ASSEMBLY AND CHARACTERISATION OF PVdF NANOFIBROUS MATERIALS WITH MAGNETIC PROPERTIES

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Introduction

Nanofibre nonwoven fabrics have been in commercial use as filter media for many years. Filtration efficiency and dirt holding capacity are strongly influenced by nanofibrous layers in the filter medium [1]. In this research an approach was developed to functionalise a nanofibrous assembly to effectively separate metal-based particles from a liquid stream[2]. Several methods are available to produce nanofibres including electrospinning, fibrillation, meltblowing and bicomponent extrusion. Of these techniques electrospinning of polymers has proved to be a versatile and facile process for the production of nanofibrous assemblies. Poly(vinylidene fluoride) (PVdF) polymer was selected for the production of nanofibres with embedded ferrous-ferric oxide in the form of iron oxide (Fe_3O_4) particles. PVdF has a high dielectric constant and is piezoelectric. Iron oxide is ferrimagnetic and can be permanently magnetised.

Materials and Methods

Nanofibrous webs were produced from a medium viscosity, multipurpose grade PVdF (Solef 1010). This polymer is highly stable and non-reactive and is used in extrusion and injection moulding. Iron oxide (Fe_3O_4) nanoparticles were <50nm (Sigma-Aldrich) and of 98% purity. The melting point was 1538^o C. PVdF powder was dissolved in Dimethylacetamide (DMA) to produce spinning solutions of different concentrations (17, 20 & 23%). The electrospinning (e-spinning) of 100% PVDF polymer was initially optimized to identify conditions that produced fibres with minimal morphological defects. All e-spinning was conducted in a fume cupboard under controlled conditions of temperature and humidity. After process optimization with PVdF alone, one polymer solution was selected and the Fe_3O_4 nanoparticles were dispersed by sonication to produce functionalized nanofibrous web samples. The Fe_3O_4 nanoparticles of 3wt%, 5wt% and 10wt% were dispersed in 20 wt% of polymer solution composed of PVdF and DMA. E-spinning was conducted with voltages of 18, 20 & 22kV and flow rates of 0.4, 0.6 &0.8ml/hr.

Characterisation techniques

The morphology of the nanofibrous nonwoven webs were studied by ESEM (Philips XL30). Micrographs were taken using an accelerating voltage of 20 kV with a spot size of 4nm and at a working distance of 5mm.Embedded nanoparticles were observed by means of FEGTEM (Philips/FEI CM200) operating at 197kV with a point resolution of 0.24 nm. The capacitance of the electrospun nanofibrous mats was tested by means of an Impedance analyzer (Agilent technologies) from which the dielectric constant was then derived. The magnetic field strength of the nonwoven samples was characterized by MFM (Agilent technologies).

Results and Discussion

A PVdF polymer concentration of 20%, spun at an operating voltage of 20kV was found to yield fibres with the fewest morphological defects. Figure 1 shows an SEM micrograph of a PVdF web containing 5% Fe_3O_4 nanoparticles.

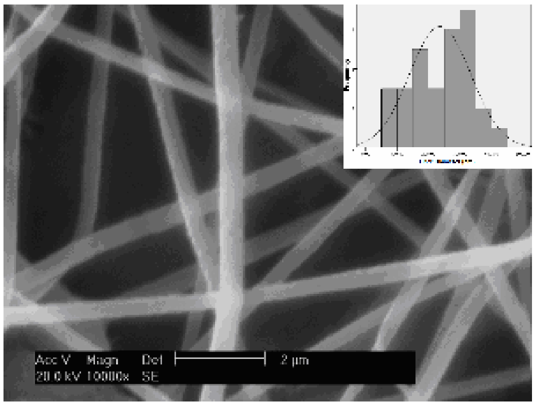

Figure 1 SEM micrograph of PVdF nanofibre with 5% Fe_3O_4 nanoparticles

The mean fibre diameter was 241 nm. TEM micrographs confirmed that particle agglomeration occurred unless sonication was employed prior to spinning; this defect has been previously observed by numerous researchers working on polymer-nanoparticle linear composite production[3]. To improve nanoparticle dispersion ultrasonic vibration can be undertaken [4]. In the present work, before electrospinning, the solution was treated in an ultrasonic bath at 3kHz. We found significantly improved dispersion after 2hr of sonication under these conditions. A TEM of a single fibre extracted from the web is given in Figure 2 that shows the dispersion of Fe_3O_4 nanoparticles at the surface.

Several papers have confirmed the presence of magnetic properties in assemblies using a SQUID magnetometer[5], hysteresis measurements[6]and vibrating sample magnetometers[7]. All these techniques provide a direct estimation of the relative magnetic field.

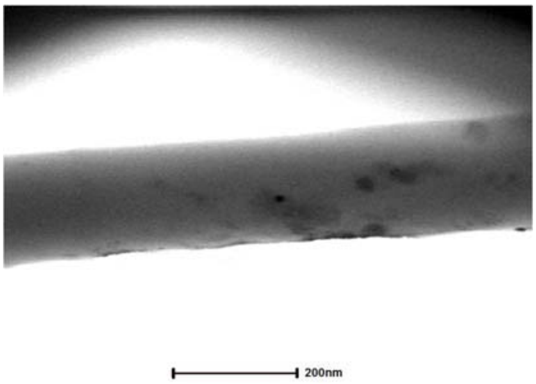

Figure 2 TEM micrograph showing PVDF nanofibre with 5% embedded Fe_3O_4 nanoparticles

In this work, MFM was adopted to characterise the magnetic field strength over the nanofibrous web. An example of the MFM evaluation is given in Figure 3. The left image shows the fibre topography and the right, the magnetic field strength. Also in Figure 3 the reducing magnetic field in the inter-fibre regions and the magnetic field over the fibre surfaces are clearly evident.

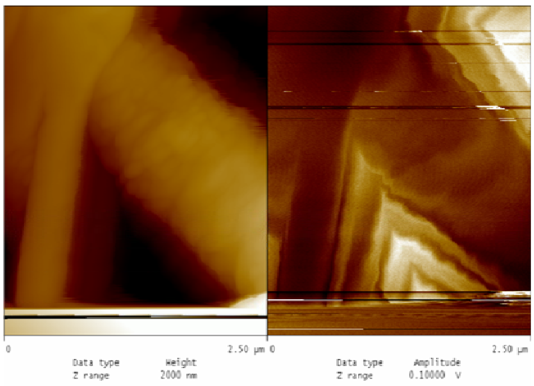

Figure 3 MFM image showing fibre topography (left) and the observed magnetic field (right)

In respect of the dielectric behaviour of PVdF webs containing 3, 5& 10% Fe_3O_4 nanoparticles shown in Figure 4, the dielectric constant approximately doubles with the addition of 10% nanoparticles compared to the 100% PVdF web. The response of a PVdF nanofibrous nonwoven composite web to a lab magnet loaded with 5% Fe_3O_4 nanoparticles is shown in figure 5.

Conclusions

Polymeric PVdF nanofibres embedded with different concentrations of Fe_3O_4 nanoparticles of <50nm were successfully produced by the electrospinning process. Agglomerations of particles within the fibres were dispersed by means of ultrasonication. MFM clearly indicated the presence of a magnetic field associated with the fibres. The relative dielectric constant approximately doubled with a 10% addition of Fe_3O_4 nanoparticles.

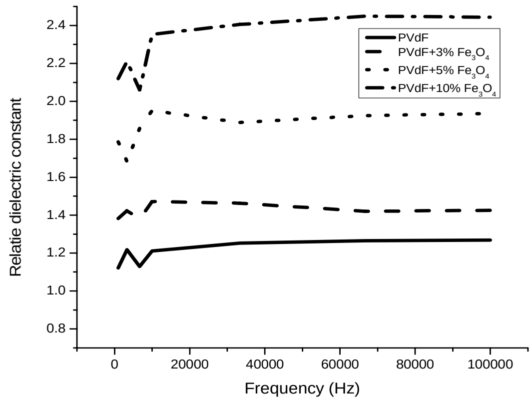

Figure 4 Dielectric behaviour of PVdF fibre webs in relation to Fe_3O_4 nanoparticle content

Figure 5 PVdF web attracted by a lab magnet

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