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Composites Science and Technology 66 (2006) 2436–2441
COMPOSITES SCIENCE AND TECHNOLOGY
www.elsevier.com/locate/compscitech

Electrospun nanocomposite fiber mats as gas sensors

R. Luoh, H. Thomas Hahn *

University of California, Los Angeles, Mechanical and Aerospace Engineering, 48-121 Engineering IV, Los Angeles, CA 90265, USA

Received 6 March 2006; accepted 7 March 2006
Available online 12 May 2006

Abstract

Electrospinning was used to spin nanocomposite fiber mats from polymer solutions containing nanoparticles. The base polymer was polyacrylonitrile (PAN), and the nanoparticles included iron oxide, antimony tin oxide and zinc oxide with diameters ranging from 10 to 70 nm. The electrospun nanocomposite fiber mats were characterized by scanning electron microscopy (SEM), scanning probe microscopy (SPM) and Fourier transform infrared (FTIR) spectroscopy. The average fiber diameter was found to decrease from 200 nm for neat PAN fibers to 50–150 nm for nanocomposite fibers. The porosity increased from 70% for PAN fiber mat to an average of 86% for nanocomposite fiber mats. The fiber mats were used as a sensor in conjunction with FTIR spectroscopy to detect CO_2 gas. The absorbance spectra showed a higher sensitivity with a fiber mat, regardless of its type, than without, indicating gas adsorption on the fiber mat. The highest sensitivity was obtained with PAN/Fe_2O_3 fiber mat. As the underlying mechanism is physisorption rather than chemisorption, the response time was short and the sensor could be used repeatedly.

Keywords: Electrospinning process; Nanocomposite fiber mat; Nanoparticles; Gas sensor; FTIR

1. Introduction

Sensors are important devices in many areas such as environmental monitoring, industrial process control, medical diagnosis, toxic chemical detection, etc. Sensors with reduced size, lower cost and more functionality such as sensitivity, selectivity and reliability are always sought after [1,2].

Compared to traditional types of sensors such as electro-chemical, catalytic, and metallic oxide semiconductor, optical fiber sensors have the following advantages [3]: absence of electromagnetic interference in sensing; absence of electric contacts in the probe; a high degree of miniaturization and geometrical versatility; multiplexity on a single network; and continuous and in situ measurement capability.

An optical fiber sensor consists of three main parts: an optoelectronic system, an optical link, and a probe, called optode or optrode. The optoelectronic system is the signal analysis unit and is decided by the type of optical property that can be used. The optical link, which is mostly silica or plastic fiber, provides the path between the optoelectronic system and the measuring optode. The optode is the sensing part that interacts with the analyte to generate changes in certain optical properties that can be monitored by the optoelectronic system. Some optical properties frequently used are refractive index, optical absorbance, fluorescence, and intensity. Fig. 1 shows a schematic of an ideal optical sensor system. In the present study, the optical fiber is missing; rather a direct light path is used.

Fourier transform infrared spectroscopy (FTIR) is one of the widely used optical methods to study the interaction of electromagnetic radiation in the infrared region with chemical compounds [4–6]. Different functional groups within a compound absorb radiation at different frequencies and yield unique IR absorbance spectra. An absorbance band may be characterized by a central wave number and the associated maximum intensity. The large band width (400–4500 cm^{-1}) and the distinct absorbance

* Corresponding author.
E-mail address: hahn@seas.ucla.edu (H.T. Hahn).

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doi:10.1016/j.compscitech.2006.03.012

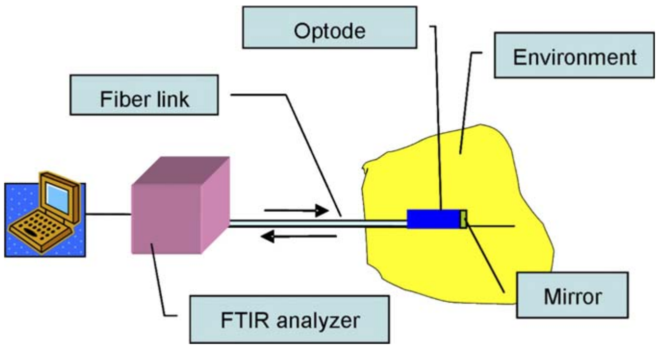

Fig. 1. A schematic of an ideal optical sensor system.

bands render the FTIR technology suitable for sensor applications [7].

Electrospinning shown in Fig. 2 is a manufacturing process that has re-emerged to produce ultra fine fibers with diameters ranging from 50 to 500 nm [8–10]. Functional nanoparticles can be incorporated into polymer solution to generate functional nanocomposite fibers [11]. Electrospun nanocomposite fiber mats have a relatively large porosity. Metal oxide semiconductors (MOS), such as tin oxide and zinc oxide, have long been used for sensing purposes based on conductivity and/or impedance changes. The conductivity of MOS changes when chemisorption occurs between MOS and the analyte [12]. The sensitivity of these sensors is very much dependent on the morphology of the sensing material. Smaller particle morphology gives a better sensing capability as surface area and active reaction sites increase [13,14]. Advances in nanotechnology are making many types of nanoparticles available. Materials with dimensions near or less than 100 nanometers are found to behave differently compared with conventional materials [1,15].

In the present paper, nanocomposite fiber mats with a small loading of metal oxide nanoparticles are used to detect gases with the help of FTIR spectroscopy. The base polymer used is polyacrylonitrile (PAN), and the nanoparticles include zinc oxide and iron oxide. The addition of metal oxide nanoparticles to the polymer improves the sensing sensitivity via enhanced gas adsorption. The morphology of fabricated fiber mats are evaluated by SEM (scanning electron microscopy) and SPM (scanning probe microscopy). The sensing performance of fiber mats is quantified by the FTIR absorbance spectra.

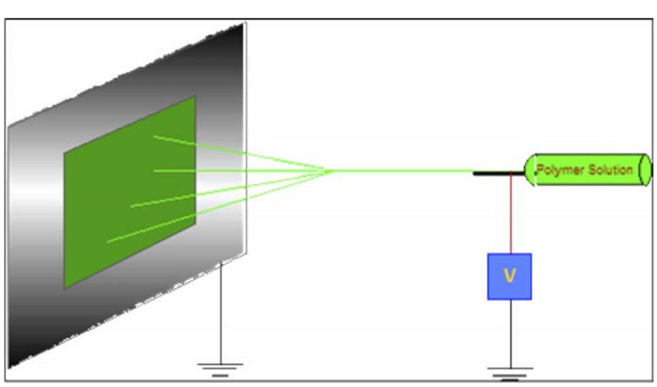

Fig. 2. A schematic of electrospinning process.

2. Experiment

In the electrospinning process an electric field is generated between a polymer solution and a metal collection screen, Fig. 2. The polymer solution is contained in a syringe with a steel capillary tip and a voltage is applied between the tip and the conductive collector. As the electrical potential is increased, the charged polymer solution is attracted to the collector. When the voltage reaches a critical value, the charge overcomes the surface tension of the polymer solution formed on the capillary tip and an electrified jet is produced. As the charged jet flies through the air, it loses the solvent through quick evaporation and impinges on the collection screen as a thin fiber mat. The fiber diameter can be controlled by varying the charge density and the polymer solution concentration. Addition of nanoparticles to the polymer solution yields the desired nanocomposite fiber mat.

In the present work, nanoparticles including iron oxide, antimony–tin oxide, and zinc oxide nanoparticles (Nanophase Technology Corp.) were used as received together with polyacrylonitrile power (Scientific Polymer Powder), Table 1 [11].

The fabricated nanocomposite fiber mats were 0.03–0.05 mm thick, and circular specimens of 12.5 mm diameter were cut out of the mats. A gas chamber with a sealed KBr window on each side with a spacing of 0.9 mm was constructed to simulate the gas environment while allowing the passage of infrared light. The fiber mat was inserted in the middle of the gas chamber as a sensor. Control valves were installed to control the gas flow without disrupting the FTIR operation.

The gas to be monitored was prepared by chemical reaction in a separate sealed chamber. Specifically, CO_2 was generated by reacting a carbonate to an acid. The gas was then pumped by an in-line pump and guided through a Teflon pipe to the gas chamber. The gas chamber was purged using compressed nitrogen gas before FTIR measurement to minimize interference with the ambient air. Absorbance spectra were recorded with a resolution of 4 cm^{-1} and each spectrum had an average of 10 scans. The spectrometer used was M2000 Series from MIDAC Inc. This spectrometer uses a Michelson-type interferometer and a room-temperature DTGS detector. The fiber mats were completely desorbed

Table 1
Properties of nanoparticles

Nanoparticle	Diameter (nm)	Density (g/cm^3)	Surface area (m^2/g)
10% Sb_3O_4, 90% SnO_2	11–29	6.8	30–80
Fe_2O_3	19–38	5.2	30–61
ZnO	24–71	5.6	15–45