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Mechanism of sonication-assisted electrophoretic deposition of carbon nano-fiber on carbon fabrics

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ABSTRACT

Uniform carbon nano-fiber (CNF) films have been deposited onto carbon fabrics by sonication-assisted Electrophoretic Deposition (EPD). To examine the effect of sonication, the distributions of voltage and pH values in the deposition bath were measured during EPD process. The degree of uniformity of CNF deposition was analyzed from the morphology of the deposited CNFs by scanning electron microscopy. The neutralization of negative charged CNFs by hydrogen ions, which were generated by electrolysis of water at the anode (carbon fabric), is essential for the adsorption of CNFs onto carbon fabrics. In addition, sonication increases the movement of ions in the suspension and accelerates the neutralization of CNFs at the anode. Moreover, sonication overcomes the aggregation and settlement of CNFs at the bottom of the deposition bath caused by gravity. The bubbles, which were generated by electrolysis of water, in the vicinity of the carbon fabrics were removed by sonication, resulting in the improvement of CNFs deposition. Based upon the results of voltage and pH values distributions during the EPD and analysis of morphologies of CNF films, a mechanism of sonication-assisted EPD has been proposed.

1. Introduction

Electrophoretic Deposition (EPD) is a colloidal process wherein charged particles are directly deposited on a substrate from a stable suspension by an electric field [1,2]. Since its discovery by Pickard [3] and the first observation of electric field induced motion of solid particles (clay) in water by Sarkar and Nicholson [4], EPD has been widely used to prepare various materials due to its low cost and simplicity. It has been used to fabricate light-weight ceramic composites combining high-temperature strength with improved fracture toughness, oxidation resistance and damage tolerance [1,5–8]. In recent years, EPD has drawn much interest as a technique to produce advanced materials, including carbon nano-filler composites [7,9–14], carbon nanotube film and buckypaper [15,16], TiO_2 nano-crystal films [17], and reduced graphene oxide composites [18].

In our previous work, vapor-grown carbon nano-fibers (CNFs) were uniformly deposited on 3k plain-woven carbon fabrics (Mitsubishi TR30) by EPD [13]. The key processing parameters such as the deposition time, the applied voltage, the concentration of CNF in a distilled water suspension, and the distance between anode and cathode have been optimized by using the Taguchi method. In the present experiment, we found it difficult to deposit CNFs onto the fabrics when 1k plain-woven fabrics were used for the substrates. This phenomenon was attributed to the following reason. Due to a low electric resistance between 1k fabric and copper plate in the suspension, a large mount of bubbles were generated by electrolysis of water which were adsorbed onto the fabric surface and made the deposition much difficult. The bubbles can be removed from the fabric by sonication during EPD process and uniform deposition was finally achieved by sonication assisted EPD. In addition, the uniformity of deposited carbon nano-fibers (CNFs) on a carbon fabric was remarkably influenced by the conductive property of the adhesive tape that covered four sides of the fabric to keep the fiber bundles from loosing during the EPD process. The deposited CNF films were much more uniform when the edges of a carbon fabric were covered by conductive tapes.

In order to understand the difference of deposition quality with and without sonication, it is necessary to address the process mechanism of EPD. Significant contributions have been made by previous researchers to understand the fundamental mechanism

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of the traditional EPD process. Hamaker and Verwey [19] proposed that the formation of a deposit by electrophoresis is due to the pressure exerted by incoming particles that enable the existing particles next to the new deposit to overcome the inter-particle repulsion. Koelmans [20] suggested that inter-particle repulsion decreases and the particles collapse in a deposit due to the increase in the electrolyte concentration in the vicinity of the electrode. Grillon et al. [21] hypothesized that particles would be neutralized while in contact with the deposition electrode. Sarkar and Nicholson [4] developed a theory in which deposition occurs via double-layer distortion and thinning during electrophoresis, followed by the coagulation of particles under the application of an electric field. Kershner et al. [22] suggested that the electrode surface also plays an important role, especially in the final arrangement of the particles. The chemical reaction that produces the pH gradient is also responsible for the agglomeration mechanism at the electrode to form the deposit [23,24]. Recently, carbon nanotubes were successfully deposited on carbon fibers by ultrasonically assisted EPD [11]. However, the deposition mechanism for sonication-assisted EPD has not been addressed, leaving the role of sonication in the deposition process unclear.

In the present work, we focus on developing an understanding of the underlying mechanism of EPD with sonication assistance. To study the deposition process, distributions of voltages and pH values in the deposition bath during EPD have been measured. Moreover, the morphology of deposited CNF film on the fabric has been analyzed at the macro and micro scales. Based on the results of the parameter measurement and morphology analysis, a deposition mechanism of uniformly distributed CNFs on carbon fabric has been proposed.

2. Experimental procedure

2.1. Materials

The nanomaterials for electrophoretic suspension were vapor grown CNFs (VGCNFs, Pyrograf III™PR-19, Applied Science, Inc.). The plain-woven carbon fabrics (T300, Toray) of 1k and 3k fiber bundle sizes were used as substrates in EPD. Detailed information of the materials can be found in our previous work [13].

2.2. Electrophoretic deposition process

For better dispersion in the suspension, VGCNFs were treated by acid oxidization to introduce negative charges. After 45 min sonication in HNO_3 solution, the carboxylic acid functional groups (—COOH) were introduced on the surface of CNFs. The functionalization of the CNFs has been confirmed by a Fourier transform infrared (FT-IR) spectrometer. The detailed procedure for the preparation of surface-treated VGCNFs can be found in Ref. [13]. A colloidal suspension of the mixture of CNFs and distilled water was sonicated at room temperature for another 45 min. Plain-woven carbon fabrics (1k and 3k) and copper plates were prepared in the same size of 125 mm × 130 mm. Four sides of a carbon fabric were taped to prevent the fibers from loosening in the suspension. Two types of tapes, copper and plastic, were used to examine the effect of their electrical resistance on EPD process.

Due to the negative charge of CNFs by surface treatment, the anodic EPD process, in which a carbon fabric and a copper plate were connected to the anode and the cathode, respectively, was adopted. The carbon fabrics with four sides covered by tapes were inserted into a picture-framed plastic holder. Then, the holder with a carbon fabric was fixed vertically in the suspension. The deposition bath was put in an ultrasonic bath to perform the EPD experiment with sonication. Fig. 1(a) shows the apparatus for sonication-assisted EPD experiments, consisting of a power supply (6035A, Agilent Technologies), a deposition bath and an ultrasonic bath (Branson B5510). A constant direct-current voltage of 120 V was applied across the 2 cm separation distance between electrodes. The concentration of CNFs was 0.1 wt%, and the deposition time was 1 min. After EPD, the CNFs-deposited carbon fabrics were dried in a vacuum oven at 120 °C for 24 h.

2.3. Voltage measurement

Voltages were measured at five positions with an equal distance of 5 mm between electrodes using FLUKE-179 multi-meter: one pole of the multi-meter fixed on the cathode and the other pole moved in the suspension from anode to cathode as shown in Fig. 1(b). A mark was made on the probe to make sure the position of pole in the same depth during the measurement Voltage distributions in the suspension were obtained at the initial and final stages during EPD. The initial stage is a short period of time (less than 10 s) after turning on the power, and the final stage is the end of deposition experiment (60 s after the deposition started).

2.4. PH value measurement

At the final stages of deposition, 50 μl suspension was carefully extracted by a micropipette with a sharp tip. The sampling locations were in the vicinity and in between of the carbon fabric and the copper plate (see Fig. 1(c)–(e)). Since it took several seconds to extract the suspension from the deposition bath, obtaining the pH value at the initial stage is meaningless. The suspension sample was carefully dropped onto a pH meter (Model H130 minilab™ one-point, HACH Company) as shown in Fig. 1(f). The pH meter houses the electrodes at the tip and displays the reading digitally. The sample quantity was enough for repeated measurements, and the pH meter was calibrated by a buffer solution of pH 7 provided by the manufacturer.

2.5. Morphology analysis

The macroscopic and microscopic morphologies of the deposited CNFs on the carbon fabric were characterized using a camera and an SEM (JSM-5800), respectively.

3. Results and discussions

3.1. Morphologies of CNFs on 3k carbon fabrics

Fig. 2 shows the morphologies of CNF films deposited on 3k carbon fabrics: Fig. 2(a) and (b) are for fabrics with plastic tapes on the edges, and Fig. 2(c) and (d) are with copper tapes. The CNF depositions on carbon fabrics in Fig. 2(a) and (c) were obtained by EPD without sonication assistance, while those in Fig. 2(b) and (d) with sonication-assisted EPD. It can be seen that dense and uniformly distributed CNFs were deposited on the carbon fabric under the condition of conductive tapes and sonication assistance (Fig. 2(d)). The CNF film deposited on carbon fabric with conductive tapes and without sonication assistance (Fig. 2(c)) was less uniform than that in Fig. 2(d). The poorest quality of CNF deposition was in the case of the carbon fabric with plastic tapes and without sonication assistance (Fig. 2(a)). Although the bottom of the fabric in Fig. 2(a) shows aggregation of CNFs caused by gravity, the deposition quality was significantly improved with sonication assistance as shown in Fig. 2(b).

For a detailed morphology of CNFs films, higher magnification images of the selected areas marked by numbers in Fig. 2(a)–(d) were made by SEM and are presented in Fig. 2(e)–(j). It can be seen