Self Cleaning Nanofiber Webs

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Abstract

The performance of chemical protective materials is an important and sensitive issue as it is associated with human safety and therefore, the development of highly efficient chemical protective materials is always a continuous process. The emergences of nanotechnology opened up so many research areas and electrospun nanocompositefiber is a potential candidate that could be used as a self detoxifying material. Incorporation of the reactive components into nanofibers makes them functionally active and depending on the nature and activity of the reactive components, nanofibers can be used in different types of filtering media, chemical protective materials, tissue engineering, drug delivery etc. In this study, nanocrystalline magnesium oxide has been considered as the functionalizing agent as it has the ability to react with chemical warfare agents and organophosphorous compounds. Electrospinning technique has been used to fabricate polyethylene oxide nanofiber embedded with nanocrystalline magnesium oxides. The nanofibers were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction method (XRD). Nanocompositefibers in the range of 50 nm to 250 nm have been produced in the laboratory. Thermogravimetric analyzer has been used to study the adsorption characteristics of nanofiber composites and impressive results have been obtained from this study.

Introduction

Electrospun nanofibers have created a new and rapidly growing research area due to its pronounced micro and nano characteristics such as high surface area with porous structure, fiber diameter at nano level, filtration properties, high permeability, layer thinness etc [1]. In addition to these, it is possible to incorporate reactive components into the nanofiber matrices. The reactive component can be catalysts, adsorbents, therapeutic agents etc. Therefore, adding the appropriate doping materials can significantly enhance the overall performance of nanofibers and the nanofiber composites can be effectively used in filtration, chemical protective materials, and tissue engineering and drug delivery. Development of highly efficient filter materials with enhanced capabilities is necessary as there are wide ranges of chemicals that possess threat to human beings. These chemicals range from pesticides to weapons of mass destruction/chemical warfare agents (CWA). Nanocrystalline metal oxides have attracted many researchers due to its potential to decontaminate hazardous substances. When the size of the metal oxides reaches nano dimensions, surface reactivity increases due to high surface concentrations of reactive edges and defect sites [2]. This high surface reactivity along with the high surface area allows their use for effective decontamination of chemical warfare agents and related toxic substances. In this study, concentration has been given to particular metal oxides and it has been observed that nano magnesium oxide reacts with organophosphorus compounds (OPs) at room temperature by dissociative chemisorption and this process involves breaking of P-O and P-F bonds and immobilizes the resultant molecular fragments [2]. Reactions of nanosize magnesium oxide with sarin, soman and VX agents have also been reported by Klabunde et.al. [2,3]. Different metal oxides including nano and micron sized magnesium oxide were reacted with half mustard and it was found that nano magnesium oxide

is more reactive than micron sized particles [4]. Due to its two-way destruction capabilities (against OPs and CWA), magnesium oxide has been chosen for this study.

It has been recently shown that electrospinning process is capable of producing fibers in the submicron range [6]. The basic theory of nanofiber spinning process and the parameters affecting the process, properties of polymer solution, thermal and mechanical properties of electrospun materials and their different applications were clearly described by Subbiah et al. [7].

Most of the published research from the US Army and other researchers has focused predominantly on the filtration and transport studies. Gibson *et al.* studied transport properties of electrospun fiber mats and they concluded that nanofiber layers give very less resistance to the moisture vapor diffusion transport [8]. Tsai *et al.* inferred that electrospun fibers have higher filtration efficiency than other nonwoven webs [9]. The possibility of using thin nanofiber layers over the conventionally used nonwoven filtration media for protective clothing was first studied by Gibson *et al.* [10]. Nanofibrous catalysts have been found to be substitutes for catalytic nanoparticles in order to overcome the limitations of catalyst recovery [11]. The recent approach of nanofiber research is focused towards the incorporation of functional structures in nanofibers for its use in catalytic applications [12]. However the use of nanofiber composites in chemical warfare protective clothing and decontamination wipes has not been reported in the literature yet. Most recently, Drew et al. [13] have produced polyacrylonitrile nanofibers using the well-established electrospun experimental setup and have applied thin coating of titanium oxide and stannum oxide. The authors immersed the electrospun webs in the coating, which completely covered the nanofibers that would affect the pore size of the web thus interfering with the functionalities that are achieved through large surface area. Therefore, this dip immersion method may not be a good technique and will affect the accessible surface area of nanofibers which in tern cannot validate the purpose of using electrospun nanofibers [14].

The goal of this research is to disperse the nanocrystalline metal oxides on to the nanofibers surfaces without harming any properties of nanofibers. Different characterization techniques have been used to examine the physical structure of nanofibers. X-ray diffraction has been used for the crystallinity of metal oxides. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used to see the overall structure of nanofiber webs and the close view of nanofibers respectively. The overall end-use application of the destructive adsorbent nanofiber web is a toxic chemical countermeasures substrate and therefore measuring the adsorption/protection properties is an important and integral part of this research. A thermogravimetric analyzer (TGA) has been used to study the adsorption characteristics of metal oxide coated nanofibers.

Materials and Methods

Polyethylene oxide with average molecular weight of 400,000 was supplied from Sigma-Aldrich, USA and nanocrystalline magnesium oxide (MgO) was obtained from Nanoscale Materials Inc., USA. The overall concentration of magnesium oxide and polyethyle oxide in water was 4% (w/w). Magnesium oxide is in the suspended form in the solution. The solution was then transferred to a syringe (10ml capacity, Hamilton Company, Reno, USA), which is then adjusted with the pump (PHD 22/2000, Harvard Apparatus, and USA). High voltage potential (16 KV) is applied to the polymer solution inducing free charges into the polymer solution. A collector screen (grounded to the earth and 10 cm from the tip of the needle) is

used on which the grids (SEM, TEM, XRD) for samples are placed so that nanofibers can be directly collected on those grids. The flow rate of the solution is kept at 50ul/min at 20^0 C (room temperature) with 40% relative humidity.

A thermogravimetric analyzer (Pyris1 TGA from Perkin Elmer) has been used to characterize the adsorption characteristics of chemical protective substrates. TGA can be used to quantitatively evaluate the adsorption of toxic chemicals as a function of increase in weight at a constant temperature.

Results and Discussions

Characterization of Nanocompositefibers

These fibers will be mostly used for filtration and chemical protective clothing and it is therefore essential to have random web-like structures that will enhance the filtration efficiency. The best way to observe the overall structure of nanofibers is to use scanning electron microscopy. The PEO-MgO nanofibers has been gone through under scanning electron microscopy (SEM) first and the SEM image shows that the electrospun PEO-metal oxide fibers form a web-like cluster with criss-crossing fibers like a sieve (Figure 1.1). The individual nanofiber is shown in Figure 1.2 which was taken using TEM. It is also observed that electrospun PEO fibers are long up to 50 microns. Nanofibers in the range of 50 nm to 250 nm have been observed from the images.

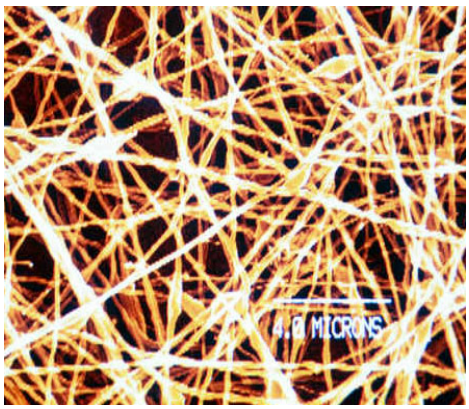

Figure 1.1: SEM image of MgO-PEO nanofiber

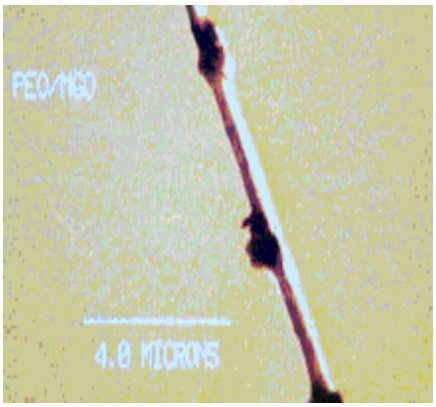

Figure 1.2: TEM image of MgO-PEO nanofiber

The state of nano-metal oxides whether they are amorphous or crystalline is the most important factor for the overall performance of nanofibers. It has been found in the literature that nano crystalline metal oxides can break down the phosphorous-oxygen bonding and immobilizes the fragmented parts. Therefore, X-ray diffraction has been done for both types of nanofibers at the beginning. The diffraction pattern for PEO-MgO nanofibers show that magnesium oxides are present at crystalline states.

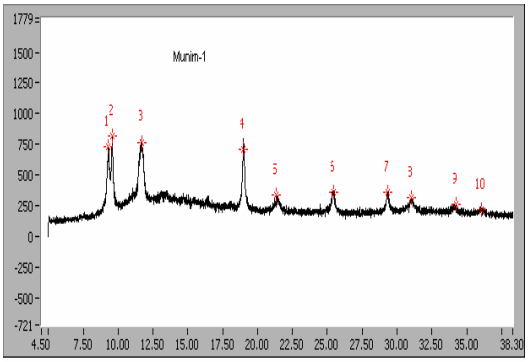

Figure 2: XRD pattern of PEO-MgO Nanofibers (Intensity vs.

Table 1. Powder Diffraction Data

n	Theta	Integrated Intensity	Relative Intensity	d in nm	Identification
1	9.29	21081	83	0.477	brucite
2	9.60	13121	52	0.462	PEO
3	11.67	25367	100	0.381	PEO
4	19.01	17930	71	0.236	brucite
5	21.37	7080	28	0.211	MgO

A strong presence of $Mg(OH)_2$ has also been observed. It is due to the use of water as PEO solvent and $Mg(OH)_2$ has been formed by water. Figure 2 shows the XRD pattern of PEO-MgO nanofibers.

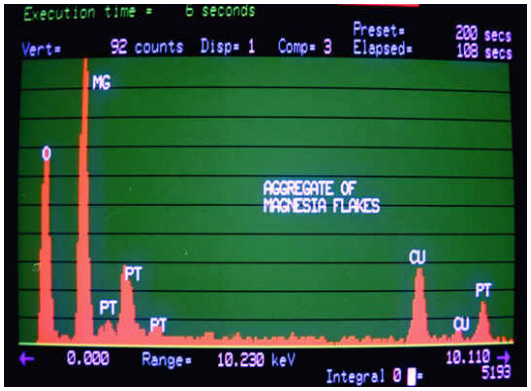

Figure 3.1: X-ray spectra obtained at nodes (MgO)

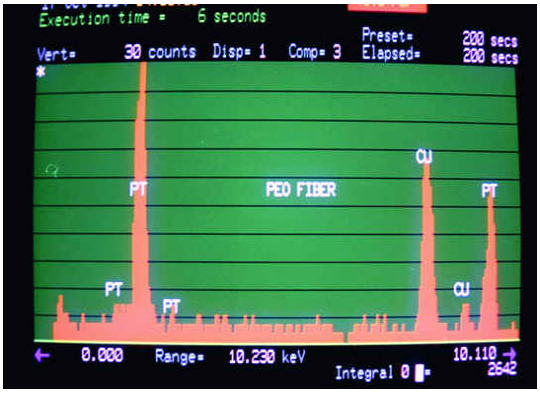

Figure 3.2: X-ray spectra obtained between nodes (PEO-MgO)

Another approach has been done to make sure the elements of nodes and between the nodes. In order to do this, X-ray spectra's for nodes and between the nodes have been performed. The characteristic X-ray spectra obtained from the nodes (Figure 3.1) show strong Mg and O-lines. The Pt and Cu-lines in the same spectrum belong to sample coating metal and to sample holder respectively. The X-ray spectra in Figure 3.2 were obtained from the sections of the PEO fibers between the nodes. There are no MgO on these sections of the fibers.

Performance of Nanocompositefibers

The PEO-MgO nanofibers were collected on to the surface of activated carbon fabric and its adsorption performance has been compared with that of activated carbon fabric alone. The results obtained from TGA are promising and it can be used to quantitatively characterize the adsorption properties of chemical protective substrates. The protection/adsorption properties can be characterized by the percentage weight gain at a predetermined time, saturation time and rate of adsorption. Toluene has been used as a test chemical for these materials at 30^{o} C. The percent weight gain and instantaneous adsorption rates were found higher for PEO-MgO nanofibers. Typical adsorption images are shown in Figure 4.1 and Figure 4.2 for activated carbon fabric alone and for the nanofiber composite respectively. Therefore it is evident that the metal oxide nanofiber composites have higher adsorption capacities than that of ACF alone.

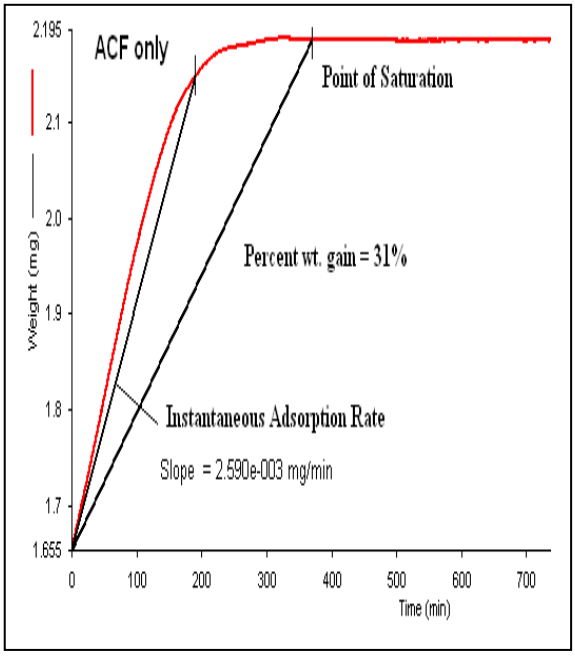

Figure 4.1:Adsorption of Toluene by ACF alone (31% wt. gain)

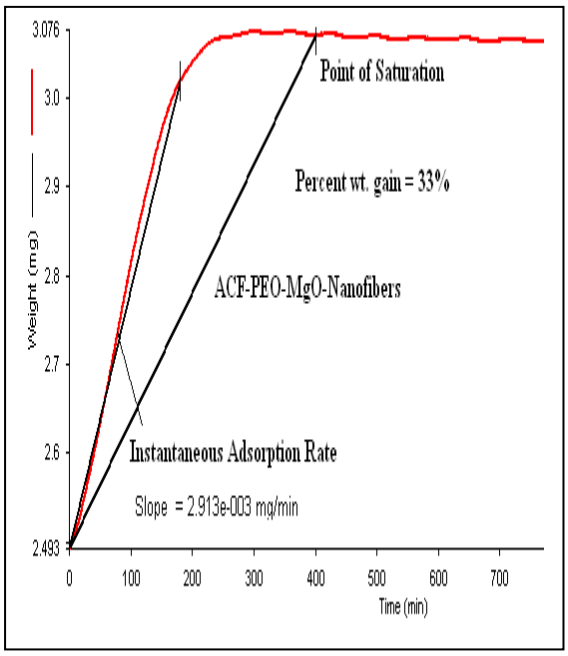

Figure 4.2:Adsorption of Toluene by ACF-PEO-MgO Nanofibers (33% wt. gain)

In summary, we have demonstrated nano metal oxide embedded nanofibers by the electrospinning technique using a single solution. These nanofibers are particularly useful as self-cleaning materials. The authors will investigate the adsorption studies in details in future.

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