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Characterization of Electrospun Carbon Nanofiber Doped Polymer Composites

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***Abstract*—**Ceramic, polymer and composite nanofibers are nowadays begun to be utilized in many fields of nanotechnology. By the means of dimensions, these fibers are as small as nano scale but because of having large surface area and microstructural characteristics, they provide unique mechanic, optical, magnetic, electronic and chemical properties. In terms of nanofiber production, electrospinning has been the most widely used technique in recent years. In this study, carbon nanofibers have been synthesized from solutions of Polyacrylonitrile (PAN)/ N,N-dimethylformamide (DMF) by electrospinning method. The carbon nanofibers have been stabilized by oxidation at 250 °C for 2 h in air and carbonized at 750 °C for 1 h in H2/N2. Images of carbon nanofibers have been taken with scanning electron microscopy (SEM). The images have been analyzed to study the fiber morphology and to determine the distribution of the fiber diameter using FibraQuant 1.3 software. Then polymer composites have been produced from mixture of carbon nanofibers and silicone polymer. The final polymer composites have been characterized by X-ray diffraction method and scanning electron microscopy (SEM) energy dispersive X-ray (EDX) measurements. These results have been reported and discussed. At result, homogeneous carbon nanofibers with 100-167 nm of diameter were obtained with optimized electrospinning conditions.

***Keywords*—**Electrospinning, characterization, composites, nanofiber.

I. Introduction

ELECTROSPINNING is a method to create nano-size fibers from polymer solutions. This process is both an interesting and well known physicochemical phenomena. In addition to electrospinning is the most effective method that applies to synthetic and natural polymers, polymer alloys, as well as to metals and ceramics composites [1], [2]. Carbon nanofibers and ceramic nanofibers can be fabricated by pyrolysis of nanofibers made from polymers that contain carbon or metal atoms [3].

In electrospinning method, a high voltage is applied to a polymer solution. When charges within the solution reached a critical value, a fluid jet will erupt from the droplet at the tip of the needle resulting in the formation of a Taylor cone (as shown in Fig. 1).

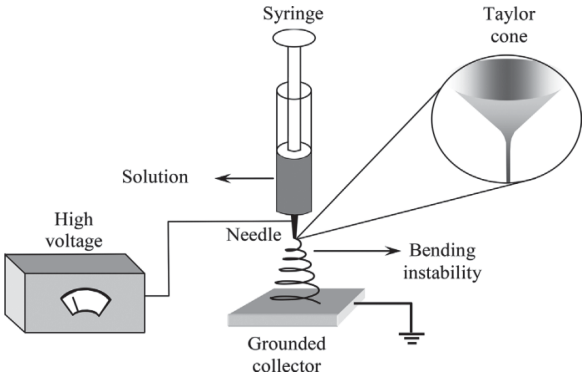

Fig. 1 Schematic diagram of the electrospinning [4]

A typical electrospinning equipment has three components: a high voltage power source, a syringe pomp (or nozzle), and a collector (as shown in Fig. 1).

The jet will move towards the region of lower potential, which is a collector. There are many parameters that will influence the structure and morphology of the electrospun fibers. The electrospinning of polymer solutions is affected by different variables, classified as solution parameters: process parameters and ambient parameters. These variables are listed in Table I [2], [5], [6].

TABLE I
ELECTROSPINNING PARAMETERS

Solution parameters	Process parameter	Ambient parameter
Molecular weight of the polymer	Applied voltage	Temperature
Concentration of solution	Distance between collector and spinneret	Humidity
Viscosity	Type of collector (static or moving)	
Surface tension	Flowrate of polymer solution	
Conductivity		
Solvent properties		

By reducing fiber diameters down to the nanosize, a significant increase in surface area is feasible. The downsizing in dimension and increase in surface area greatly affect the physical, chemical, biological reactivity and electroactivity of polymeric nanofibers [7].

Carbon nanomaterials have become candidates for many applications in fuel cells, nanocomposites, micro electric devices, sensors, energy storage, microelectronics,

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biomedicines, and mechanical resonators. For example; carbon nanotubes, graphene (oxides), carbon nanofibers, and fullerenes [8]. Some kinds of organic polymers that can be fabricate into nanofibers can be converted to carbon nanofibers [3]. Carbon nanofibers (CNF) can be made by using as-spun PAN nanofibers as a precursor followed by thermal treatment, which can affect the final properties of carbon nanofibers, such as diameter, structure, composition, homogeneity, electrical properties, flexibility, etc. [5]. The morphological microstructures and the related physical, mechanical or electrical properties of the electrospun carbon nanofibers are still largely unknown [1].

Polymer fibers synthesized from PAN/DMF solution undergo further modification by pyrolysis processes. Pyrolysis is defined as the decomposition of organic material by a thermochemical process at certain temperature in the absence of oxygen. Pyrolysis involves the change of chemical composition and physical phase. It is an irreversible process. The stabilization process occurs at a temperature between 180 and 300 ºC. After accomplishing the oxidative stabilization stage, carbonization process is applied to convert the polymer fibers into carbon fibers with increased strength [9].

Recently, many types of nanofibers have doped with various elements. The performance of the carbon nanomaterials for many applications is further improved by doping of elements (S, N, O, P, B). Furthermore, loading metal, metal oxide/ hydroxide on carbon nanomaterials enhances the performance [9]. Nowadays, many investigations have been made on noble metal nanoparticles to fabricate carbon nanomaterials, including Au, Ag, Pt and Pd nanoparticles. Among these metal nanoparticles, Ag nanoparticles have stirred up great research concern because of their high surface area, good stability, excellent biocompatibility and higher electrical conductivity [10].

This paper aims at investigating the Ag-CNF doped polymer composite.

II. Materials and Methods

For the preparation of the carbon nanofibers, we used Polyacrylonitrile (PAN, (C3H3N)x , Mw=150,000 g/mol) as the starting polymer reagents and N,N-dimethylformamide (DMF, HCON(CH3)2 , Mw=73,09 g/mol) as solvent. Silver nitrate (AgNO3, >99% Mw= 169,87 g/mol) is used as doping precursor. RTV664 A/B is a silicone rubber. The silicone rubber used as the matrix was RTV664 A/B, obtained from local company in Turkey. The preparation of the solutions of the carbon nanofiber samples has been achieved as follows. Firstly, we poured 96 g of N,N DMF and 4 g of PAN in a beaker and this mixture was stirred for an hour. Then AgNO3 was dissolved as 1% mol of polymer and stirred for 1 hour at 25°C. These obtained homogeneous solutions were loaded into a plastic syringe of the pump of the electrospinning set-up constructed by us [4]. Ag doped CNFs have been developed at constant voltage of 25 kV, at a height of 6 cm, and with constant flow rate of 2 ml/h. Then the Ag doped CNFs have been stabilized by oxidation at 250 °C for 2 h in air and carbonized at 750 °C for 1 h in H2/N2 atmosphere. Finally Ag-doped CNFs were added to RTV664 A/B mixture (1% mol of mixture). They were stirred homogenously and poured the mold. Polymer composite were obtained and then characterized by using SEM-EDX, goniometer (contact angle, CA).

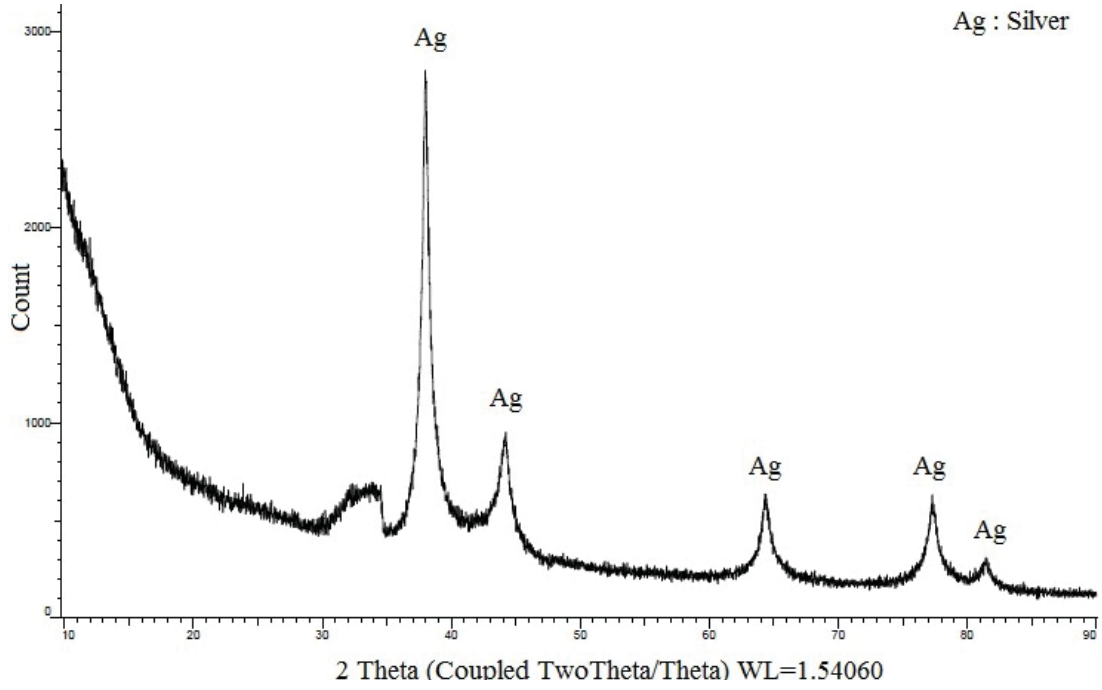

Fig. 2 XRD spectra of Ag doped CNFs

TABLE II
CARBON NANOFIBER DIAMETER

Description	Diameter			Measurement
	Average	Std Dev	Median	
Before stabilization	204	140	167	246
After stabilization	144	74	128	995
After carbonization	111	56	100	396

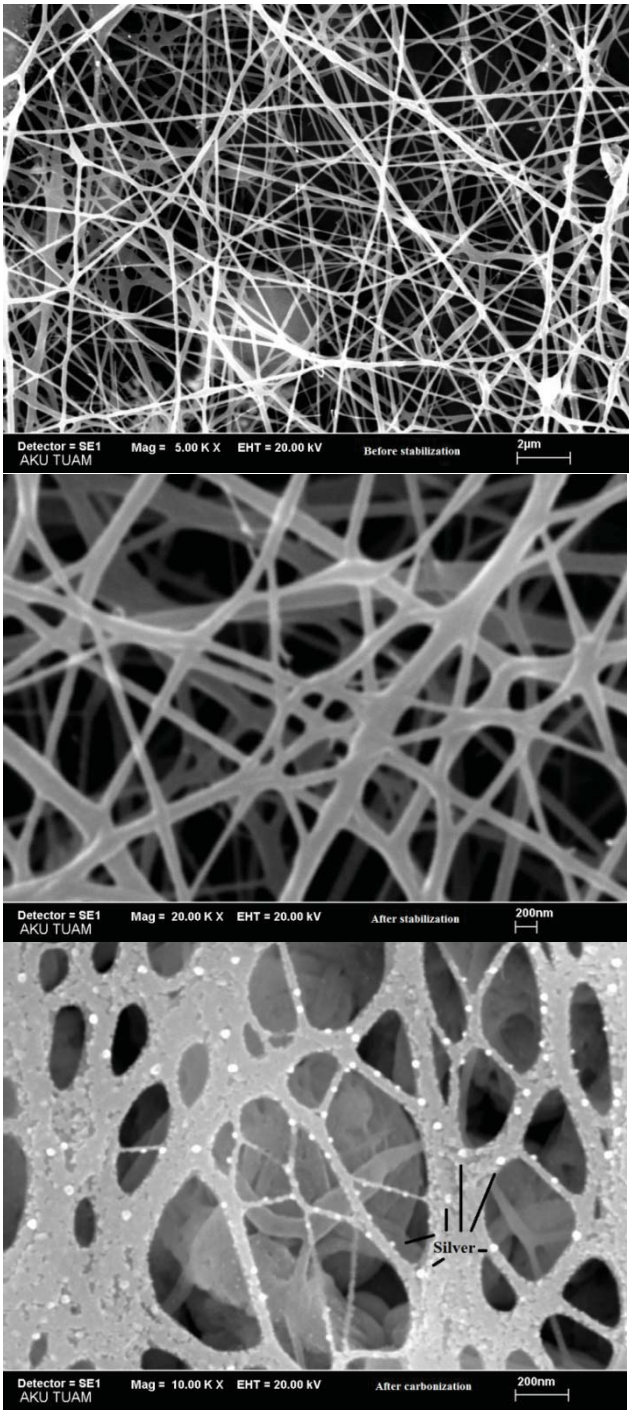

Fig. 3 SEM images of Ag doped CNFs

III. RESULTS AND DISCUSSION

The formation of silver NPs was characterized using X-ray diffraction (XRD) (XRD 6000- Shimadzu). The XRD spectra of the silver nanoparticle in the CNFs are shown in Fig. 2. The morphology and structure of as-prepared, after stabilization and carbonization of Ag doped CNFs were investigated by SEM (JEOL 6360 LV). In Fig. 3, SEM images are shown for the nanofibers.

Ag doped CNFs have been analyzed to study the fiber morphology and to determine distributions of the diameter fiber thicknesses using FibraQuant 1.3 Software (as shown in Table II).

As seen from Table II and Fig. 3 diameters of Ag doped CNFs are at the nanometer scale. The measured average diameter of these nanofibers depends on the thermal treatment.

In Fig. 4, SEM-EDX result of Ag doped CNFs are shown. Loaded metal particles have uniform size and distribute on the surface homogeneously. SEM-EDX also provides Ag metal doping.

The SEM-EDX elemental mapping scan was introduced to clearly identify the spatial distribution of Ag and C in the Ag doped CNFs structure, as shown in Fig. 5.

The tensile testing was measured through the ASTM D 412 method, using dumb-bell shaped test specimens, at ambient temperature (Fig. 6). Young's modulus (E) was derived from compression tests for Ag doped CNFs/RTV664 composite. Elastic module of RTV664 was measured as 3.1 MPa. In literature elastic modules of silicone elastomer is between 0.5-3.6 MPa. Because E of silicone polymer is related to the samples' base/agent ratio [11]. E of Ag doped CNFs/RTV664 composite was found 6 MPa. Novel polymer composite (Ag doped CNFs/RTV664 composite) with high modulus were successfully prepared in this study.

Fig. 7 shows that addition Ag doped CNFs (hydrophobic particles) increased hydrophobicity of polymer composite material. Contact angles changed from 104,41° to 111,83°. Contact angle measurements are sensitive to changes in surface roughness. Carbons tend to be hydrophobic character. Depending on the preparation method of your samples, local (nanoscale) roughness of the test surfaces could be affected by the addition of the CNTs to polymer.

In summary, the pure and Ag-doped CNFs and their polymer composite with high module were successfully synthesized through a simple and facile electrospinning technique and their mineralogical, morphological and surface properties were investigated.

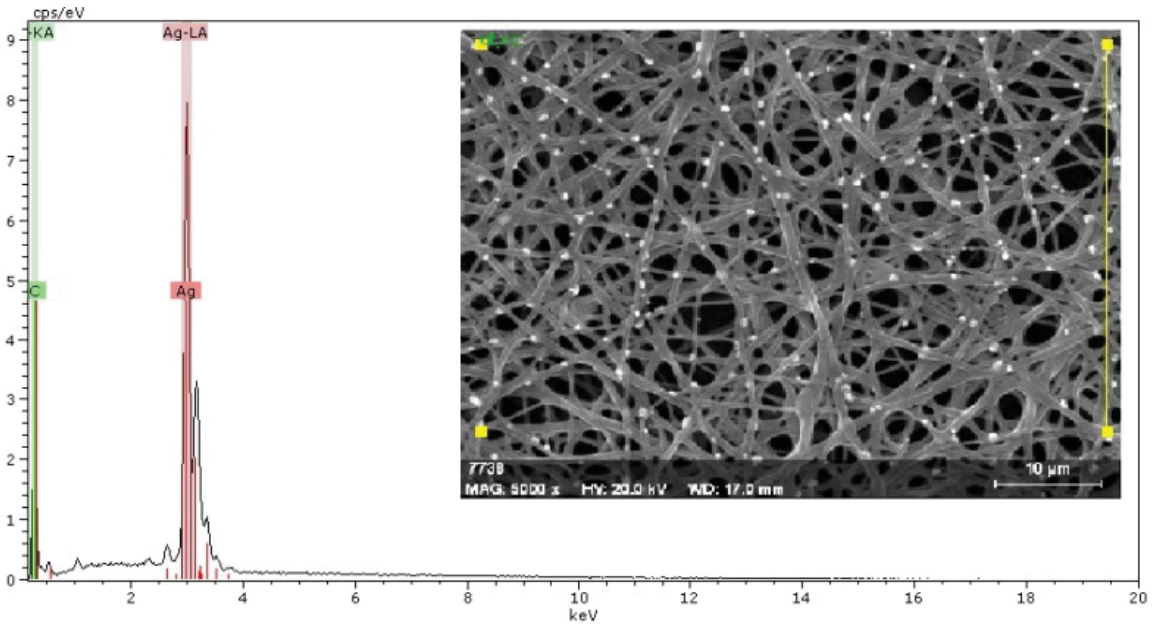

Fig. 4 SEM-EDX diagram of Ag doped CNFs

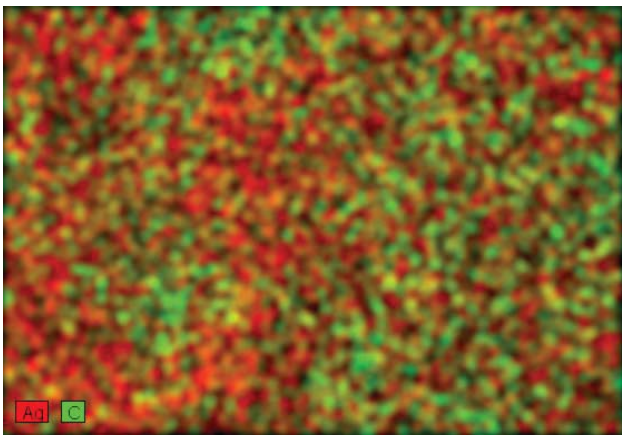

Fig. 5 SEM-EDX images of Ag doped CNFs for elemental mapping

Fig. 6 Moulded Ag doped CNFs/RTV664 composite

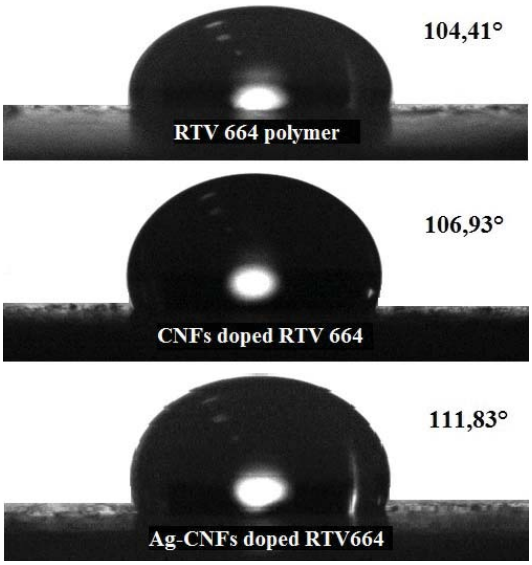

Fig. 7 Contact angles of polymer composite samples

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