MULTI SCALE AND GEOMETRY EFFECT ON THE ELECTROMAGNETIC BEHAVIOUR OF Fe_3O_4/CARBON COMPOSITE NANOFIBERS

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1 Introduction

Multifunctional composite nanofibers have attracted increasing interest in the recent years due to their potential for a broad range of applications. These composite nanofibers can be produced by incorporating various functionalities into the polymer solution using different nanofillers with specific properties. For example electrical and magnetic properties are suitable candidates for a wide range of applications such as electrodes for Li-ion batteries, microwave absorbers and electromagnetic device applications [1, 2]. In order to generate the electromagnetic properties, both electrically conductive and magnetically permeable components are needed. Fe_3O_4 nanoparticles (two different sizes: 10-20nm superparamagnetic (SPM) Fe_3O_4 nanoparticles and 20-30nm ferromagnetic properties (FM) Fe_3O_4 nanoparticles) are employed as one of these constituents as a magnetic filler. In combination with a polymer matrix, Fe_3O_4 can be used as microwave absorption structures and dampers [3] therapy medical applications [4] such as drug delivery and therapy [5].

We have selected PAN which is a predominant carbon fiber precursor that can be processed by thermal stabilization and subsequent high temperature carbonization. The carbonization induces electrical conductivity into the produced carbon fibers [6]. Electromagnetic multifunctional composite nanofibers can be produced by using Fe_3O_4 precursor dissolved in PAN followed by electrospinning and carbonization to fabricate magnetic composites which are electrically conductive [1, 7, 8]. On the other hand, the morphology of electrospun magnetic Fe_3O_4/PAN nanofibers with direct dispersion of Fe_3O_4 nanoparticles into a polymer solution has been studied by others [9, 10].

Different sizes and contents of nano-magnetite (Fe_3O_4 nanoparticles) along with the microstructure of electrically conductive carbon nanofibers (CNF) matrix has been found to affect on the electromagnetic properties of the composite material. In this study the effect of size and content of nanofiller and geometry of nanofiber matrix on the electromagnetic properties of the Fe_3O_4/CNF composite nanofibers are investigated.

2 Experimental

2.1 Materials

The materials used in this study are Polyacrylonitrile (PAN) (Mw. 150,000), N,N-Dimethylformamide (DMF), Fe_3O_4 (20-30nm) and (10-20nm) nanoparticles, Triton X-100 (contains less than 3% Polyethylene glycol).

2.2 Sample Preparation

0 and 10wt.%Fe_3O_4 (either 20-30nm or 10-20nm) to the PAN were dispersed in 10wt.% PAN/DMF solution using Triton X-100 as surfactant and DMF as solvent for PAN.

2.3 Electrospinning and Carbonization

The prepared composite solutions were electrospun using electrostatic forces [11]. In this study, the voltage applied to the polymer solution was in the range of 11-12kV for all the prepared samples. The non-woven fibers were collected on the aluminum foil. The as-spun nanofibers were placed in the furnace. They were then heated to 250°C at a ramping rate of 5°C/min and then stabilized for 100min under air atmosphere. The stabilized samples were then exposed to nitrogen at 250°C for 20min and heated to 900°C with the ramping rate of 5°C/min and carbonized at this temperature for 60min. Carbon fibers were then cooled down to the room temperature under nitrogen atmosphere. Carbonization process is summarized in Figure 1.

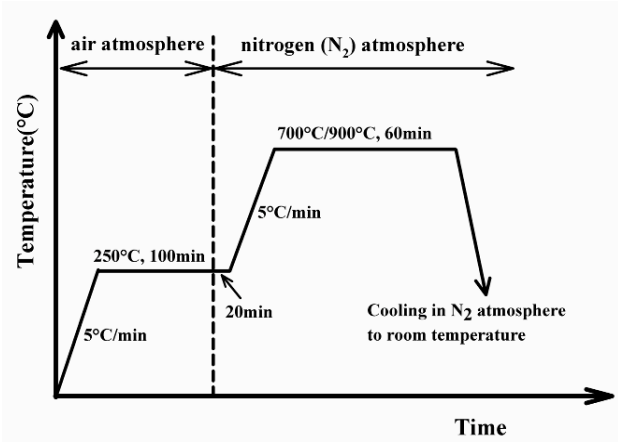

Fig. 1 Carbonization process of electrospun nanofibers.

2.4 Analysis Methods

To characterize the microstructural feature of samples, particles size or distribution and chemical composition, the Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray diffractometry (XRD) and Raman spectroscopy have been employed. Electrical conductivity and magnetic moment versus magnetic field plots known as M-H or hysteresis curves of composite nanofibers were also measured using four-point probe method and Superconducting Quantum Interference Device, respectively.

3 Results and Discussion

3.1 Effect of size and content of nanoparticles

The size of Fe_3O_4 nanoparticles as fillers is proved to affect the microstructure, carbon matrix crystallinity and electromagnetic properties of composite nanofibers.

Relatively uniform fibers with random distribution are acquired for both pristine carbon nanofiber and composite materials containing different sizes of Fe_3O_4 nanoparticles. Figure 2 shows the SEM micrographs of as-electrospun pristine and composite PAN-based nanofibers made of 10wt.% GB:10-20nm Fe_3O_4. The average fiber diameter increases from 390± 40 for pristine carbon nanofiber to 538±60nm and 837±52nm for as-electrospun composite PAN based nanofibers containing 10wt.%Fe_3O_4 with 20-30nm and GB:10-20nm nanoparticles, respectively.

This might happen as a result of an increase in the viscosity of the solution [12] or aggregation of nanoparticles since smaller nanoparticles have higher tendency to aggregate with each other.

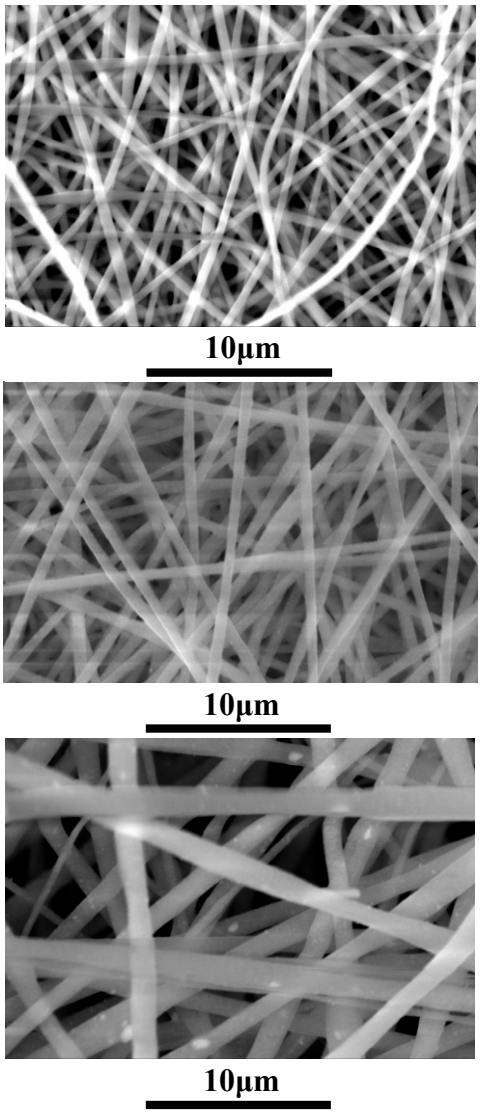

Fig. 2 SEM images of (a) pristine CNF and (b) 10wt.%Fe_3O_4 (20-30nm)/carbon nanofiber composite, (c) 10wt.%Fe_3O_4 (10-20nm)/carbon nanofiber composite.

It is also observed that the electrical conductivity is varied for pristine carbon nanofiber and composite carbon nanofibers fabricated with various sizes of Fe_3O_4 nanoparticles. First of all, electrical conductivity is proved to improve via addition of GA:20-30nm Fe_3O_4 nanoparticles. Raman spectroscope revealed that the graphitization of carbon fiber matrix is slightly enhanced by Fe_3O_4 nanoparticles.

Besides, XRD results demonstrated that after carbonization of composite nanofibers containing GA:20-30nm Fe_3O_4 nanoparticles, other magnetic

phases such as metallic α-Fe and Fe_3C are formed [13]. The electrical conductivity increases from 1.94±0.7S/cm for 10wt.% GB:10-20nm Fe_3O_4 carbon nanofiber to 9.20±0.50S/cm for 10wt.% GA:20-30nm Fe_3O_4 carbon nanofiber composite. The enhanced electrical conductivity for composite containing larger Fe_3O_4 nanoparticles can be attributed to the catalytic effect of GA:20-30nm Fe_3O_4 nanoparticles as well as the formation of some magnetic phases as mentioned above. The catalytic graphitization of carbon matrix by iron oxide is reported in other references [14, 15].

However, it is found that GB:10-20nm Fe_3O_4 nanoparticles do not contribute to the electrical conductivity of composite carbon nanofibers made of these nanoparticles. This observation is also confirmed with Raman spectroscopy and XRD results. No change in graphitization degree is seen nor the formation of any metallic phases such as Fe. The degree of carbon fiber graphitization ($R=I_G/I_D$) of pristine carbon nanofibers (10PAN900), 10wt.%GA:20-30nm Fe_3O_4/CNF (A10F900) and 10wt.% GA:20-30nm Fe_3O_4/CNF (B10F900) composite nanofibers is summarized in Table 1. I_G/I_D is the ratio between graphitized carbon structure to disordered carbon structure which can be determined using Raman spectroscopy.

Table 1. Raman spectroscopy results ($R=I_G/I_D$) and electrical conductivity (S/cm):

Sample	$R=I_G/I_D$	Electrical conductivity (S/cm)
10PAN900	0.559±0.020	2.60±0.90S/cm
A10F900	0.613±0.002	9.20±0.50S/cm
B10F900	0.568±0.010	1.94±0.7S/cm

XRD patterns of GA:20-30nm Fe_3O_4, GB:10-20nm Fe_3O_4, pristine carbon nanofibers (10PAN900), 10wt.%GA:20-30nm Fe_3O_4/CNF (A10F900) and 10wt.% GA:20-30nm Fe_3O_4/CNF (B10F900) composite nanofibers are demonstrated in Figure 3 with the corresponding reference numbers. Jade software was employed to identify the formation of different phases after carbonization process.

According to the XRD results shown in Figure 3, except for the carbon peaks at 2θ=22° and 44°, Fe_3O_4 (Reference number: 01-071-6337), α-Fe (Reference number: 98-000-0064) and Fe_3C (Reference number: 99-000-0796) are three identified phases formed after carbonization for 10wt.% GA:20-30nm Fe_3O_4/CNF composite. However, it is demonstrated that only Fe_3O_4 peaks exist for 10wt.% GB:10-20nm Fe_3O_4/CNF composite.

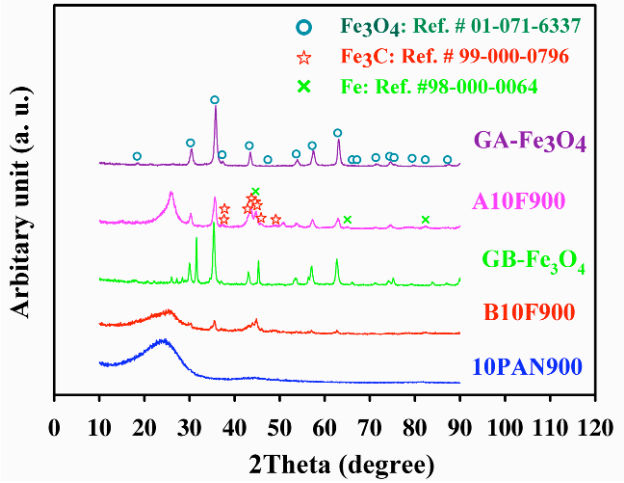

Fig. 3. XRD patterns of GA:20-30nm Fe_3O_4, GB:10-20nm Fe_3O_4, pristine carbon nanofibers (10PAN900), 10wt.%GA:20-30nm Fe_3O_4/CNF (A10F900) and 10wt.% GA:20-30nm Fe_3O_4/CNF (B10F900) composite nanofibers

Further, various magnetic strength and hysteresis are obtained for composite made of different sizes of Fe_3O_4 nanoparticles. Saturation magnetization (M_s), remanence magnetization (M_r) and coercivity (H_c) of pure nanoparticles, as-spun composite nanofibers and carbonized composite nanofibers at 900°C are shown in Table 2.

It is revealed that 20-30nm Fe_3O_4 nanoparticle provides a higher level of saturation magnetization (M_s=53emu/g). This value is lower (M_s=32emu/g) for 10-20nm nanoparticles. Reduction of the size of ferromagnetic particle results in increasing the surface area. The large surface area of nanoparticle leads to the formation of disordered spin configuration on its surface which is effectively capable of lowering the net magnetization level [16, 17].

Comparison of the magnetic properties of as-electrospun composite nanofibers made of different sizes of Fe_3O_4 nanoparticles reveals that electrospinning process does not affect the magnetic properties such as magnetic strength and hysteresis.

By embedding magnetic nanoparticles into the polymer matrix (PAN) to form composite nanofibers by electrospinning the nanoparticles can be arranged into higher order micro and macro structures. A key objective in this study is to answer the question of whether inherent superparamagnetic properties of

the magnetite nanoparticle can be preserved and transferrable to the fibrous structures.

Table 2 lists the magnetic parameters M_s, M_r, and H_c of GA:20-30nm, GB:10-20nm Fe_3O_4 nanoparticles and as-electrospun composite nanofibers containing 10wt.% GA:20-30nm Fe_3O_4 and GB:10-20nm Fe_3O_4 at room temperature. As shown in Table 2, the M_s value of the as-spun composite nanofibres either formed by GB:10-20nm Fe_3O_4 or GA:20-30nm Fe_3O_4 nanoparticles is proved to follow the rule of mixture and is dependent on the amount of magnetic Fe_3O_4 as previously reported [15].

The M_s values of A10F and B10F samples are equal to 5.8emu/g and 3.0emug corresponding respectively to 10% of the M_s values of GA:20-30nm Fe_3O_4 nanoparticle (56.5emu/g) and GB:10-20nm Fe_3O_4 nanoparticle (32.0emu/g). In addition, the as-spun composite nanofibers exhibit the same H_c value as that of the pure Fe_3O_4 nanoparticles (H_c=32.5Oe for those made of GA:20-30nm Fe_3O_4 nanoparticles and no coercivity for those made of GB:10-20nm Fe_3O_4 nanoparticles).

Accordingly we can conclude that the magnetic properties of Fe_3O_4 nanoparticles are successfully transferred into the electrospun nanofibrous mat for all the samples

Table 2. The M_s, M_r and H_c of GA:20-30nm, GB:10-20nm Fe_3O_4 nanoparticles and as-electrospun composite nanofibers containing 10wt.% GA:20-30nm Fe_3O_4 and GB:10-20nm Fe_3O_4 at 300K:

Sample	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
GA: 20-30nm Fe_3O_4	56.50	3.75	32.50
A10F	5.8	0.34	30
GB: 10-20nm Fe_3O_4	32.00	0.02	0
B10F	3.00	0.0133	0

In comparison to electrospun composite nanofibers, different magnetic properties are obtained for carbonized composite nanofibers containing the two different sizes of Fe_3O_4 nanoparticles. The carbonized samples made of both GB:10-20nm and GA:20-30nm Fe_3O_4 nanoparticles show larger M_s values as compared to their corresponding electrospun nanofibers.

The M-H curves of as-spun nanofibers and carbonized nanofibers are shown in Fig. 4 (B stands for 10-20nm Fe_3O_4 and A stands for 20-30nm Fe_3O_4 nanoparticles). Table 3 also summarizes the magnetic parameters for these carbonized samples. It can be seen that higher values of magnetic strength are obtained for samples made of larger nanoparticles (A10F(c) and A10F900 (d) samples).

The increase in M_s value due to carbonization process can be partly attributed to the loss of constituents of PAN known as carbon yielding which results in the rise in the proportion of Fe_3O_4 in the composite. Furthermore it was found that during the carbonization process the nanoparticles become larger as a result of the effect of high carbonization temperature. The TEM images provide further evidence that nanoparticles grow bigger after the carbonization process. Figure 5 shows the TEM micrographs of composite carbon nanofibers containing 10wt.% GA:20-30nm Fe_3O_4.

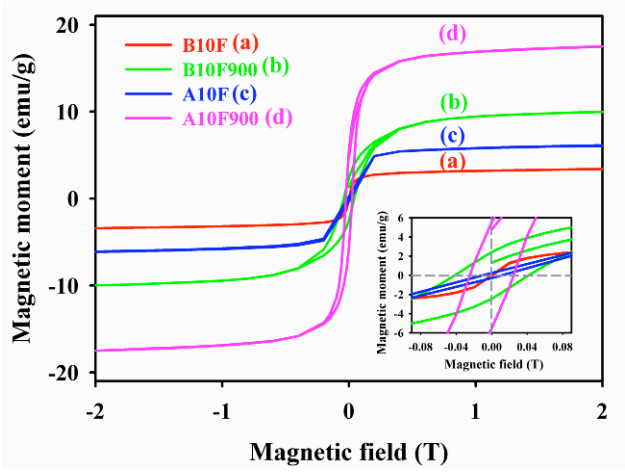

Fig. 4 M-H curves of as-spun and carbonized composite nanofibers.

Table 3. The M_s, M_r and H_c of composite carbon nanofibers containing 10wt.% GA:20-30nm Fe_3O_4 and GB:10-20nm Fe_3O_4 at 300K:

Sample	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
A10F900	16.00	5.50	250
B10F900	9.00	2.44	400

Another possible explanation for the higher M_s values of carbonized samples is the formation of new magnetic phases during the pyrolysis process such as α-Fe and Fe_3C. However, these phases are only formed in carbonized composite nanofibers made of GA:20-30nm Fe_3O_4 nanoparticles (Figure 3).

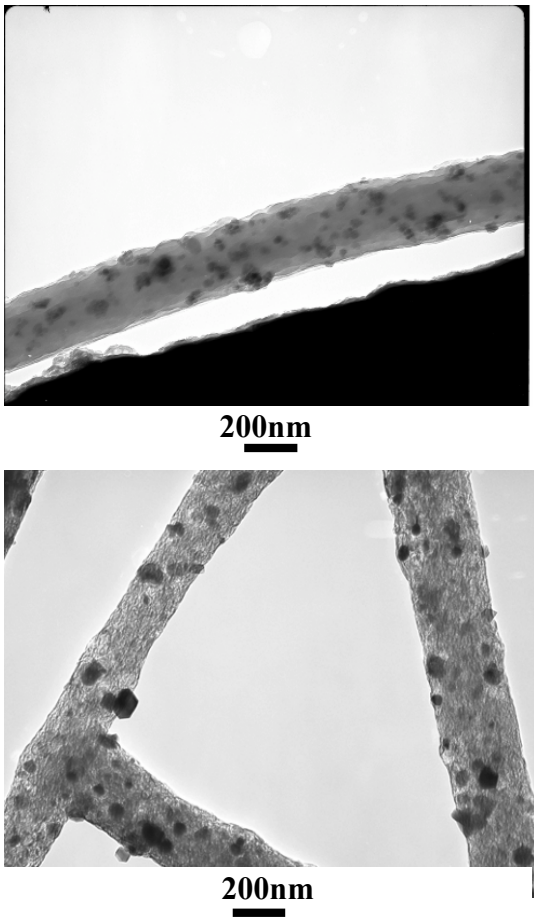

Fig. 5 TEM images of (a) 10wt.%Fe_3O_4 (20-30nm)/PAN nanofiber composite, (b) 10wt.%Fe_3O_4 (20-30nm)/carbon nanofiber composite.

In addition, higher level of hysteresis (larger M_r and H_c values) is induced in carbonized composite nanofibers as compared to the uncarbonized electrospun composite nanofibers. The reported superparamagnetic size of Fe_3O_4 nanoparticles is 25nm [18]. Therefore, GB:10-20nm Fe_3O_4 nanoparticles behave like superparamagnetic materials. However, when the size of Fe_3O_4 nanoparticles exceeds 25nm, they behave like ferromagnetic materials, meaning that coercivity (H_c) increases, as the particles grow larger. According to the TEM micrograph shown in Figure 5 nanoparticles fuse together and grow to the sizes larger than 25nm. For example, the measured size of Fe_3O_4 nanoparticles for the A10F900 sample is 66±30nm which is larger than 25nm. It is known that for nanoparticles above superparamagnetic size, increasing the size of magnetic nanoparticles results in increasing the magnetocrystalline anisotropy. Increasing the magnetocrystalline anisotropy of magnetic particles raises the required magnetic field to switch the magnetic moment direction. Consequently, the H_c increases with the size of nanoparticles after carbonization process [19]. The value of H_c reaches its maximum as the particles grow larger to 128nm which is the critical size for Fe_3O_4 [20]. For particles larger than 128nm (which is not observed in our samples) the magnetocrystalline anisotropy drops with increasing the size and hence H_c increases as shown in Figure 6.

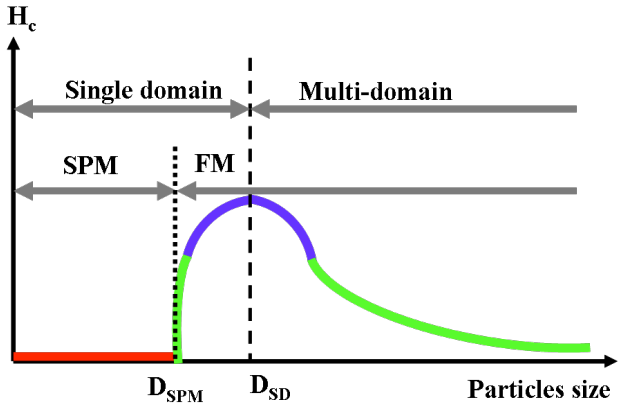

Fig. 6 The variation of coercivity (H_c) with the size of magnetic particles.

It is also of interest to mention that carbonized sample containing 10wt.% GB:10-20nm Fe_3O_4 nanoparticles (B10F900) shows larger H_c (400Oe) than the one made of GA:20-30nm Fe_3O_4 (250Oe). The reason can be explained perhaps as the higher agglomeration and diffusion of GB:10-20nm Fe_3O_4 nanoparticles obtained for B10F900 sample due to their small size and high surface energy of smaller nanoparticles.

Conclusion

PAN based carbon nanofibers containing two different sizes of Fe_3O_4 nanoparticles have demonstrated multifunctional and electromagnetic properties. Nanofibrous mats with uniform distribution of Fe_3O_4 nanoparticles have been produced by the electrospinning process. Both electrical conductivity and magnetic properties are demonstrated to depend on the particle size and the presence of nanoparticles.

Electrical conductivity was shown to increase with the addition of GA:20-30nm Fe_3O_4 nanoparticles while smaller GB:10-20nm Fe_3O_4 nanoparticles do not contribute to the electrical conductivity.

The feasibility of transferring magnetic properties of both GA:20-30nm and GB:10-20nm Fe_3O_4 nanoparticle into the fibrous structure has been

successfully demonstrated for non-carbonized samples.

The enhancement of the saturation magnetization level in carbonized samples can be attributed to the formation of larger magnetic particles, carbon fiber weight loss during the carbonization and the formation of magnetic phases such as α-Fe which is observed for the composites made of GA:20-30nm Fe_3O_4 nanoparticles. For the samples made of GB:10-20nm Fe_3O_4 nanoparticles, the higher level of saturation magnetization may only be attributed to the growth and fusion of nanoparticles.

Magnetic hysteresis was observed through carbonizing the as-spun nanofibers as a result of particle growth during heat treatment. Furthermore, the level of saturation magnetization was higher in the carbonized fibers.

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