

UV Resistibility of a Carbon Nanofiber Reinforced Polymer Composite

A. Evcin, N. Çiçek Bezir, R. Duman, N. Duman

Abstract—Nowadays, a great concern is placed on the harmfulness of ultraviolet radiation (UVR) which attacks human bodies. Nanocarbon materials, such as carbon nanotubes (CNTs), carbon nanofibers (CNFs) and graphene, have been considered promising alternatives to shielding materials because of their excellent electrical conductivities, very high surface areas and low densities. In the present work, 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. We present the fabrication and characterization of transparent and ultraviolet (UV) shielding CNF/polymer composites. The content of CNF filler has been varied from 0.2% to 0.6 % by weight. UV Spectroscopy has been performed to study the effect of composition on the transmittance of polymer composites.

Keywords—Electrospinning, carbon nanofiber, characterization, composites, nanofiber, ultraviolet radiation.

I. INTRODUCTION

RADIATION is the emission of energy from any source. There are many types of radiation. Ultraviolet (UV) radiation is electromagnetic radiation with a wavelength from 10 nm to 400 nm. The main source of UV radiation is the sun, although it can also come from man-made sources such as tanning beds and welding torches [1]-[2].

Radiation exists through a spectrum from very high-energy (high-frequency) radiation to very low-energy (low-frequency) radiation. UV rays have more energy than visible light, but not as much as x-rays. UV light is part of the electromagnetic spectrum. It is at the higher end of energy compared to visible light and is followed in energy by X-rays and the Gamma rays (Fig. 1) [3].

Nowadays, ultraviolet radiation (UVR) which attacks human bodies has attracted a great concern due to photochemical effect within the polymer structure. A common failure mechanism for organic materials is photodegradation due to UV exposure. In order to minimize such disadvantages polymer composite coatings are prepared with UV resistant polymer and additives [4]-[5]. These additives not only protect the coating, but they can also protect the substrate, which may

be vulnerable to UV degradation [6]. Polymer composite materials incorporating nanomaterials such as zinc oxide, titanium oxides, iron oxide [7] carbon black, carbon nanotubes (CNTs) and graphene (Gr) have been used in many applications due to control the transmittance and absorbance in these nanocomposites [8]-[11].

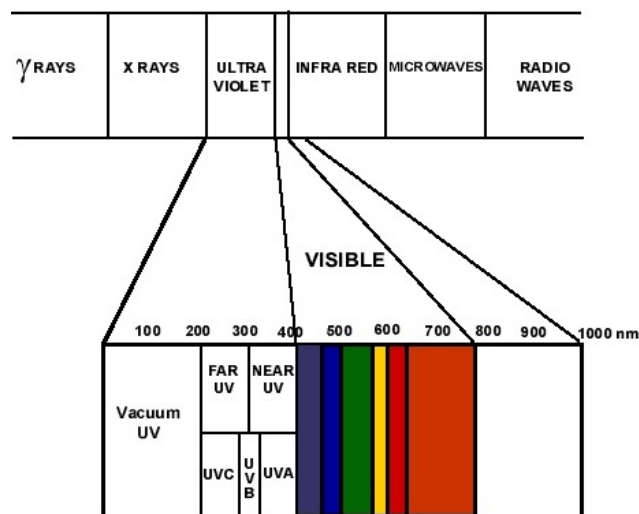


Fig. 1 Electromagnetic spectrum [3]

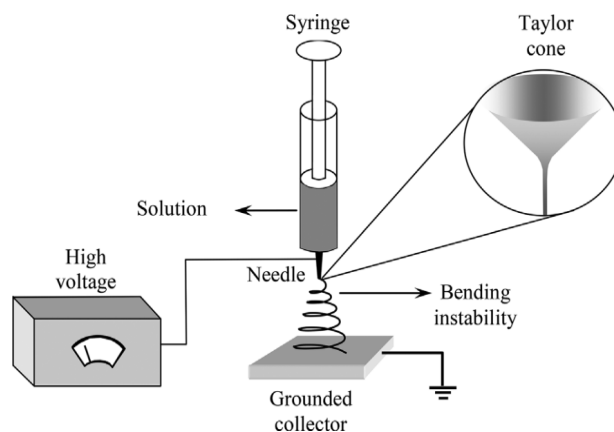


Fig. 2 Electrospinning setup [13]

A. Evcin is with the Department of Materials Science and Engineering, Afyon Kocatepe University, 03200 Afyonkarahisar Turkey (e-mail: evcin@aku.edu.tr).

N. Ç. Bezir, was with the Department of Physics, Süleyman Demirel University, Isparta, Turkey. (e-mail: cicekn@gmail.com).

R. Duman and N. Duman are with the Faculty of Medicine, Afyon Kocatepe University, 03200 Afyonkarahisar Turkey (e-mail: resatduman@gmail.com, nilybayram@hotmail.com).

UV radiation is split into four major bands as described in the Table I [12].

TABLE I
TYPES OF UV RADIATION

Description	Wavelength Range (nm)	Common Effect
UVA	320 - 400	Skin Tanning
UVB	280 - 320	Skin Tanning
UVC	200 - 280	Germicidal
VUV	40 - 200	Absorbed by oxygen

Recently, many types of nanofibers have attracted a great attention due to their properties in many fields. Electrospinning is a relatively simple and inexpensive method to produce nanofibers with diameters in the nanometer range. Electrospinning process has many parameters such as polymer, solution, ambient and equipment. Equipment parameters are field strength, electrode distance and arrangement, flow rate, delivery volume, and needle diameter. Typical electrospinning equipment has three components: a high voltage power source, a syringe pump (or nozzle), and a collector (as shown in Fig. 2).

Various organic based polymers have been used to produce nanofibers by electrospinning process; however the polymers available as carbon precursors are relatively limited. In order to convert electrospun polymer nanofibers to carbon nanofibers, a carbonization process at around 750-1000 °C has to be applied. For carbon precursors, such as PAN, a so-called stabilization process before carbonization is essential to keep the fiber morphology [14], [15].

This paper aims at investigating the UV resistibility of a carbon fiber reinforced polymer composite (CFRPC).

II. MATERIALS AND METHOD

For the preparation of the carbon nanofibers, we used Polyacrylonitrile (PAN, $(C_3H_3N)_x$, $M_w=150,000$ g/mol) as the starting polymer reagents and N,N-dimethylformamide (DMF, $HCON(CH_3)_2$, $M_w=73,09$ g/mol) as solvent. RTV664 A/B is a silicone rubber. The silicone rubber used as the matrix and 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. These obtained homogeneous solutions were loaded into a plastic syringe of the pump of the electrospinning set-up constructed by us [13]. Nanofibers 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 carbon nanofibers have been stabilized by oxidation at 250 °C for 2 h in air and carbonized at 750 °C for 1 h in H_2/N_2 atmosphere. In Fig. 3, SEM images are shown for the nanofibers prepared from the mixture of PAN/DMF. For the investigation of the percent dependences of the UV resistivity, the CNF/polymer composites with 0.2–0.6% weight fraction of filler were prepared (Fig. 4)

Carbon nanofibers have been analyzed to study the fiber morphology and to determine distributions of the diameter fiber thicknesses using FibraQuant 1.3 Software (Fig. 4 and Table I).

TABLE II
CARBON NANOFIBER DIAMETER

Description	Diameter			Measurement
	Average	Std Dev	Median	
Before calcination	192	95	199	559
After calcination	148	105	117	517

As seen Table II and Figs. 3 and 4, diameters of Carbon nanofiber samples are at the nanometer scale. The measured average diameter of these nanofibers depends on the calcination.

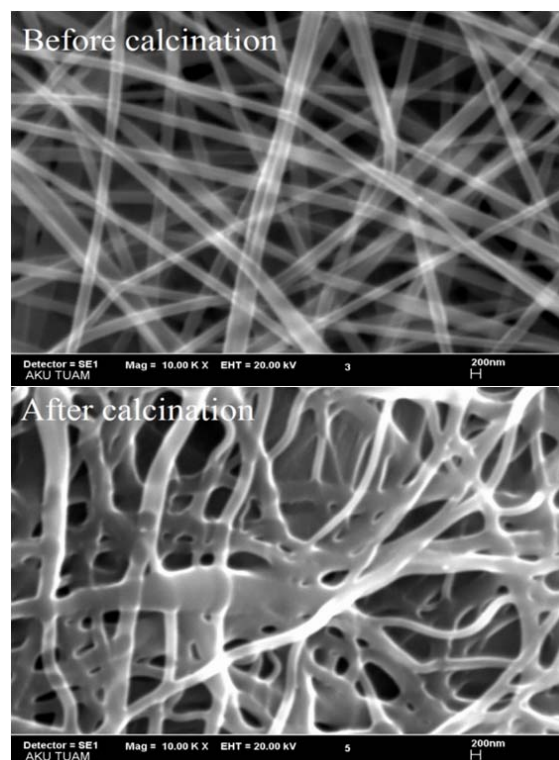


Fig. 3 SEM images of carbon nanofibers before and after calcination

III. RESULT AND DISCUSSION

The well-dispersed nature of CNF particles in the produced composite is supported by scanning electron microscopy (SEM) (Figs. 6 and 7).

Figs. 6 and 7 illustrate the microscopic morphology of the carbon nanofibers in the RTV664 silicone polymer matrix.

The UV absorbability (Abs) and % Transmittance (%T) of CNF nanoparticles varies with the content of CNF nanoparticles in the polymer matrix. The UV absorbability and % Transmittance of the control sample, and the samples with 0,02-0,06 wt% CNF nanoparticles are shown in Figs. 8 and 9 respectively.

In Fig. 8, it shows that the control sample has an excellent absorption of UV radiation in the wavelength ranges from 190 to 280 nm, however, it has no fully absorption of UV radiation in the wavelength ranges from 280 to 400 nm which the UV absorbability increases with the decrease of wavelength.

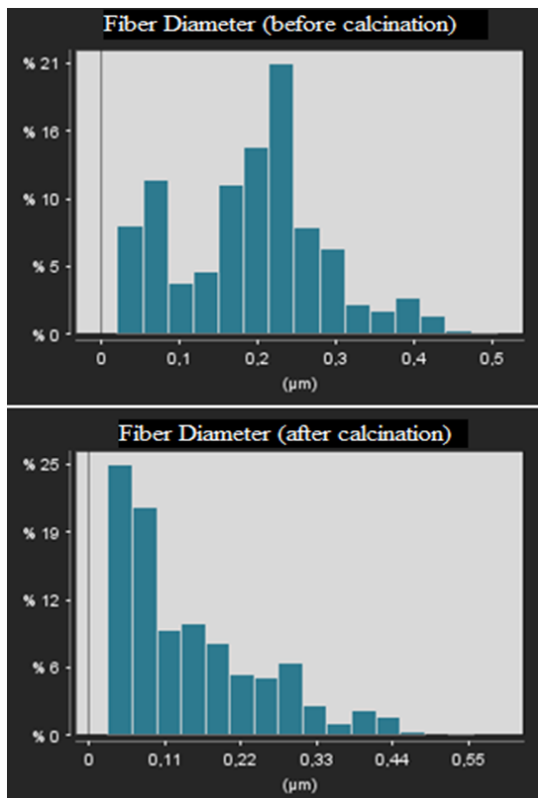


Fig. 4 Fiber diameter histograms

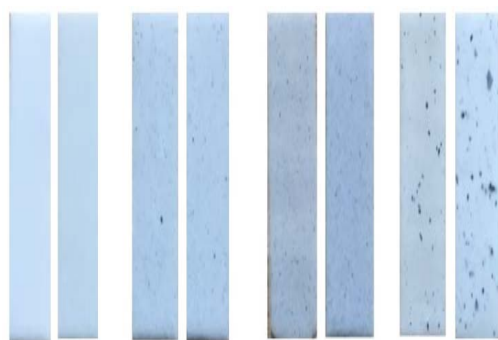


Fig. 5 CNF/RTV664 polymer composites (0-0,02-0,04-0,06% respectively)

In Fig. 9, it shows that polymer composites with excellent homogeneity and transmittance under 400 nm are for example between 0,02% and 0,06% with transmittance <1%. The control sample has also low transmittance in the wavelength ranges from 190 to 280 nm. It shows that transmittance increases with the increase of wavelength in the wavelength ranges from 320 to 400 nm for all samples. The lowest transmittance is for 0,06% CNF doped polymer composite.

By comparing with the Figs. 5 and 6 and the other samples, the samples with 0,02-0,06% show an excellent UV absorption through the whole range of wavelength from 190 to 400 nm. Then we have stated that the criterion for complete

UV protection is defined as less than 1% UV transmission (more than 99% absorption). Results of UV analysis are in agreement with literature [4]-[7].

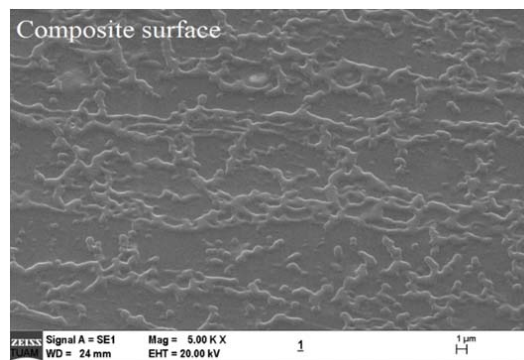


Fig. 6 SEM image of composite surface

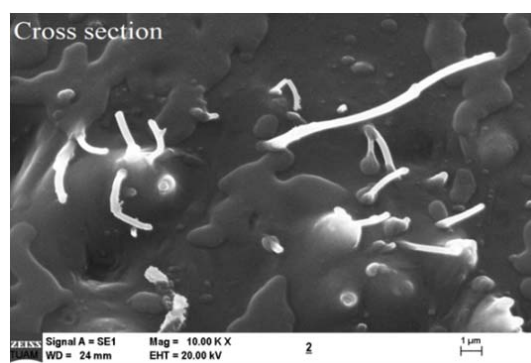


Fig. 7 SEM image of composite cross section

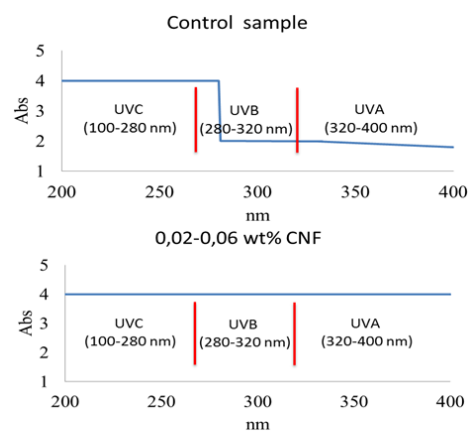


Fig. 8 UV absorbability of the control sample and sample with 0,02-0,06 wt% CNF

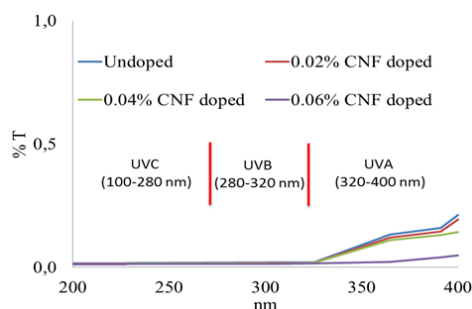


Fig. 9% Transmittances of samples

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