MAGNETIC PROPERTIES OF ELECTROSPUN POLYVINYL BUTYRAL/Fe_2O_3 NANOFIBROUS MEMBRANES

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Abstract

In this contribution, magnetic Fe_2O_3 nanoparticles (MNPs) were successfully incorporated into the polyvinyl butyral (PVB) nanofibrous membranes using the electrospinning process. The effects of the MNP concentration on the morphology of the nanofibres and their magnetic properties were investigated. Scanning electron microscopy and transmission electron microscopy confirmed their concentration-dependent, yet uniform diameter, and the presence of well-embedded MNPs inside the PVB nanofibres. The magnetic properties of the PVB/MNP membranes were studied using the vibrating-sample magnetometry. The saturation magnetization increased from 6.4 to 45.5 emu/g as the MNP concentration in the feedstock solution increased from 1 to 15 wt%. The fabricated PVB/MNP nanofibrous membranes possessed the ability to respond to the external magnetic fields, which determines their potential in the development of the advanced smart textiles.

Keywords: Electrospinning, polyvinyl butyral, nanofibres, nanoparticles, magnetic properties

1. INTRODUCTION

Recently, magnetic nanofibrous composites fabricated using the electrospinning technology have attracted a considerable attention due to possibility to easily convey a novel function to the conventional nanofibers, *i.e.* the activity in the external magnetic field. Such field-responsive composites have aroused much interest in the bio-medical technology (tissue engineering [1], cell carries [2], hyperthermia [3]), separation technology [4] or the electromagnetic devices (sensors [5]).

Until now, Fe_2O_3 nanofibrous membranes have been successfully prepared by electrospinnig from various synthetic polymers such as polyurethane [3], polylactic acid [2], polyvinyl alcohol [6], polyaniline [7] etc. Kim et al. [8] incorporated magnetic nanoparticles (MNPs) into the polyvinylpyrrolidone fibres in order to develop highly efficient air filters. Their material exhibited the magnetic saturation of 10.5 emu/g, which might be a limiting factor for certain applications. Besides that, the preparation and characterization of PVB/MNPs nanofibrous composite was not systematically investigated yet. Polyvinylbutyral is the environmentally-friendly, non-toxic, odourless polymer with a very good adhesion to metallic and ceramic surfaces and compatibility with many types of synthetic polymers [9]. The possible applicability and advantages of the PVB in the electrospinning process were summarized in detail by Peer et al. [10]. Polyvinylbutyral is also frequently added to the various solutions in order to improve their spinnability and fabricate for example the superhydrophobic nanofibres [11], the membranes with photocatalytic activity [12] or the sensors for the detection of H_2S [13].

The aim of this contribution was to analyse the effect of the MNP concentration on the morphological, structural and magnetic properties of the electrospun nanofibrous composites. The correlations between the spinnability process and the magnetic properties were discussed in the view of potential applications.

2. EXPERIMENTAL

2.1. Materials and sample preparation

Polyvinylbutyral (M_w = 60,000 g/mol; Mowital B 60H; kindly provided by Kuraray Specialities Europe, Germany) was dissolved in methanol (PENTA; quality of p.a.; Czech Republic). Magnetic nanoparticles consisting of iron (III) oxide produced by NanoArc (Germany) were mixed with the PVB solution at the concentrations of 1, 5, 10, 15, and 20 wt%. According to the datasheet, the size of the MNPs ranged between 20 - 40 nm, and their surface areas equalled to 30 - 60 m^2/g.

Polyvinylbutyral/methanol solutions (8 wt%) with various MNP concentrations were prepared by mechanical stirring at 25 °C for 15 minutes. The nanofibrous webs were produced using a laboratory device with the carbon steel stick (10 mm in diameter) and the flat collector. The electrospinning process of PVB solutions with the MNPs was carried out at a voltage of 20 kV, and the tip-to-collector distance was fixed at 10 cm. Volume of a drop of polymer solution placed on the tip was approximately 0.2 mL. The temperature and relative humidity for electrospinning was 23 °C and 45 %, respectively.

2.2. Characterizations

Morphology of the nanofibres sputtered by a thin gold layer was observed using Vega 3 high-resolution scanning electron microscope (SEM; Tescan, Czech Republic) and a high-resolution transmission electron microscope (TEM), JEOL (JEM 2100, Japan) fitted with LaB6 cathode operated at 80 kV. The mean fibre diameter was determined by help of Adobe Creative Suite software taking into account 300 fibres from 3 different images. The magnetic properties of the PVB nanofibrous membranes with the MNPs were determined using vibrating-sample magnetometer (Model 7407, Lake Shore, USA) in the magnetic field ranging up to 14 kOe (~1150 kA/m) at the laboratory temperature (23 °C).

3. RESULTS AND DISCUSSION

The PVB nanofibrous membranes with various MNP concentrations were prepared by a simple electrospinning system under the optimal experimental parameters (voltage of 20 kV and a tip-to-collector distance of 10 cm) favouring the fabrication of uniform nanofibres. To analyse the effect of the MNP concentration on the morphology of resulted nanofibres, the SEM and TEM were employed, as shown in **Figure 1**. As can be observed, the MNPs possessed the spherical shape with approximate size of 30 nm. The incorporation of the MNPs into the PVB nanofibres was dependent on their concentration. It seems that the most homogeneous structure was obtained at the concentration of 10 wt% MNPs, however, when the concentration of the MNPs increased (above 15 wt%) the particulate clusters were created and protruded from the nanofibres. Structural non-uniformity of the nanofibers represents limiting factor for scaling-up the process to the industrial applications [14]. Considering this presumption, the PVB nanofibres with 20 wt% concentration of the MNPs were therefore excluded from the characterization of their magnetic properties.

The average diameter for pure PVB nanofibres is around 230 nm for the concentration of 8 wt%. **Figure 2** displays the nanofibre diameter versus the MNP concentration. As clearly seen, the incorporation of the MNPs into the PVB nanofibres remarkably affected their average diameter. The progress is non-monotonic, and local maximum of the fibre diameter is arguably located at the MNP concentration around ca. 7 wt%. Above this concentration, the fibre diameter is decreasing with increasing MNP content with simultaneous standard deviation increase (which might indicate lower stability of the process). This result is in partial agreement with the recent studies [8,15]. For instance, Kim et al. [8] found that the fibre diameter is increasing with the MNP content. This can be explained as follows; the electrospinning process is driven by the competition between electric and hydrodynamic forces. Once the viscosity of the solution increases by the addition of the MNPs, at the same electric potential, the elongation is suppressed resulting in the production of thicker fibres [8]. It appears that beyond a certain MNP concentration, this balance is impaired most probably by particle clustering (**Figure 1**) leading to the lower diameter of the fibres.

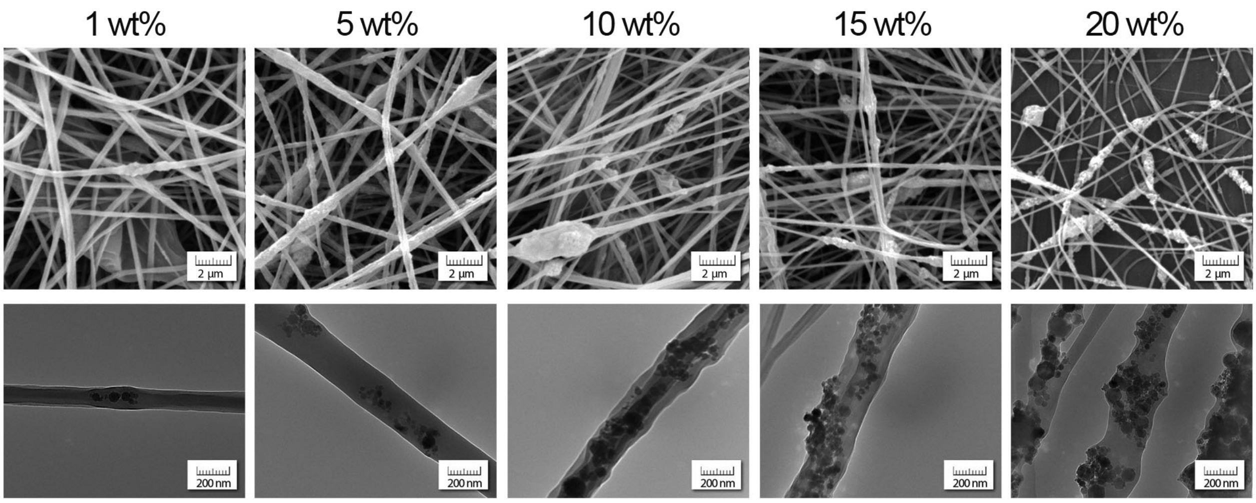

Figure 1 The SEM (*upper line*) and TEM images (*bottom line*) of PVB nanofibres with various MNP concentrations

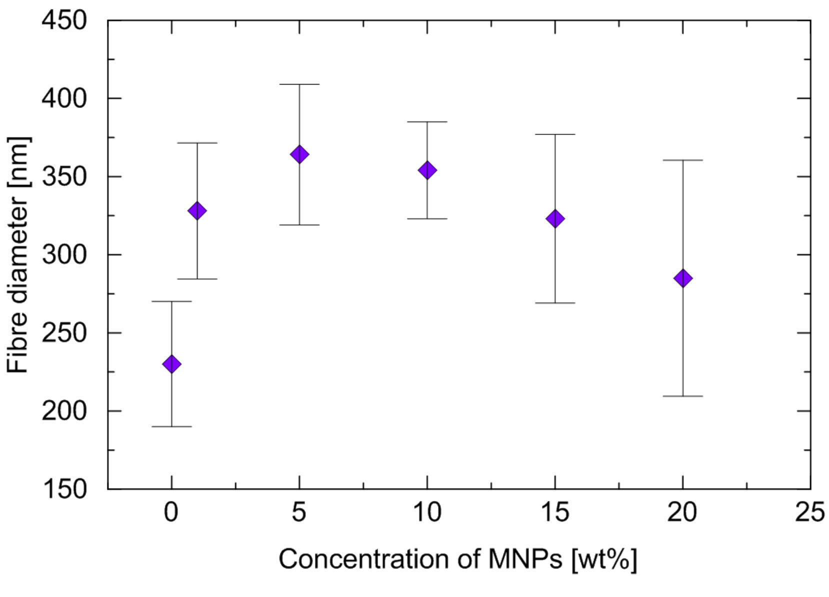

Figure 2 The fibre diameter dependence on MNP concentration

To investigate magnetic properties of the PVB/MNPs nanofibrous membranes with various MNP concentrations, the hysteresis loops were recorded using vibrating sample magnetometer. As shown in **Figure 3**, the saturation magnetization (M_s), which occurs when all of the magnetic domains are aligned in the direction of the applied magnetic field, clearly depends on the MNP concentration [8]. Expectedly, the higher concentration of the MNPs in fibrous membranes leads to higher magnetization. Therefore, the M_s increased from 6.4 to 45.5 emu/g as the MNP concentration increased from 1 to 15 wt%, respectively. It is worth mentioning that the M_s values of herein produced electrospun PVB/MNPs membranes exceeded those of similar magnetic membranes [3,6-8]. The high magnetic performance of the nanofibres is of particular interest in the industrial wastewater treatment. As shown recently, the magnetic nanofibres exhibit higher adsorption rate of heavy metals and dyes when compared to the traditional adsorbents [16].

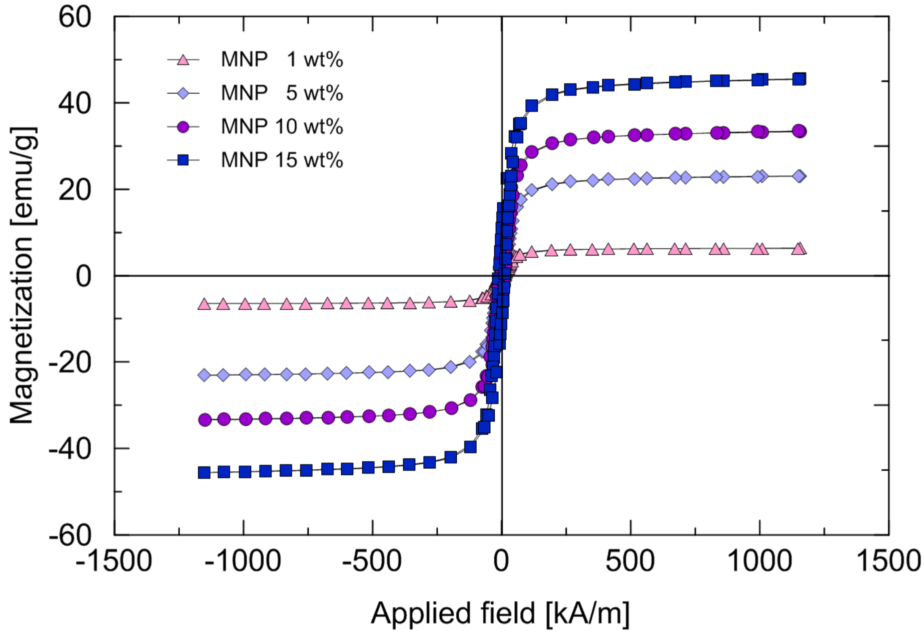

Figure 3 Magnetic properties of PVB nanofibres with various MNP concentrations

4. CONCLUSION

The magnetic PVB nanofibrous membranes were successfully fabricated using the electrospinning process. The effects of the MNP concentration on the morphology and magnetic properties of nanofibres were investigated. It was found that the fibre diameter is a non-monotonous function of the MNP concentration, which is driven by the competition between electric forces and the viscous forces. Nevertheless, the higher MNP concentrations (above 15 wt%) caused cluster protrusion from the nanofibres. The saturation magnetization of the membranes strongly depended on the MNP concentration, and the highest value of 45 emu/g was obtained for PVB/MNPs membrane at 15 wt%. All the fabricated PVB/MNPs nanofibrous membranes possessed the ability to response to the external magnetic field, which is the important prerequisite for the effective filtration.

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