrix, whereas the traditional papermaking method is simple and low cost.

One of the most common metals, copper, has received wide attention in both academia and industry. Copper has excellent thermal conductivity at about  $400 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  (Nath and Chopra 1974; Ye and Tang 2002; Miyake *et al.* 2008). However, the difficulty of molding and the low strength of copper powder film tend to limit its applications. Combining the excellent properties of copper powder and plant fiber could be a good way

to expand the application of cellulose. In our pre-experiment, if the particle size of the copper powder is not small enough, copper paper has poor physical strength and is even difficult to mold because of the poor combination between copper particles and fiber. Therefore, the particle size of copper powder should be small enough to improve copper paper molding and dispersion, which significantly affects the thermal conductivity (Agari *et al.* 1991).

In this work, ultrafine copper powders were added into the cellulosic pulp as conductive fillers, and guar gum was appended into the mixture as a retention aid. Copper paper was made by a traditional papermaking method. The structural characteristics of the copper papers were investigated by scanning electron microscopy (SEM). The mechanical properties and thermal conductivity of the copper paper were examined. This study provided possibilities to improve the thermal conductivity of the papers in a traditional papermaking method.

## EXPERIMENTAL

### Materials

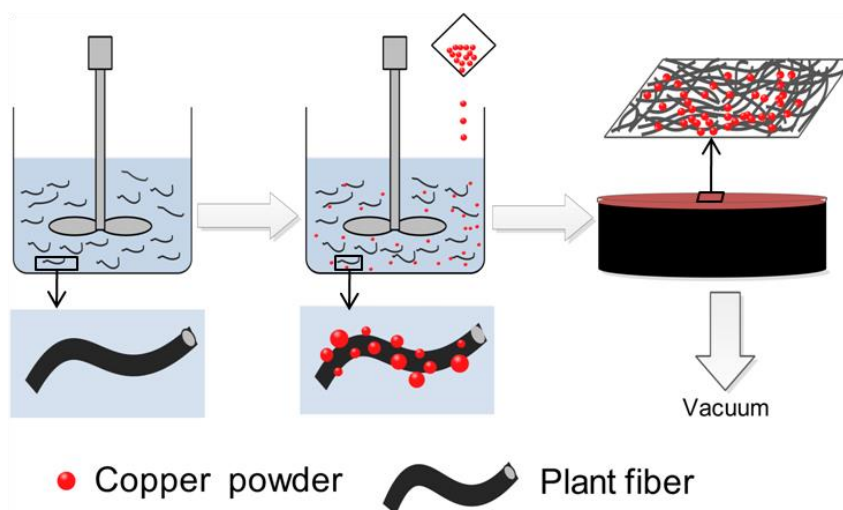
Bleached softwood pulp was supplied by China Tobacco Mauduit (Guangdong, China), with cellulose content of 91.61% and hemicellulose content of 7.70%. Guar gum GP-Z201) with a viscosity from 2000 mPa•s to 5000 mPa•s in 1 wt% aqueous solution, were purchased from Shandong GP Natural Products Company Ltd (Shandong, China).

Copper powders (Cu-P5) with an average particle diameter of 13.4  $\mu\text{m}$ , oxygen content of 0.2%, and tap density from 5.7  $\text{g}/\text{cm}^3$  to 5.8  $\text{g}/\text{cm}^3$ , were purchased from Dongguan Hyper Tech Company Ltd (Dongguan, China).

### Methods

#### *Preparation of copper paper*

As shown in Fig.1, copper paper was prepared by using a model 1600 Econo-Space automatic sheet former system (Réalisations Australes Inc., Quebec, Canada) according to TAPPI T205 om-88 (1988).



**Fig. 1.** The preparation of copper paper

The dry component of the soft wood pulp was 1 g, and the dosage of guar gum was 6 mL with a mass percent concentration of 1%. The variable amounts of copper powder were 30 g, 40 g, 50 g, and 60 g. The sheets were dried at 102 °C using a Formax 12 drum dryer (Thwing-Albert Instrument Company, West Berlin, NJ, USA). The calendaring processes were carried out on the rolling calender at 10 MPa and 15 MPa. The oven dry copper paper was weighed to determine the weight ratio of pulp and copper powder.

### Characterization

SEM observations of copper paper samples were carried out using a scanning electron microscope (SEM; S-3700N, Hitachi, Ltd., Tokyo, Japan). The paper sample surfaces were coated with gold before observations.

The thermal conductivity of the copper paper was calculated by Eq. 1,

$$C_t = \alpha \times \rho \times C \quad (1)$$

where  $C_t$  is the thermal conductivity ( $\text{w}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ),  $\alpha$  is thermal diffusivity ( $\text{m}^2\cdot\text{s}^{-1}$ ),  $\rho$  is density ( $\text{kg}\cdot\text{m}^{-3}$ ), and  $C$  is the specific heat capacity ( $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ ).

The thermal diffusivities of copper paper (diameter of 12.7 mm) were measured at 30 °C with an LFA 457 analyzer (Netzsch, Selb, Bavaria, Germany). Each  $\rho$  value of copper paper was determined by the weight and dimension of samples. In addition,  $C$  was measured at 30 °C with DSC 200 F3 (Netzsch).

The tensile index values of paper sheets were measured using a L&W CE062 tensile strength tester (Kista, Sweden).

## RESULTS AND DISCUSSION

### The Thermal Conductivity of Copper Paper

Table 1 shows the thermal conductivities, thermal diffusivities, densities, and the specific heat capacities of copper paper with different weight ratio of pulp/copper. As shown in Fig. 2, the thermal conductivity of pure plant fiber paper was  $0.234 \text{ w}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ , and the addition of copper powder improved the thermal conductivity of paper. With increasing amounts of copper powder, the thermal conductivity of copper paper increased to a maximum value of  $0.5608 \text{ w}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  in the 1:12 weight ratio of pulp/copper.

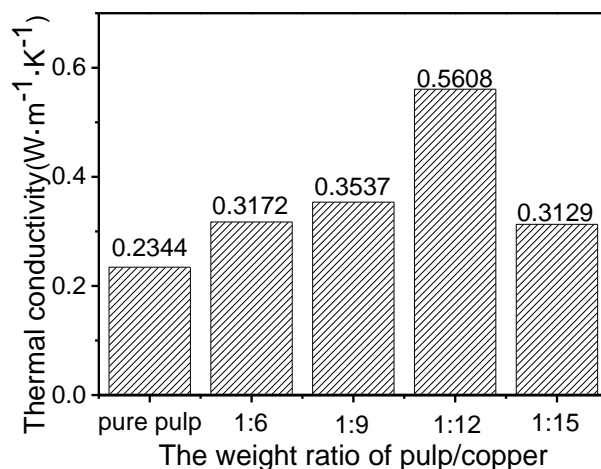
**Table 1.** Thermal Conductivities, Thermal Diffusivities, Densities and the Specific Heat Capacities of Copper Paper with Different Weight Ratio of Pulp/Copper

The weight ratio of pulp/copper	Thermal diffusivity ( $\text{mm}^2\cdot\text{s}^{-1}$ )	Density ( $\text{kg}\cdot\text{m}^{-3}$ )	Specific heat capacity ( $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )	Thermal conductivity ( $\text{w}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ )
Pure pulp	$0.2250\pm 0.003$	$450.0\pm 5.7$	$2314\pm 6.9$	$0.2344\pm 0.01$
1:6	$0.1300\pm 0.002$	$2947\pm 4.6$	$828.8\pm 7.2$	$0.3172\pm 0.01$
1:9	$0.1880\pm 0.005$	$3289\pm 3.4$	$572.0\pm 5.0$	$0.3537\pm 0.02$
1:12	$0.2660\pm 0.003$	$3491\pm 5.9$	$604.0\pm 4.3$	$0.5608\pm 0.02$
1:15	$0.1320\pm 0.006$	$2934\pm 3.3$	$808.0\pm 6.5$	$0.3129\pm 0.02$

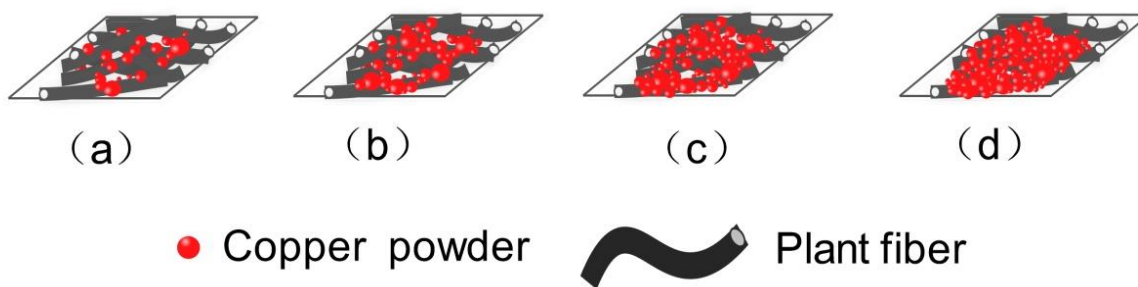
A schematic illustration of copper paper is shown in Fig. 3. When the weight ratio of pulp/copper was lower than 1:12, the thermal conductivity increased slowly. When the dosage of copper powder was low, the copper particles were distributed sparsely on the

fiber, so they were not in close enough contact to form the thermal conductive chain. When the dosage of copper powders reached a certain value, as shown in Fig. 3(b), the contact became firm and then formed a thermal conductive chain, which enhanced the thermal conductivity of copper paper noticeably.

However, when the dosage of copper was too high (Fig. 3(d)), copper particles would stack, which was equivalent to the addition of the thermal diffusion path distance, slowing down the diffusion of heat, which finally led to the decrease of thermal conductivity. This was consistent with the observation from SEM.



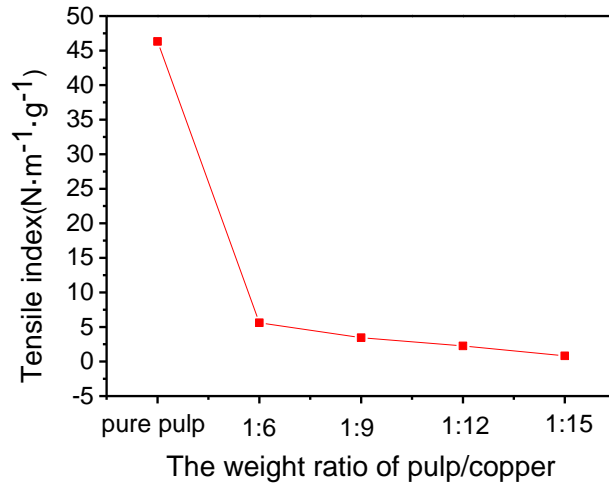
**Fig. 2.** The effect of the weight ratio of pulp/copper on thermal conductivity



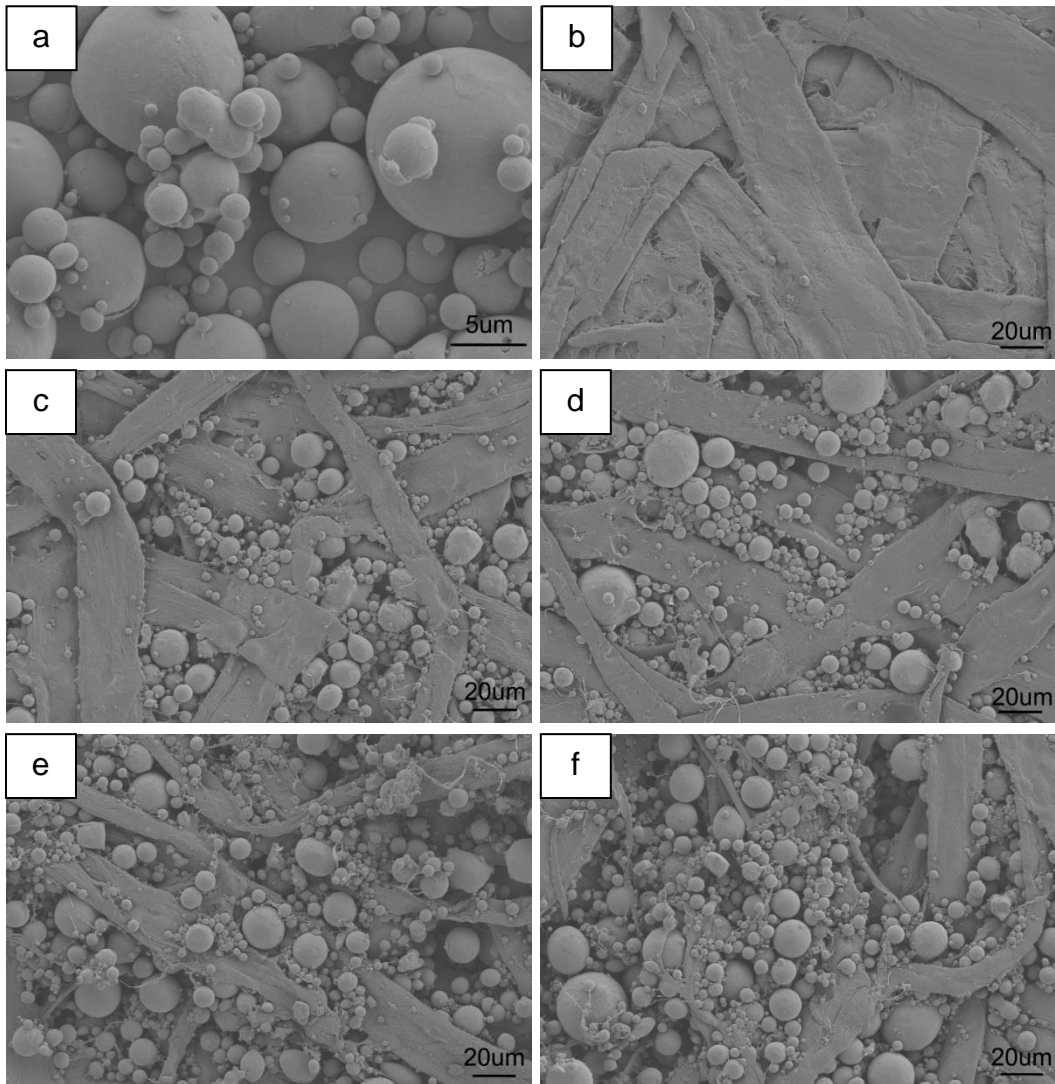
**Fig. 3.** Schematic illustration of copper paper with the weight ratio of pulp/copper is (a) 1:6; (b) 1:9; (c) 1:12; and (d) 1:15, respectively

### Tensile Index of Copper Paper

The tensile index curve of copper paper with five different weight ratios of pulp/copper is plotted in Fig. 4. The tensile index of the paper without copper was 46.3 N·m<sup>-1</sup>·g<sup>-1</sup>. The tensile index curve of copper paper showed a decreasing trend with the increase of quality percentage of copper. The tensile index of copper paper whose weight ratio of pulp/copper was 1:6, represents a decrease of 88% compared with the paper without copper. This phenomenon may have resulted from the decline of binding energy between copper and plant fiber due to the destructive effect of the copper particles.



**Fig. 4.** The effect of the weight ratio of pulp/copper on tensile index of copper paper



**Fig. 5.** The SEM image of (a) ultrafine copper powder; (b) softwood pulp; and copper paper with the weight ratio of pulp/copper is (c) 1:6; (d) 1:9; (e) 1:12; (f) 1:15, respectively

### Morphology Observation of Copper Paper

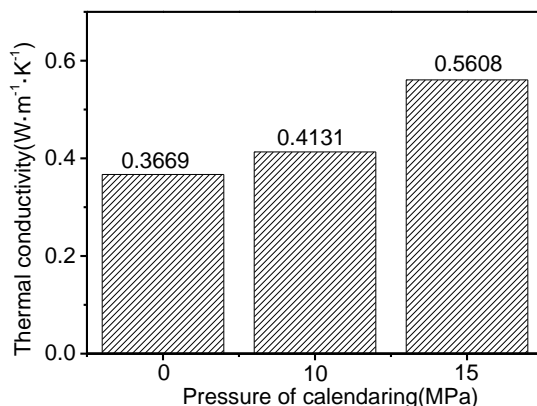
The morphology of ultrafine copper powder, softwood pulp, and copper paper with different weight ratios of pulp/copper in 1:6, 1:9, 1:12, and 1:15, were observed by SEM (Fig. 5). SEM imaging showed that copper papers consisted of copper powder particles roughly 2  $\mu\text{m}$  to 20  $\mu\text{m}$  in diameter that tended to be randomly distributed on the paper surface. As shown in Fig. 5(c), when the dosage of copper was low, copper particles in the fiber matrix were mainly present in an isolated form, having less impact on each other. With the increase of the quality percentage of copper, copper powder particles tended to contact with each other and form a thermal chain, and the local thermal chain was interconnected and penetrated to form a thermal network throughout the cellulose matrix material, which resulted in higher thermal conductivity that was supported by the above change rule of thermal conductivity.

### The Influence of Calendaring

Based on the typical processing method of copper paper, copper paper can be further processed using a rolling calender with different pressures. Table 2 shows the thermal conductivities, thermal diffusivities, densities, and the specific heat capacities of copper paper with different calendaring pressure. Figure 6 shows that the thermal conductivity of copper paper without calendaring was  $0.3669 \text{ w}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ . With the increase of calendaring pressure, the thermal conductivity of copper paper increased up to  $0.5608 \text{ w}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  when the pressure was 15 MPa. Additionally, because of the increase of calendaring pressure, the thickness of copper paper decreased, and the fiber network structure became more compact, which helped the copper particles get closer and form a better thermal conductive chain.

**Table 2.** Thermal Conductivities, Thermal Diffusivities, Densities and Specific Heat Capacities of Copper Paper with Different Calendaring Pressure

Calendaring pressure(MPa)	Thermal diffusivity ( $\text{mm}^2\cdot\text{s}^{-1}$ )	Density ( $\text{kg}\cdot\text{m}^{-3}$ )	Specific heat capacity ( $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )	Thermal conductivity ( $\text{w}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ )
0	$0.2330\pm 0.005$	$2298\pm 3.6$	$685.0\pm 1.5$	$0.3669\pm 0.02$
10	$0.2190\pm 0.003$	$2413\pm 4.1$	$782.0\pm 2.4$	$0.4131\pm 0.01$
15	$0.2660\pm 0.007$	$3491\pm 2.8$	$604.0\pm 3.9$	$0.5608\pm 0.02$



**Fig. 6.** The effect of calendaring pressure on the thermal conductivity of copper paper with the pulp/copper weight ratio of 1:12

## CONCLUSIONS

1. Copper paper was prepared by the traditional papermaking process. The goal was to evaluate the suitability of such materials for applications in the thermal conductivity area. The addition of copper powder can effectively improve the thermal conductivity of paper. With the increase of the amount of copper powder, the thermal conductivity of copper paper rose and then reached its maximum of up to 0.5608 when the pulp/copper weight ratio was 1:12, which was a 143% increase compared to the paper without copper powder.
2. The copper particles were distributed randomly on the fiber surface according to the observation of SEM, which showed the favorable combination between copper powder and fiber. However, the tensile index curve of copper paper showed a decreasing trend with the increase of quality percentage of copper. The tensile index of copper paper with the weight ration of pulp/copper was 1:6, an 88% decrease compared with the paper without copper.
3. Calendering enhanced the thermal conductivity of the copper paper. With increasing pressure from 0 MPa to 15 MPa, the thermal conductivity was increased from  $0.367 \text{ w}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  to  $0.561 \text{ w}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ .

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