Percolation for Coated Conductive Paper: Electrical Conductivity as a Function of Volume Fraction of Graphite and Carbon Black

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Conductive papers were prepared *via* surface coating with graphite or carbon black using either carboxylated styrene butadiene latex or starch as the binder. It is of practical interest to determine the percolation threshold for the coated paper product made using a binary system consisting of conductive filler and binder. In this study, the electro-conductivity threshold of various conductive papers was determined based on experimental data according to the percolation law. Results showed that the conductivity of coated, conductive paper is a function of the volume fraction of conductive filler, which can be described well by the percolation theory. The percolation thresholds of graphite/latex, graphite/starch, carbon black/latex, and carbon black/starch coatings were 17.66, 12.36, 11.71, and 8.69 vol.%, respectively. At concentrations higher than the percolation threshold, the conductivity of conductive paper using graphite as the conductive filler was much higher than that achieved using carbon black at a similar volume fraction. The present paper has significant practical implications for conductive paper technology using graphite filler based on surface coating technology.

Keywords: Conductive paper; Percolation; Graphite; Carbon black; Carboxylated styrene butadiene latex; Starch

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INTRODUCTION

Conductive papers represent a new class of paper products that can be used extensively in many fields, such as antistatic packaging, electromagnetic shielding, planar heating elements, new energy and electrochemical materials, sensors, and actuators (Hu *et al.* 2009; Shen *et al.* 2010; Bendrea *et al.* 2011; Ummartyotin *et al.* 2011). The uses of these products extend beyond those of traditional papers such as products for printing and writing, packaging, tissue, and other consumer uses.

Various methods to prepare conductive paper have been described. Some of these include mixing conductive materials and pulp fibers and subjecting them to the traditional papermaking process (Oya and Ogino 2008; Agarwal *et al.* 2009; Anderson *et al.* 2010; Jabbour *et al.* 2012); coating the papers with conductive fillers (Hu *et al.* 2009; Tang *et al.* 2014); and *in-situ* polymerization and adsorption of conductive polymers onto pulp fibers before using them in paper making (Li *et al.* 2010a; Youssef *et al.* 2012).

Surface coating with electrically conductive fillers onto paper sheets is a practical and effective way to obtain conductive papers. Paper coating technology has been known to the paper industry for a long time and has several advantages, such as low production cost, high efficiency, high filler retention, and low technological risk when scaled up (Zhang *et al.* 2013). A conductive coating formula generally comprises a binder (commonly, a non-conductive material), and conductive fillers (Fig. 1). Determination of the conductive threshold and the effect of the conductive filler content on conductivity are of practical interest.

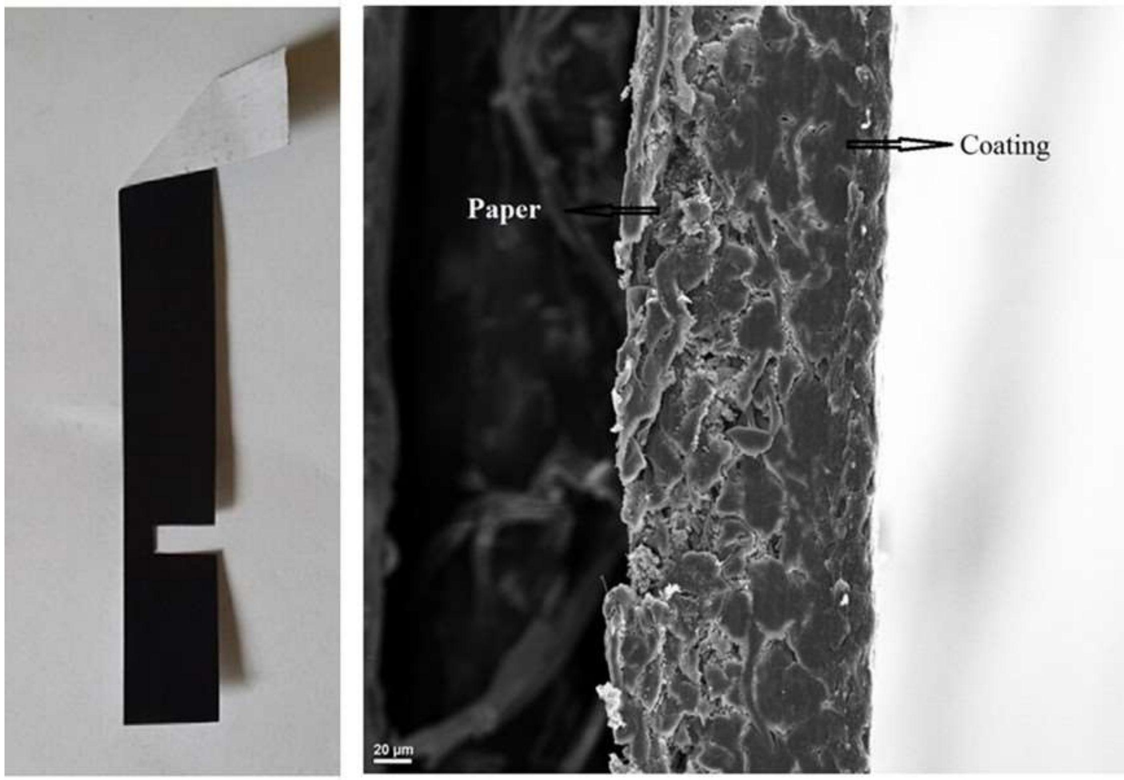

Fig. 1. Graphite-based coated paper (left) and cross-sectional SEM image of coated conductive paper (right)

Much effort has been made to increase the electrical conductivity of conductive paper. Graphite-based surface coating technology could impart high conductivity, in the range of 100 S/m (Mosseler 2014), to the paper, which may be suitable for the preparation of paper-based antennae with a wide range of potential applications.

The percolation theory has been used to describe the electrical conductive properties of different composite systems including carbon nanotubes (Hunt 2001; Bauhofer and Kovacs 2009; Likius *et al.* 2012). It has also been applied to the conductive paper system made of mixed, unmodified pulp fibers and modified polypyrrole pulp fibers, for which a threshold of 8.7 vol.% was found (Huang *et al.* 2005; Li *et al.* 2010b).

In this study, the classical percolation theory was employed to determine the conductive threshold and the effect of the conductive filler content on the conductivity of the coated paper using graphite as the filler. For comparison, carbon black was also included as a conductive filler. Four systems, including graphite/latex (G/L), graphite/starch (G/S), carbon black/latex (C/L), and carbon black/starch (C/S), were studied.

EXPERIMENTAL

Materials

Graphite (MW, 12.01 g/mol; particle size under 20 μm) was purchased from Sigma-Aldrich USA. Carbon black (C198-500) was purchased from Fisher Scientific USA. Starch (Filmkote 550) and carboxylated styrene butadiene (SB) latex (with solids content of 50%) were obtained from a mill in Eastern Canada. All chemicals were used without further treatment. Commercially available paper made of recycled fibers, with a thickness of 97 μm, was used as the substrate for the surface coating process. The volume fraction of carbon black and graphite was estimated by assuming that their densities were 1.8 and 2.2 g/cm^3, respectively (Shin and Kwon 2011). Deionized water was used for all experiments.

Experimental Procedure

Four coating formulas of graphite/latex, graphite/starch, carbon black/latex, and carbon black/starch with about 10 to 40% weight content were prepared by adding specific amounts of the above chemicals into water and stirring the mixtures with an electrical agitator (IKA T25) at 10,000 rpm for 30 min. For SB latex suspensions, the 50% water content was taken in to account. A K303 multicoater (RK Print Coat Instruments Ltd., UK) was used to apply the conductive filler suspensions to the paper sheets. The thickness of the paper was determined by a paper thickness tester (Labthink CHY-C2A, USA). The coating thickness was controlled to 40 ± 7 μm. The coated paper samples were subsequently dried at 105 °C for 60 min in an electric hot-air heating oven.

Electrical Conductivity Measurement

Real and cross-sectional SEM photographs of coated conductive paper with graphite/carbon black as the conductive fillers are shown in Fig. 1. The electrical resistance was measured using a Model 2750 multimeter/switch system (Keithley). Four electrodes were placed on the surface coating with a distance of 1 cm. The electrical conductivity was obtained from the resistivity as,

$$\sigma = 1/\omega = L/R\cdot A \tag{1}$$

where, σ is the conductivity in Siemens per meter (S/m), ω is the resistivity measured by an ohm meter (Ω·m), L is the length, R is the measured resistance of a conductor (Ω), and A is its cross-sectional area (Kamyshny *et al.* 2011; Tang *et al.* 2014).

Characterization

The morphology of surface-coated paper was characterized using an ULTRA-55 field-emission scanning electron microscope (SEM, JEOL JSM-6400, Tokyo, Japan).

RESULTS AND DISCUSSION

The relationship between conductivity of the paper coated with G/L, G/S, C/L, or C/S coatings and the volume fraction of conductive filler (graphite or carbon black) is shown in Fig. 2. The volume fraction was limited to no higher than about 30% for graphite and carbon black due to rheological issues. Too high a content of conductive filler could lead to process and operational difficulties (Zhang and Chen 2004; Huang *et al*. 2011).

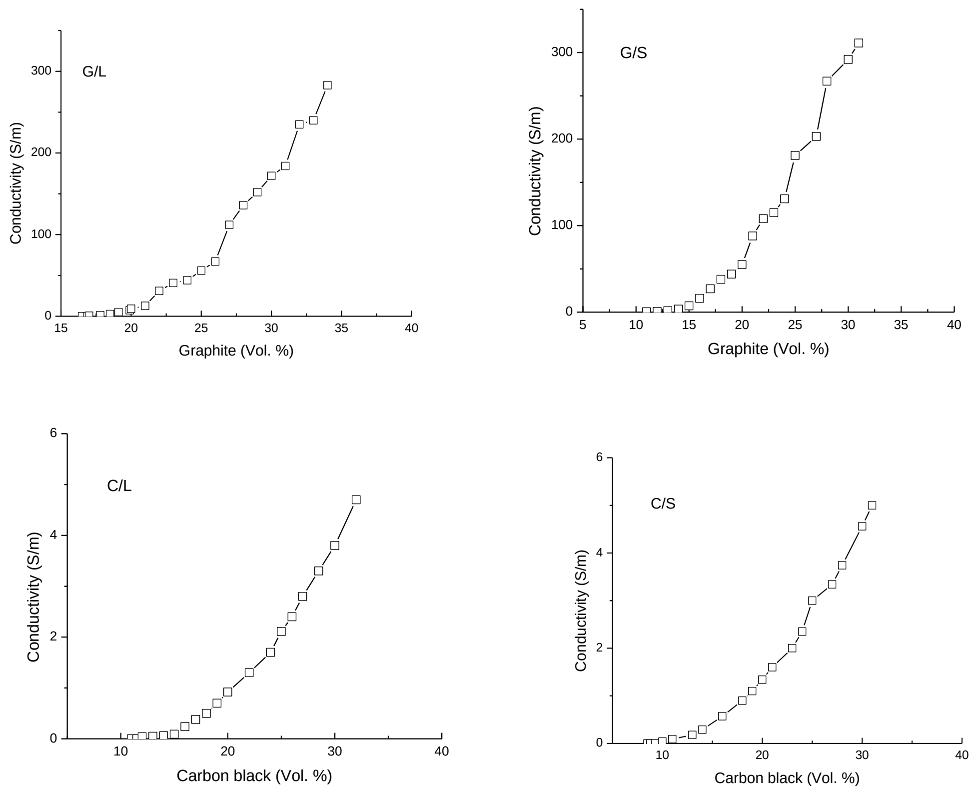

Fig. 2. Electrical conductivity of G/L, G/S, C/L, and C/S coated conductive papers as functions of the volume fraction of conductive filler

The percolation theory gives a statistical-geometric description of the conductivity of a disordered system. According to this theory, the percolation threshold is the critical volume fraction of the conducting component at which the infinite conducting network is first formed (Sherrington and Kirkpatrick 1975; Sahini and Sahimi 1994). Using the percolation concept, the electrical conductivity above the percolation threshold can be correlated to the conductive filler volume fraction as follows (Huang 2002),

$$\sigma = \sigma_0(V - V_c)^t \tag{2}$$

where, σ is the conductivity in Siemens per meter (S/m), σ_0 is a constant, V is the filler volume fraction, V_c is the percolation threshold, and t is an exponent. These parameters were determined for each of the four systems studied based on the experimental results shown in Fig. 1. These parameters are shown in Table 1.

Table 1. σ_0, V_c, and t of Various Coatings

Coating	V_c (vol. %)	σ_0 (S/m)	t
G/L	17.66	7493.33	1.81
G/S	12.36	5968.90	1.74
C/L	11.71	96.57	1.90
C/S	8.69	91.21	1.94

The percolation threshold values, V_c, of the G/L, G/S, C/L, and C/S coated samples were 17.66, 12.36, 11.71, and 8.69 vol.%, respectively. For a spherically shaped particle system, the percolation threshold is typically high. Kirkpatrick (1973) and Zallen (2008) cited a percolation threshold of 16 vol.% for geometrical models in systems consisting of statistically distributed, spherical particles.

As shown in Table 1, under otherwise identical conditions, using carbon black as the filler yielded a lower value of V_c. Janzen (1975) examined the effects of the filler structure on the percolation threshold and proposed Eq. 3 to relate V_c to the density and DBP (dibutyl phthalate) value of the conductive fillers,

$$V_c = 1 / (1 + 4\rho v) \tag{3}$$

where, V_c is the percolation threshold (volume fraction), ρ is the density of the conductive filler, and v is the DBP (dibutyl phthalate) value of the conductive filler. Equation 3 shows that higher values of v correspond to lower values of V_c. Carbon black usually has a higher DBP value than that of graphite (Zou *et al.* 2002). This explains why, within the conductive network, the percolation threshold of carbon black-filled composite is lower than that of graphite-filled samples.

Equation 3 illustrates the effect of the physical properties of conductive fillers, namely the density and DBP value, on the percolation threshold. It does not consider the effects of the matrix (for example, the binder). As shown in Table 1, the binder used can also affect the percolation threshold; under otherwise identical conditions, starch yielded a lower threshold than latex. It has been reported previously that the percolation threshold of a tertiary CB/PP/EVA system was 3.8 vol.% as compared to 7.8 vol.% for a binary CB/PP composite without EVA (Zhang and Chen 2004). In addition, the physical state can also affect the threshold. For instance, the percolation threshold of carbon black/ butyl-acrylate solid composite was found to be 10.9 vol.%, but decreased to 5.8 vol.% of carbon black for a foam product with the same composition (Pelíšková *et al.* 2014).

As shown in Table 1, the σ_0 values of the G/L and G/S samples were much higher than those of the C/L and C/S samples. This is in agreement with the fact that graphite is more electrically conductive than carbon black when used as a conductive filler *via* surface coating (Tang *et al.* 2014). Graphite is an anisotropic conductor whose conductivity is much greater than that of carbon black. σ_0 has a great influence on the conductivity of the final product, so choosing material with good conductivity is critical in producing conductive paper products with very high conductivity.

The exponent values, t, were in the range of 1.74 to 1.94 (Table 1). The results were lower than those of the EBA/carbon black composites (2.24), the ethylene butyl-acrylate/carbon black composites (3.4), and the acrylonitrile butadiene styrene/graphite composite (3.37) (Dahiya *et al.* 2007; Thompson *et al.* 2010; Pelíšková *et al.* 2014). This may be because the present coating was rather thin, nearly a two-dimensional system, in accordance with prior literature (Stauffer and Aharony 1991; Li *et al.* 2010c).

The morphology of coated paper samples was characterized by SEM, as shown in Fig. 3. The conducting network of conductive filler does not completely form when the volume fraction is lower than the percolation threshold. This assumption can be confirmed by comparing the micrographs of coated papers with filler concentrations lower or higher than the percolation threshold. Cracks can be clearly observed in images (a), (c), (e), and (g), supporting the conclusion that a conductive network was not formed. However, in Figs. 3(b), (d), (f), and (h), the conductive fillers were well-connected. The formation of cracks depends on interaction between the binder and filler phases.

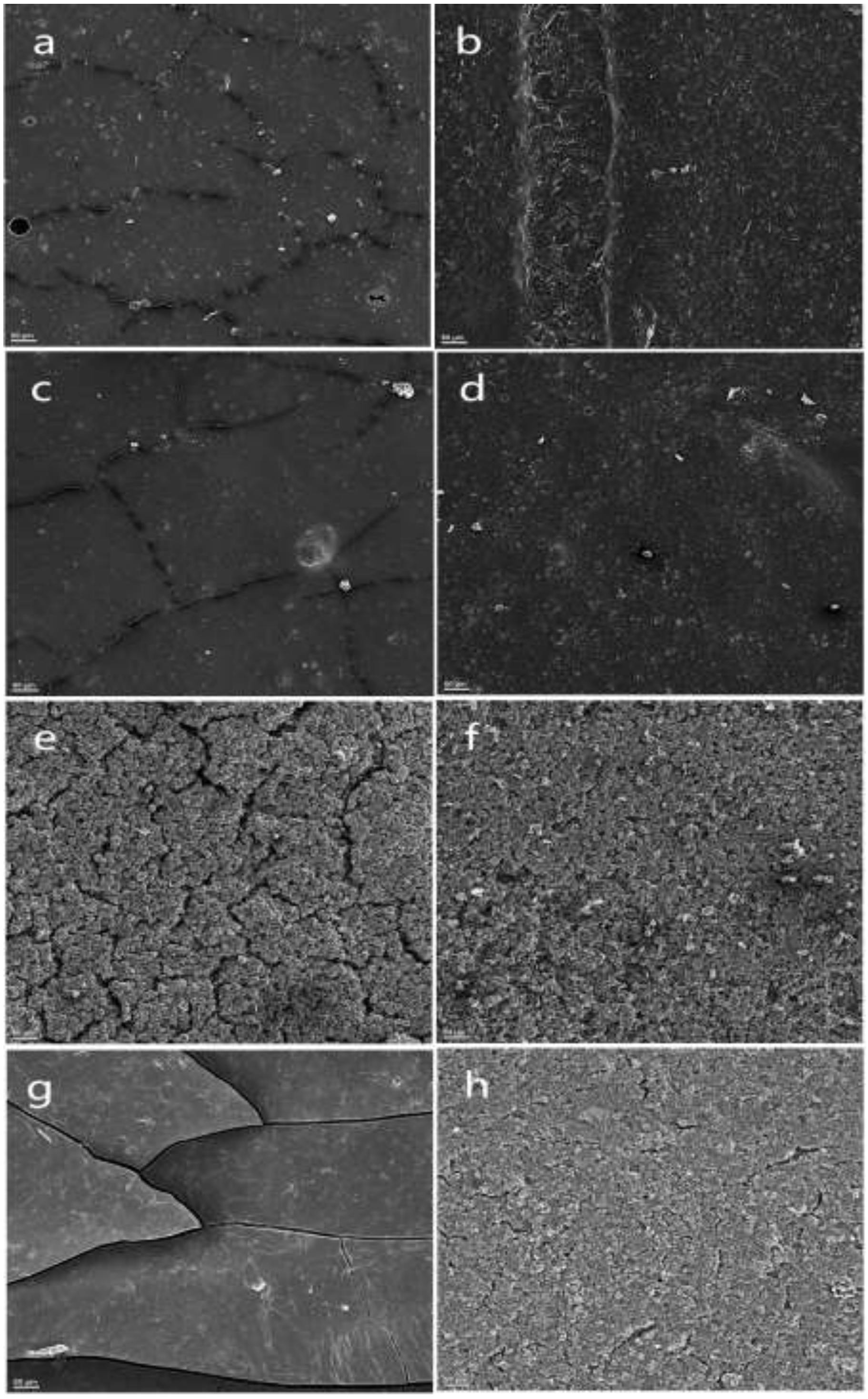

Fig. 3. SEM images of coated papers with different graphite or carbon black concentrations: (a) SB latex with 13 vol.% graphite, lower than the percolation threshold of 17.66 vol.%; (b) SB latex with 19 vol.% graphite, higher than the percolation threshold; (c) SB latex with 10 vol.% carbon black, lower than percolation threshold of 11.71 vol.%; (d) SB latex with 12 vol.% graphite, higher than the percolation threshold; (e) starch with 10.5 vol.% graphite, lower than the percolation threshold of 12.36 vol.%; (f) starch with 20 vol.% graphite, higher than the percolation threshold; (g) starch with 5.0 vol.% carbon black, lower than the percolation threshold of 8.69 vol.%; and (h) starch with 18.1 vol.% carbon black, higher than the percolation threshold

There was a relatively higher binder content when the conductive filler concentration was below the percolation threshold. In this case, a significant amount of cracks were formed. These results suggest that graphite or carbon black filler particles of different sizes were randomly dispersed within the matrix. Clusters of randomly distributed conductive filler particles formed with increases in the volume ratio. Carbon black particle aggregates in the polymers were clearly shown by Zhang and Chen (2004). The formation of cracks, as seen in Figs. 3(a), (c), (e), and (g), may have been due to the lack of sufficient amounts of conductive filler aggregates when the conductive filler volume fraction was below the percolation threshold.

CONCLUSIONS

1. The percolation theory was successfully applied to explain the relationship between the conductivity of coated conductive paper and the volume fraction of conductive filler applied.
2. The percolation thresholds of graphite/latex, graphite/starch, carbon black/latex, and carbon black/starch coatings were 17.66, 12.36, 11.71, and 8.69 vol.%, respectively.
3. The exponent t of the percolation law varied from 1.74 to 1.94 for the graphite and carbon black systems studied.
4. The σ_0 values of the percolation law when using graphite as the conductive filler ranged from 5968.90 to 7493.33 S/m, much higher than those when using carbon black as the conductive filler (91.21 to 96.47 S/m).
5. The keys for preparing conductive paper with high conductivity *via* surface coating technology are to choose a filler with high electrical conductivity and to increase the volume fraction of the conductive filler.

ACKNOWLEDGMENTS

The authors thank Dr. Zhibin He and Dr. Qiang Wang of the Limerick Pulp and Paper Center, University of New Brunswick for their invaluable help and useful discussion. Financial support was provided by the Canada Research Chairs Program of the Government of Canada and the Fundamental Research Funds for the Central Universities of NEFU, Grant No. DL11CB10.

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Article submitted: March 13, 2015; Peer review completed: May 8, 2015; Revised version received: May 31, 2015; Accepted: June 13, 2015; Published: June 18, 2015.
DOI: 10.15376/biores.10.3.4877-4885