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Colossal permittivity of carbon nanotubes grafted carbon fiber-reinforced epoxy composites

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ABSTRACT

Giant dielectric-constant-ceramic materials have been paid much attention for their potential applications in high-capacity capacitors due to their high energy storage density. Dielectric constants of composite materials are generally low compared with ceramic materials. In this paper, carbon nanotubes (CNTs) were successfully prepared on carbon fibers (CFs) surface by chemical vapor deposition (CVD) and CNTs-CFs/epoxy composites were obtained by hot-pressure molding. Effects of CVD atmosphere on composites dielectric performance were investigated. The composites exhibited a surprisingly high dielectric constant about 200,000 (60 kHz) when the ratio of C_2H_2, H_2 and N_2 was 6:6:12 in the CVD process.

1. Introduction

Elaborate efforts have been reported on ceramic materials owing to their giant dielectric constant [1–4]. In contrast, the dielectric constant of polymer material is relatively low. However, polymer composites are arousing considerable interest since they exhibit good physical and mechanical properties which meet the requirements for advanced electric materials [5]. Adding conductive fillers such as carbon materials and metals can dramatically improve dielectric properties of polymers [6,7]. Due to the combination of excellent electrical properties, mechanical properties and low density [6,8], dielectric properties of CFs reinforced composites and CNTs reinforced composites have been extensively explored respectively, the significant changes in permittivity of composites have been observed [9–12]. Mirkhani et al. [13] investigated the effect of synthesis catalyst on electrical properties of nitrogen-doped CNTs/polyvinylidene fluoride nanocomposites and Ameli et al. [10] successfully synthesized nitrogen-doped CNTs/polymer nanocomposites exhibiting relatively high and frequency independent real permittivity together with low dielectric loss.

Nevertheless, van der Waals forces make it difficult to obtain a uniform dispersion of CNTs, which restricts the interface combination of CF and epoxy [14]. In this paper, uniform dispersion of CNTs was achieved on CFs surface by CVD. The yield and ordering degree of CNTs play important roles in dielectric properties of composites. The process that C_2H_2 cracking into activated carbon atoms is a reversible reaction which is carried out rapidly and the concentration of carbon atoms increased significantly [15,16]. H_2 can be used to control the reaction rate since hydrogen atoms facilitate the process to a reverse reaction and amorphous carbons will be substantially reduced.

In this study, different sorts of CFs specimens were prepared using C_2H_2 as carbon source and N_2 as protective gas. The permittivity of composites was greatly improved and influences of CVD atmosphere on dielectric properties were systematically studied.

2. Experimental

Materials and synthesis: The PAN-based CFs (Physical features of CFs are shown in Table S1) were calcined to remove sizing and immersed into an 0.05 mol/L ethanol solution of $Co(NO_3)_2{\cdot}6H_2O$ to deposit catalyst precursors. Catalyst coated CFs were placed in CVD furnace (Fig. S1 shows the details of CVD furnace) which was evacuated and heated to 450 °C under the protection of N_2, then catalyst precursors were reduced by H_2. A mixture of C_2H_2, H_2 and N_2 was introduced into the reactor to synthesize CNTs on CFs surface at 600 °C for 10 min. The flow of mixed gas is listed in Table 1. The ratio of sample 4 was the same as sample 3 while the gas flow increased by 2 times which led to a higher volume concentration. Composites were prepared using CFs and TDE-85

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Table 1
CVD atmosphere ratio of acetylene, hydrogen and nitrogen.

Sample No.	C_2H_2 (L/min)	H_2 (L/min)	N_2 (L/min)
1	3	0	9
2	3	9	0
3	3	3	6
4	6	6	12

(4,5-epoxycyclohexane-1,2-dicarboxylic acid diglycidyl ester) epoxy resin by hot-pressure molding. The mass ratio of CNTs-CFs loading in composite was 52 wt% and the volume fraction of CNTs-CFs was 45 vol%. The flow chart of synthesizing CFs/epoxy composites is shown in Fig. 1.

The morphology of CNTs was examined by SU-70 field emission scanning electron microscopy (SEM) operated at 15 kV. Dielectric properties and AC conductivity were investigated by LCR meter (Agilent, E4980AL). Further detailed structure study of CNTs was carried out by a high resolution trans-mission electron microscopes (HRTEM, EOL, JEM-2100) operated at 200 kV.

3. Results and discussion

The ratio of C_2H_2, H_2 and N_2 has a demonstrable effect on the morphology and yield of CNTs, definition of yield can be found in Supplementary materials. As shown in Fig. 2a, a large amount of amorphous carbons are generated with the ratio of 3:0:9. Extra carbon atoms are directly deposited on CFs surface since catalyst particles are not in sufficient quantities to catalyze all of them. However, the cracking reaction rate of C_2H_2 can be inhibited obviously with high hydrogen content. The concentration of activated carbon atoms is greatly reduced, meanwhile, the yield of CNTs decreases as shown in Fig. 2b. When the hydrogen content is moderate, as shown in Fig. 2c–d, CNTs grown on CFs surface are uniform. Meanwhile, the yield of CNTs increases with the improving of gas volume concentration.

Fig. 3a shows Raman spectra of CNTs grafted CFs, the relative intensity of D peak and G peak (I_D/I_G) is used to characterize the order degree of carbon materials. When the ratio is 3:0:9, massive amorphous carbons lead to a low graphitization degree (I_D/I_G = 1.2093), corresponding to SEM images, TGA results shown in

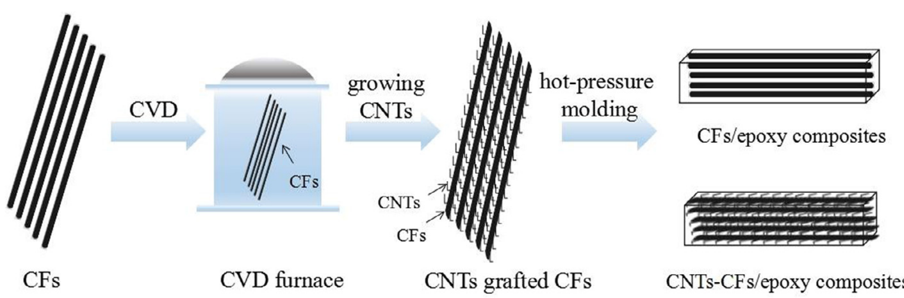

Fig. 1. Schematic diagram of synthesis of CNTs-CFs/epoxy composites.

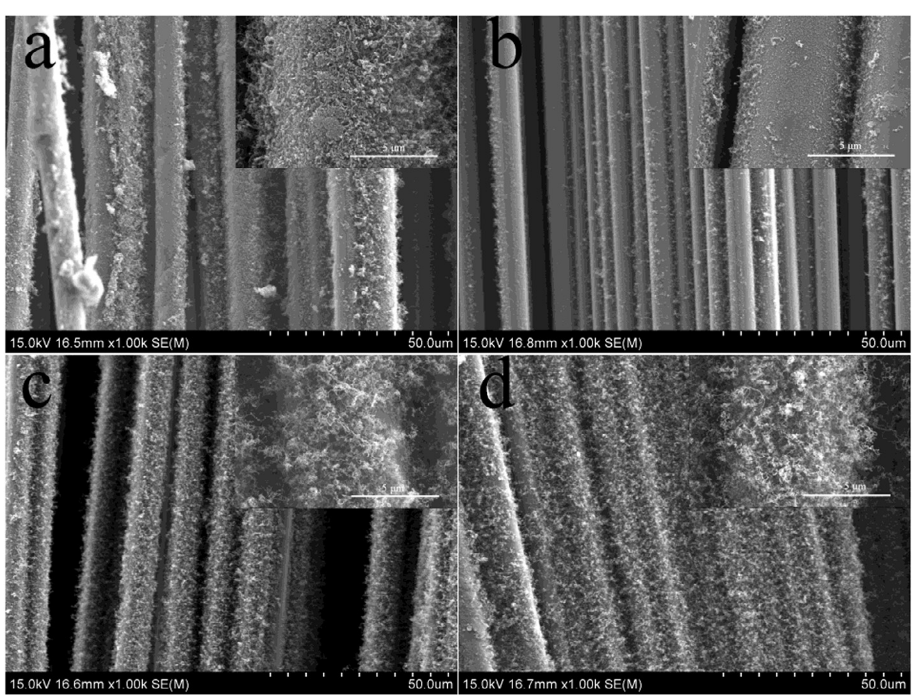

Fig. 2. SEM image of CNTs grafted CFs under different CVD atmospheres (a) C_2H_2:H_2:N_2 = 3:0:9, (b) C_2H_2:H_2:N_2 = 3:9:0, (c) C_2H_2:H_2:N_2 = 3:3:6, (d)C_2H_2:H_2:N_2 = 6:6:12.