PREPARATION OF AL_2O_3 NANOFIBRES AND THEIR SURFACE PLASMA TREATMENT

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Abstract

In this work, the electrospinning process was used for the preparation of ceramic nanofibres from PVA/$Al(NO_3)_3 \cdot 9H_2O$ precursor solutions. Six solutions with different weight concentrations were prepared and nanofibres from each solution were made. Precursor nanofibers were treated in DCSBD plasma (diffuse coplanar surface barrier discharge) for 10 minutes. Later fibres were thermally treated in furnace. Obtained calcinated nanofibers were analysed by FTIR analysis, scanning electron microscopy and thermogravimetry.

Keywords: Electrospinning, alumina, nanofibres, plasma

1. INTRODUCTION

Electrospinning is a highly versatile method to process solutions or melts, mainly polymers, into continuous fibres with diameter ranging from few micrometers to several tens of nanometers. Electrospinning is very simple and, therefore, easily controlled technique for fibre production with dimension in nanometer range. In a typical electrospinning experiment polymer solution is pumped through the nozzle with diameter in the order of 100 μm. The nozzle also serves as an electrode, to which high electric field is applied. A distance of electrodes is adjusted usually in the range of 100-250 mm. The substrate on which nanofibres are collected is typically in contact with the counter electrode [1].

A needle-free technique was used for nanofibre preparation in this work. Nanofibres were prepared using Nanospider technology (Elmarco, Czech Republic), which provides a high voltage electrospinning process. The technology is based on the possibility to create spinning process from thin film of polymer solution. [2].

Al_2O_3 inorganic fibres are widely employed as engineering material used in various applications mainly due to high ratio of the surface area to the volume and high desirable porosity. Al_2O_3 nanofibres play an important role as a promising material for filtration [3], bio-template [4] and catalyst support in high temperature reactions [5]. Nanomaterials in the fibrous form have low basis weight, high permeability and small pore size that make them appropriate for the wide range of filtration applications, for example, reducing NO_x and CO emission [6]. However, Al_2O_3 nanofibres are more often used in high-temperature composites with elastic modulus, thermal and chemical stability as streighteners [7].

Nowadays, plasma treatment is widely used as an effective tool for physical and chemical modifications of the polymer surface, leaving the bulk material unchanged [8][9][10]. Plasma treatment leads to degradation of polymeric chains, chemical bond cleavage, creations of free radicals and release of gaseous degradation products due to irradiation by highly energetic photons (UV, soft X-ray) and substrate bombardment with electrons, ions excited species and radicals. Subsequent chemical reactions of transient, highly reactive species can result in formation of excess double bonds, large cross-linked and oxidized structures [11]-[14] The effect of plasma on ceramic materials has also been studied. On the one hand, the effect to increase the calcination process of ceramic precursors was verified, and on the other hand phenomena changing the physical properties of the ceramic material were observed [15], [16].

2. EXPERIMENTAL

Six different polymeric solutions were prepared for electrostatic spinning. Each mixture had different weight concentration of PVA/$Al(NO_3)_3 \cdot 9H_2O$ (see **Table 1**). The solutions for spinning were prepared as follows: The appropriated amount of PVA was diluted with water than the calculated amount of $Al(NO_3)_3 \cdot 9H_2O$ was added and mixed together at 80 °C overnight till to complete homogenization. Prepared solutions were spun using Nanospider™ NS LAB 500 (ELMARCO). The applied voltage was changed according to optimal spinning conditions (**Table 1**), distance between electrodes was fixed to 140 mm. Spinning was performed at ambient air, laboratory temperature and humidity between 40 - 60 % RH.

Table 1 Sample labelling and composition

Sample labelling	PVA [wt%]	$Al(NO_3)_3 \cdot 9H_2O$	Applied voltage
16 PVA_0	16	0	45
14 PVA_0	14	0	65
16 PVA_{15}	16	15	60
14 PVA_{15}	14	15	55
16 PVA_{20}	16	20	60
14 PVA_{20}	14	20	56

The final alumina fibres were obtained by the calcination process up to 1000 °C (100, 250 and 1000 °C). For the final comparison of plasma effect, half of samples were treated by plasma for 10 minutes before calcination process. DCSBD electrode was used as a source of plasma generating non-isothermal plasma.

3. RESULTS

In **Figure 1** the plasma treated samples before (left) and after (right) calcination process are shown. The shape of plasma treated nanofibers has significantly changed. These nanofibers are after calcination flatter, longer and more divided while the shape of porous membrane is preserved.

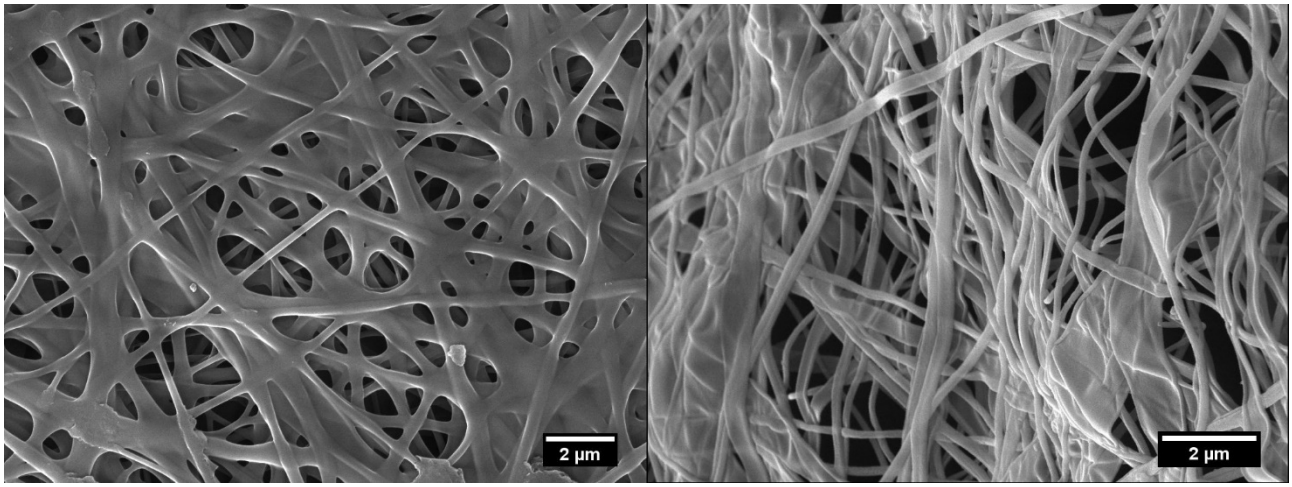

Figure 1 Representative SEM images of prepared 16 PVA_{20} nanofibers before (left) and after calcination (right) to 1000 °C

The originally round fibres gradually flattened resulting in an increase of their diameter. This phenomenon was explained as a “baking or melting” of nanofibres in plasma process. We assume that in the case of nanofibres containing aluminium nitrate nonahydrate it was possible, that the water bonded in crystalline structure was released. Then this water could partly disrupt nanofibrous structure. The elemental composition of fibres is shown in **Table 2**. After calcination weight percentage of carbon and nitrogen was lowered (not to zero value). This is probably caused by the melting and baking process. This could be a key step in the formation a membrane-like structure. Moreover, plasma had also a low impact on material composition. An increase of oxygen-bonded chemical groups was revealed by ATR-FTIR analysis (**Figure 2**). As can be seen in **Figure 2**, the FTIR spectra of samples measuring before calcination kept signals belonging to polyvinyl alcohol - (-OH vibration between 3500 - 3200 cm^{-1}, C-H aliphatic stretch at 2980 cm^{-1}, C=O at 1730 cm^{-1} and C-O-C at 1350 cm^{-1}. There is also visible vibration of N-O groups from nitrate at 1573 and 1383 cm^{-1}. After calcination there were visible vibrations in a region around 2980 cm^{-1} which belong to carbon chain, 1250-1160 cm^{-1} which belong to Al-OH stretch and at 900 - 620 cm^{-1} representing Al-O groups [16], [17].

Table 2 EDX analysis of 16 PVA_{20} nanofibres before and after the calcination process. (*) -up to 1000 °C

Sample	O [wt%]	Al [wt%]	C [wt%]	N [wt%]
16 PVA_{20}	46.7 ± 1.0	5.9 ± 0.7	38.2 ± 1.8	8.6 ± 0.2
16 PVA_{20} /plasma	38.4 ± 3.5	5.1 ± 1.7	46.7 ± 0.9	7.6 ± 0.5
16 PVA_{20} /calcination*	49.3 ± 2.8	31.9 ± 3.0	15.5 ± 2.1	0.9 ± 0.1
16 PVA_{20} /plasma/ calcination*	46.4 ± 2.9	18.3 ± 3.9	33.2 ± 7.4	0.7 ± 0.4

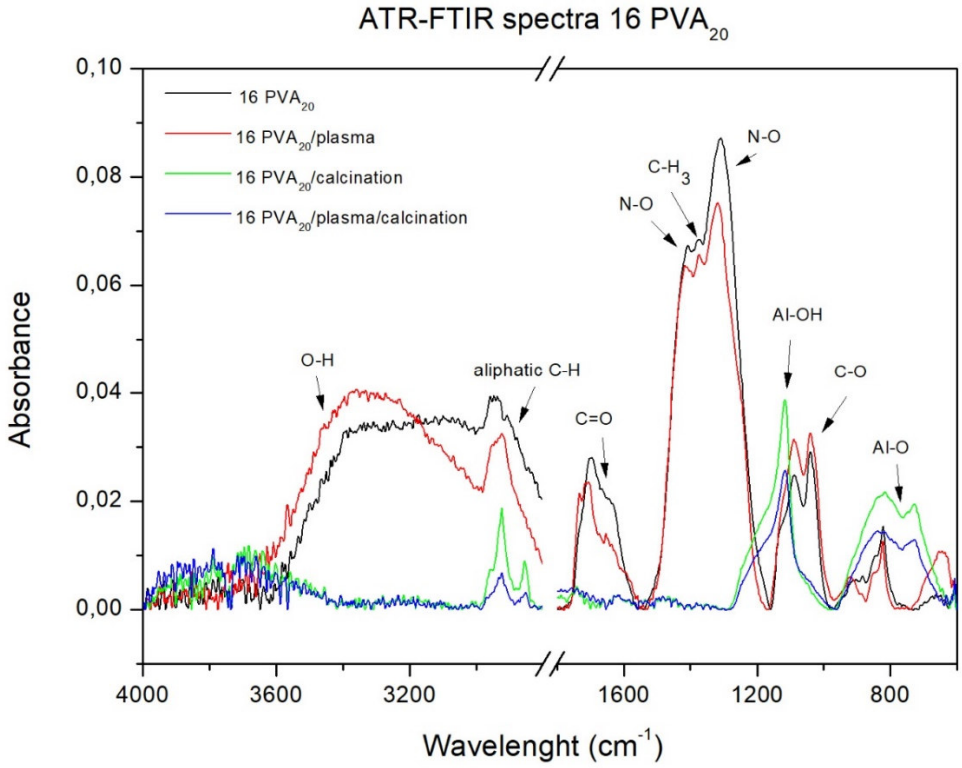

Figure 2 FTIR spectra of pure sample 16 PVA_{20} (black), 16 PVA_{20} after plasma treatment (red), 16 PVA_{20} after calcination to 1000 °C (green) and 16 PVA_{20} after plasma and calcination process (blue)

Plasma treatment of obtained nanofibers has also a significant effect on the calcination process. As shown in **Figure 2** after 10 minutes of plasma treatment there is a significant decrease in all carbon groups absorbances. After longer period of plasma treatment there is total vanishing of C-H_3 aliphatic vibrations in region 1370 cm^{-1}.

4. CONCLUSION

In this work we confirmed preparation of ceramic nanofibers from aluminium nitrate nonahydrate and polyvinylalcohol. Six different spinning solutions were prepared and it was possible to prepare nanofibers from all the precursor solutions. For spinning nanofibers was used electrospinning process via Nanospider™ technology. Before calcination nanofibers were modified using DCSBD plasma for 10 minutes. After nanofibers underwent calcination process which led to remove all the organic phases and nitrogen oxides. All the samples were characterized by SEM, ATR-FTIR, TGA and EDX analysis. The conclusion after comparison is that plasma treatment has a significant impact on the final structure of material, final composition of nanofibres. Plasma treatment can be considered as a novel method for the preparation of ceramic materials with membrane-like structure.

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