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ScienceDirect
Materials Letters 61 (2007) 1307–1310
materials letters
www.elsevier.com/locate/matlet

Froth floatation integrated into electrodeposition to prepare Ni/short carbon fibers composites with network and sheet structures

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Received 13 October 2005; accepted 7 July 2006
Available online 25 July 2006

Abstract

A new method of electrodeposition to prepare Ni/short carbon fibers (CFs) composites with network and sheet structures is described. The key point of the electrodeposition process is to obtain a sheet like preform floating on the electrolyte surface by froth flotation. The preform was composed of short homogeneous CFs. During the electrodeposition process, the preform was uniformly coated by nickel and the coating gradually grew from cathode to anode. The electrodeposits retained the network and sheet structures. The coating thickness can be controlled by appropriate electroplating conditions. The composites of epoxy resin reinforced by the electrodeposits were prepared successfully, and its electrical resistivity and electromagnetic shielding properties are reported.

Keywords: Short carbon fiber; Nickel; Electrodeposition; Froth floatation; Network; Sheet

1. Introduction

Carbon fibers (CFs) possess excellent mechanical characteristics, such as high specific strength, specific modulus, low expansion coefficient and high thermal and electric conductivity, which were widely used into resins and metals as reinforcements to fabricate high performance composites [1–3]. Recently the research field of sheet or two-dimensional (2d) plane materials of CFs has been extensively focused, for example carbon fiber felt, carbon fiber paper, short CFs reinforced sheet molding compound (SMC), etc, and the applications in electromagnetic shielding materials, antistatic materials, wave absorbing materials and electrode materials of battery are discussed [4–8]. Metal-coated fibers are considerably superior to neat fibers, and not only can improve the conductivity of the composite but also reduce the production cost. However, it was difficult to obtain the composite with uniform metal coatings by simple preparation process [9,10].

Electrodeposition is an important surface treatment to fabricate protective, decorative and conductive metallic coatings [11,12]. Based on the previous works of authors [13], we obtained a novel network composite sheet of Ni/short CFs by the simple technique using froth flotation. The plane network structure, being built up by Ni-coated short CFs, offers the innovative properties of Ni/short CFs composite, such as high porosity, large specific area and high conductive, thus the composite is expected to be a promising precursor for functional material, especially as a conductive filler applied in laminated resin or paper. And the Ni/short CFs composite is a promising reinforcement for bulk materials of metal matrix composites (MMCs) using lamination or infiltration. Moreover, the improved electrodeposition not only can obtain uniform metallic coatings on carbon fiber sheets, but also presents a new and feasible way to fabricate sheet materials.

2. Experimental

Short CFs used in this paper, were T300 provided by Japan Toray Co., Ltd. The Polyacrylonitrile (PAN)-based CFs were desized after being dispersed, and were cut into 2–3 mm length. The PAN-based fibers have a density of 1.76 g/cm^3 and a mean

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doi:10.1016/j.matlet.2006.07.019

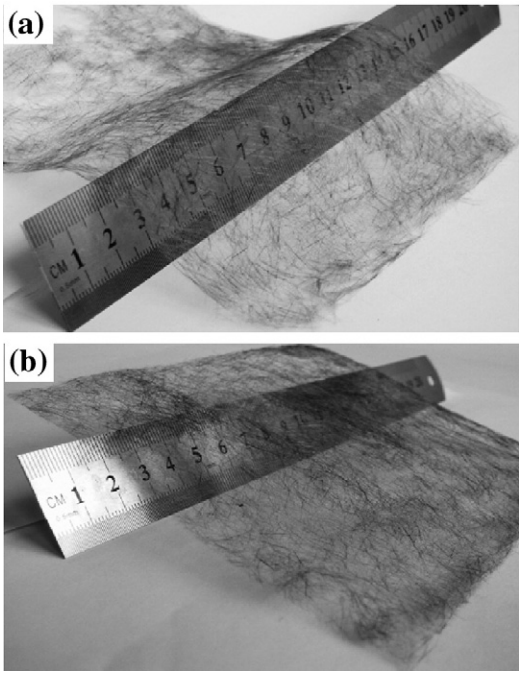

Fig. 1. Photographs of the two electrodeposits prepared at: (a) 0.5 A dm^{-2}, 35 min, (b) 1.0 A dm^{-2}, 30 min.

diameter of 7 μm. Prior to use, the fiber surfaces were cleaned of any contaminants by immersing them into the acetone solution for about 40 min.

The Ni-plating bath composed of 400 g/l $Ni(SO_3NH_2)_2 \cdot 4H_2O$, 5 g/l nickel chloride, and 40 g/l boric acid was prepared. The concentration of short CFs in bath is about 2 g/l. Before being plated, in order to enhance the interfacial adhesion the short CFs were activated in nitric acid for about 10 min, and then mixed with surfactant (0.05 g/l polyethylene glycol and 0.05 g/l 2-octanol, respectively), and at last agitated to uniformity by ultrasonic wave. A pure Cu plate with an exposed surface of 10 cm^2 (2 × 5 cm) was used as the cathode and a pure Ni plate (99.98 wt. %) was used as the anode. The experiment was operated at 40 °C. Lots of foams were produced in the bath by air agitator, and the short CFs rose with the foam. Then all the short CFs floated uniformly on the liquid surface to be a plane network preform. One edge of the preform was contacted with the cathode. Two electrodeposits with different coating thickness were obtained by selecting different current densities. The electrodeposition was stopped when the preform was coated entirely, which can be observed by the naked eye.

The epoxy resin composites with the electrodeposits were prepared using the following procedure. The appropriate amounts of the epoxy resin (E-44) and the hardener (polyamide 203#) were mixed at room temperature. The mould was preheated. Then the

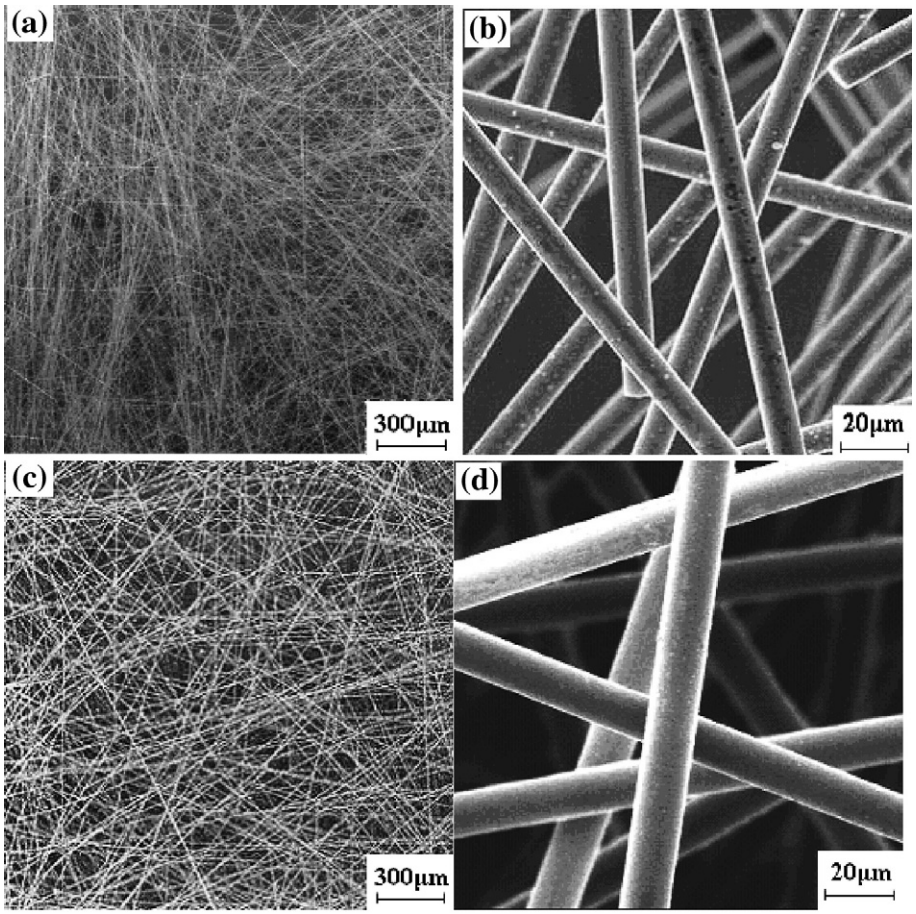

Fig. 2. SEM images of the two electrodeposits: (a), (b) are the images of sample A; (c) and (d) are the images of sample B.

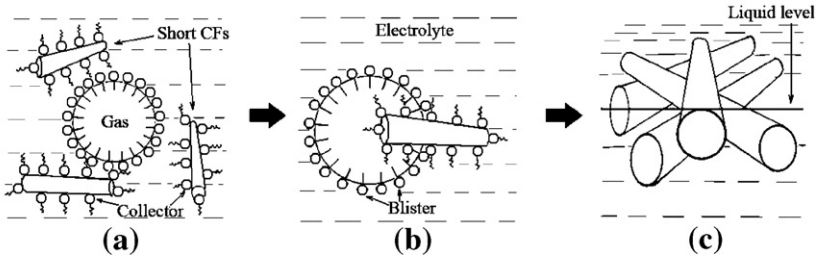

Fig. 3. Schematic diagram of the short CFs rising and the plane network preform forming: (a) Hydrophobic surfactant and foaming agent adsorbed in the surface of short CFs and foams, respectively. (b) Foams impacted short CF and carried it to rise. (c) Short CFs overlapped each other and floated on the electrolyte.

epoxy resin and the electrodeposits were put into the mould. The composites were cured at 80 °C, 10 MPa. The fiber weight fractions of the composites were controlled at about 5 wt.%.

The morphology of the short CFs and the separated electrodeposits were observed by scanning electron microscopy (SEM: S520). The cross-section of coated CFs was observed by optical microscope (Olympus B071). The electrical resistivity of composites was measured in the direction perpendicular to the pressure by four-probe method. The flanged circular coaxial transmission line method, ASTM Standard D 4935-99, was used to test the EMI SE.

3. Results and discussion

In other parameters controlled condition, the various coating thickness of electrodeposits were obtained at various current densities. The macrographs of the electrodeposits are shown in Fig. 1(a) and (b), which were obtained for 35 min with 0.5 A dm^{-2} and for 30 min with 1.0 A dm^{-2}, respectively. It shows us clearly that the electrodeposits have the sheet and network structure. And from the images sample A (Fig. 1(a)) is more flexible than sample B (Fig. 1(b)). The average thickness of the two samples, being measured by spiral micrometer, is 56 μm and 93 μm.

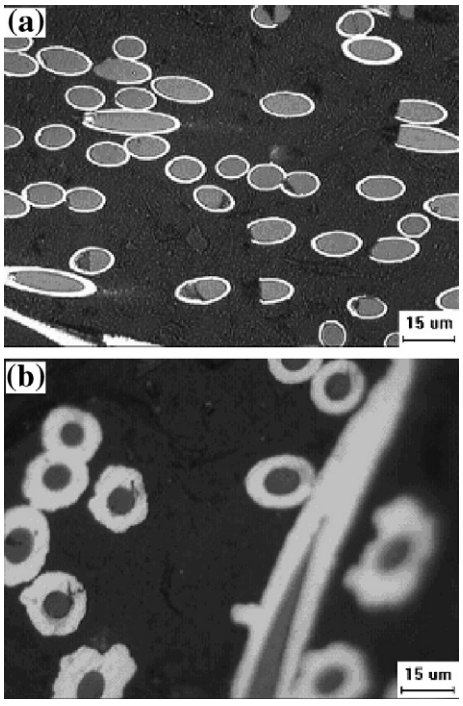

Fig. 4. Cross-section of the electrodeposits: (a) is the image of sample A, (b) is the image of sample B.

Fig. 2 presents the SEM morphologies of the two electrodeposits. Fig. 2(b) and (d) is the corresponding locally enlarged images of the two electrodeposits. Fig. 2 shows obviously that the electrodeposits have the plane network structure and the short CFs distributed uniformly. Almost all of the short CFs are not disorderly dispersed in the space but they are regularly distributed in paralleled planes. It is clear from Fig. 2(b) and (d) that the short CFs lapped with each other and built up to the electrodeposits layered and homogeneously. In sample A the average diameter of the short CFs with Ni coatings is equal to about 10 μm, and in sample B it is about 16 μm.

It is known that CF is a turbostratic structure, and it has hydrophobicity. The density of the electrolyte is about 1.26 g/cm^3 measured by a density meter, which is close to that of CFs 1.72 g/cm^3. It's reasonable to believe that, due to the resultant effect of surface tension and buoyancy, the short CFs is prone to rise to the surface of the electrolyte. The process of short CFs rising is very similar to froth floatation in mineral separation. The hydrophobic surfactant 2-octanol is collected to increase the hydrophobicity of short CFs, and the foaming agent polyethylene glycol is blistered to produce abundant foam. The proposed process of the short CFs rising and the plane network preform forming is sketched in Fig. 3. The hydrophilic group of collector adsorbed to the surface of short CFs, and the hydrophobic group extended into fluid phase. After adding the foaming agent polyethylene glycol and blasting air, the blister acted on foams. The orientation of blister groups is different from that of collector, the hydrophilic and hydrophobic groups entered into gas phase and fluid phase, respectively, as shown in Fig. 3(a) and (b). In the course of foams' rising, foams impacted with short CFs inevitably, and foams carried short CFs to rise (Fig. 3(b)). Then more and more short CFs became suspended on the surface of the electrolyte, finally the short CFs distributed uniformly and overlaid to be the sheet network perform. Due to the effect of surface tension and buoyancy, the preform floated on the electrolyte (Fig. 3(c)).

Anode and cathode were installed in the bath after the sheet like preform formed, and the cathode was contacted with one edge of the preform. During the process of electrodeposition, the growth of coating can be observed by the naked eye. The cathode vicinal region was the

Table 1
The properties of the two composites: composite A was reinforced by the electrodeposit of sample A; composite B was reinforced by sample B

Properties / Samples	Electrical resistivity (mΩ cm)	EMI SE (dB)				
		100 MHz	300 MHz	600 MHz	800 MHz	1000 MHz
Composite A	16.8	37.5	35.2	32.6	38.6	37.1
Composite B	13.2	40.4	39.3	38.7	41.6	42.5

origin of nickel deposition place and then the coating extended to the whole preform from cathode to anode gradually. Finally the electrodeposit with the sheet and network structure was obtained.

It is known that CF is a conductor, so the preform is more like an extended cathode when it was contacted with cathode. Because the preform was composed of naked fibers and the contact was loose, the conductivity was very poor and it decreased gradually from the cathode to the anode. Therefore, at the initial stage of electrodeposition, the short CFs near the cathode have higher nickel deposit rate than that of far short CFs. However, the deposit rate of the back CFs decreased slowly because of protective screens of the front Ni-coated CFs. Finally, to all short CFs in the preform, the amount of nickel deposition is approximately equal and the Ni coatings obtained are uniform.

The visual cross-sectional pictures of the electrodeposits indicate that the Ni coatings are uniform, as shown in Fig. 4. The average coating thickness of sample A is about 1.5 μm, and sample B is about 5.0 μm, which is accord with Figs. 1 and 2.

The epoxy resin matrix composites reinforced by the electrodeposits were prepared, and the properties such as electrical resistivity and EMI SE were tested. The results are presented in Table 1, which reveal that the composite B has lower electrical resistivity and higher EMI SE than that of composite A, the reasons may be that composite A has the thicker nickel coating than composite B. The uniform nickel coatings and the connected network structure in the electrodeposits lead the composites to have lower electrical resistivity and good EMI shielding.

4. Conclusions

In the new electrodeposition, froth flotation was used to obtain a novel preform with the network and sheet structure floating on a liquid surface, and the network composite sheet of Ni/short CFs was successfully prepared. The preforms were composed of short CFs homogeneously and the electrodeposits were coated by nickel uniformly. By observing and analyzing the special electrodeposition process, the present authors pointed out that the poor conductivity of short CFs and the protective screens of coated short CFs were the main reasons to obtain the uniform coatings. Two electrodeposits were prepared for 35 min with 0.5 A dm^{-2}, and 30 min with 1.0 A dm^{-2}, the average thickness of the coatings was 1.5 μm and 5.0 μm, respectively. The composites of epoxy resin reinforced by the electrodeposits were prepared, and their electrical resistivity and electromagnetic shielding properties are tested. The results showed that the composites have good properties, and implied that the special electrodeposit sheet has promising applications in electromagnetic wave shielding materials.

Acknowledgements

The authors are grateful for the financial support from the National Natural Science Foundation of China (No. 50401004) and the National High Technology Research and Development Program of China (No. 2002AA334010).

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