THE ROLE OF SOLVENTS IN THE PREPARATION OF HYDROPHOBIC NANOFIBROUS MEMBRANE CONTAINING FUMED SILICA

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Abstract

It is well-known that a type of used fumed silica nanoparticles plays a dominant role in wettability of the corresponding nanofibrous mats. As a result, the desired contact angle can be approximately achieved by a choice of adequate fumed silica nanoparticles. However, less attention has been hitherto paid to an active role of solvents in connection with the tailoring this contact angle. For analysis we used poly(vinyl butyral) representing electrospun-friendly material, various types of fumed silica nanoparticles and two solvents - methanol and ethanol. It is demonstrated that a choice of polymer solvents plays a significant role in contact angle changes. Hence, in combination of the type of fumed silica nanoparticles and the type of solvent it is possible to achieve a finer partition of the required contact angles.

Keywords: PVB solution, solvents, fumed silica, electrospinning, rheology

1. INTRODUCTION

Wettability represents a very important property of solid surfaces in various industrial applications as documented e.g. in [1-3]. Natural surfaces, like the lotus leaf, show that these biological superhydrophobic properties are induced by a hierarchical surface roughness in micro- and nanometer scale. For example, the superhydrophobic surfaces may be used for advanced applications, like as self-cleaning or separation membranes [4,5]. The required properties from the viewpoint of wettability can be achieved by surface treatment of the final products or during their manufacturing (as e.g. polymer processing) or by a combination of these two approaches.

Electrospinning, a polymer process during which the nanofibrous mats are prepared through a formation of viscoelastic jets in high electrostatic field, is an excellent representative how wettability of the resulting products can be widely varied. An application of various combinations of the entry parameters (as e.g. type of solvent [6,7], polymer concentration [8,9], relative humidity, applied high voltage, tip-to-collector distance) results in specific morphology of the resulted nanofibres that is generated by different cross-sections of the individual nanofibres (circular, flat or branched) and their possible porosity. The solvent properties and concentration of polymer solution significantly participate in a degree of wettability. Another factor contributing to tailoring wettability of nanofibrous mats is an application of additives. A family of fumed silica nanoparticles cover a broad range from hydrophilicity to hydrophobicity. Dufficy et al. [10] incorporated various fumed silica nanoparticles into polyacrylonitrile nanofibres by electrospinning process to produce mats with controlled wettability. Koysuren and Koysuren [11] reinforced poly(methyl methacrylate) nanofibrous mats with silica nanoparticles to make better dye adsorption capacity possible through higher contact angle of mats.

In this contribution, the wetting properties of nonwovens textile from poly(vinyl butyral) (PVB) dissolved either in methanol or ethanol solutions are analysed by water contact angle (CA) measurements. To enhance the wettability of mats, various types of fumed silica differing in surface modification, size and specific surface area were added into polymer solutions and consequently electrospun. The wetting properties of nanofibrous mats and cast films were compared.

2. EXPERIMENTAL

Material and Sample Preparation

Polyvinyl butyral (PVB, with butyral content of 75-81 %, M_w = 60,000 g/mol) was kindly provided by Kuraray Specialities Europe and it was dissolved in methanol and ethanol (quality of p.a., Penta, Czech Republic) at concentration 10 wt.%. Fumed silica nanoparticles (NPs) were kindly provided by Evonik Degussa Corporation (Germany). Characterization of the individual nanoparticles (specific surface area (BET), diameter of particles and surface modification) is described in **Table 1**.

PVB solutions with fixed concentration (2 wt.%) of fumed silica NPs were prepared by magnetic stirring at 250 rpm and at 25 °C over 48 hours using a magnetic stirrer (Heidolph, Germany). The PVB solutions were cast onto glass Petri dishes, left at room temperature until the solvents were evaporated. The nanofibrous webs were produced using a laboratory device [12] with the carbon steel stick (10 mm in diameter) and the flat metal collector. The electrospinning process of PVB solutions with silica NPs 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 about 23 °C and 45 %, respectively.

Table 1 Characterization of various fumed silica nanoparticles

Fumed silica	Diameter (nm)	BET (m^2/g)	Modification
R 812	8	230-290	Trimethylsilyl $O\text{-}Si\text{-}(CH_3)_3$
R 805	10-12	125-175	Octyl $(O)_3\text{-}Si\text{-}C_8H_{17}$
A 200	12	175-225	Hydrophilic/none
R 972	12-16	90-130	Dimethylsilyl $(O)_2\text{-}Si\text{-}(CH_3)_2$

Characterizations

Morphology of the nanofibres sputtered by a thin gold layer was observed using a Vega 3 high resolution scanning electron microscope (Tescan, Czech Republic). The mean fibre diameter was determined by help of Adobe Creative Suite software taking into account 300 fibres from 3 different images.

The wettability of PVB films and fibres was determined by the sessile drop method by a Drop Shape Analyzer - DSA30E (KRÜSS, Germany), using deionized water as the liquid.

3. RESULTS AND DISCUSSION

To compare solvent effect on the morphology of PVB nanofibres, methanol and ethanol were selected. Under the optimal experimental parameters (voltage of 20 kV and a tip-to-collector distance of 10 cm) favouring the fabrication of uniform nanofibres, a series of polymer solutions were electrospun. The PVB nanofibres created from the PVB/methanol solutions with mean diameter around 291 nm are of a circular shape and relatively thinner than the flat nanofibres electrospun from PVB/ethanol solution with mean diameter around 414 nm. To evaluate the changes in surface properties, the contact angle (CA) was measured by the sessile drop method. The shape of nanofibres influenced wetting properties. The SEM images and mapping of the contact angles of the neat PVB nanofibres created from the two solvents are shown in **Figure 1**. The circular nanofibres with smaller diameter exhibit higher average CA of 137° than the flat ones with higher diameter and CA of 129°.

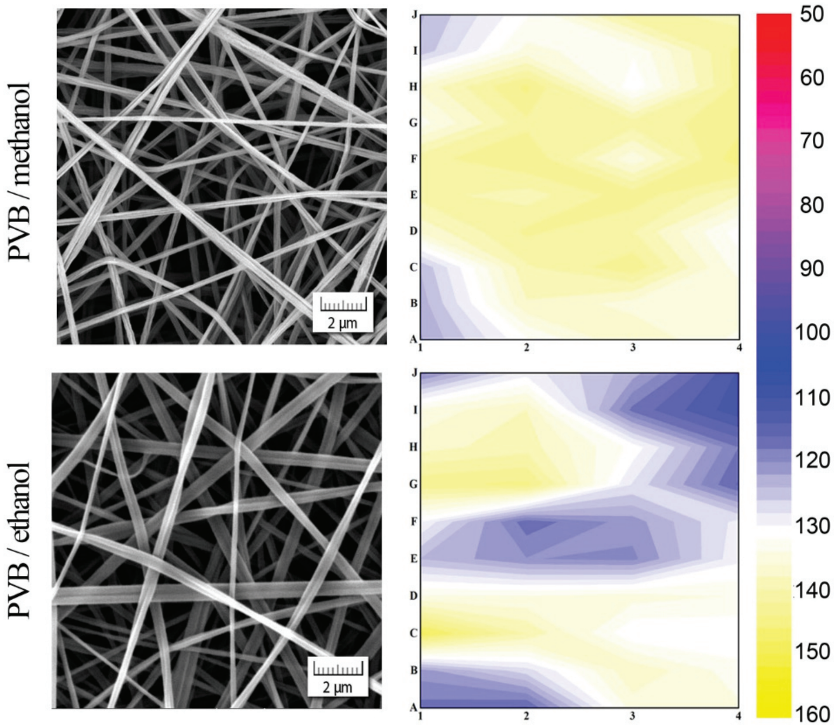

Figure 1 The SEM images and mapping of contact angles of neat PVB fibres

To increase the water repellency of nanofibrous web, the fumed silica nanoparticles at fixed concentration of 2 wt.% were added to the 10 wt.% PVB solutions and nanofibres were successfully produced. The fumed silica differing in surface modification, size and specific surface area has effect on the roughness of fibres which is the dominant factor for wettability. The results of nanofibres diameters and their corresponding CA are presented in **Table 2**.

Table 2 The diameters of nanofibres and their wetting properties

	PVB in methanol		PVB in ethanol	
	Diameter of fibres [nm]	Contact angle [°]	Diameter of fibres [nm]	Contact angle [°]
Neat PVB	291 ± 56	137 ± 6	414 ± 73	129 ± 9
PVB / R 812	350 ± 106	146 ± 3	476 ± 74	132 ± 12
PVB / R 805	346 ± 68	137 ± 7	468 ± 83	133 ± 4
PVB / A 200	349 ± 70	140 ± 8	501 ± 76	135 ± 7
PVB / R 972	363 ± 130	152 ± 4	536 ± 108	141 ± 5

It was found that the surface morphologies were substantially changed by solvent due to polymer-particle-solvent interactions. In the case of PVB dissolved in methanol the fumed silica nanoparticles cover nanofibres in a better way in comparison with the nanofibres produced from PVB dissolved in ethanol. **Figures 2** and **3** depict the morphologies of nanofibres obtained from PVB dissolved in methanol and ethanol and their corresponding mappings of water contact angles. In the case of silica R 972 it was found that the contact angle increased up to 152° which indicates superhydrophobic behaviour.

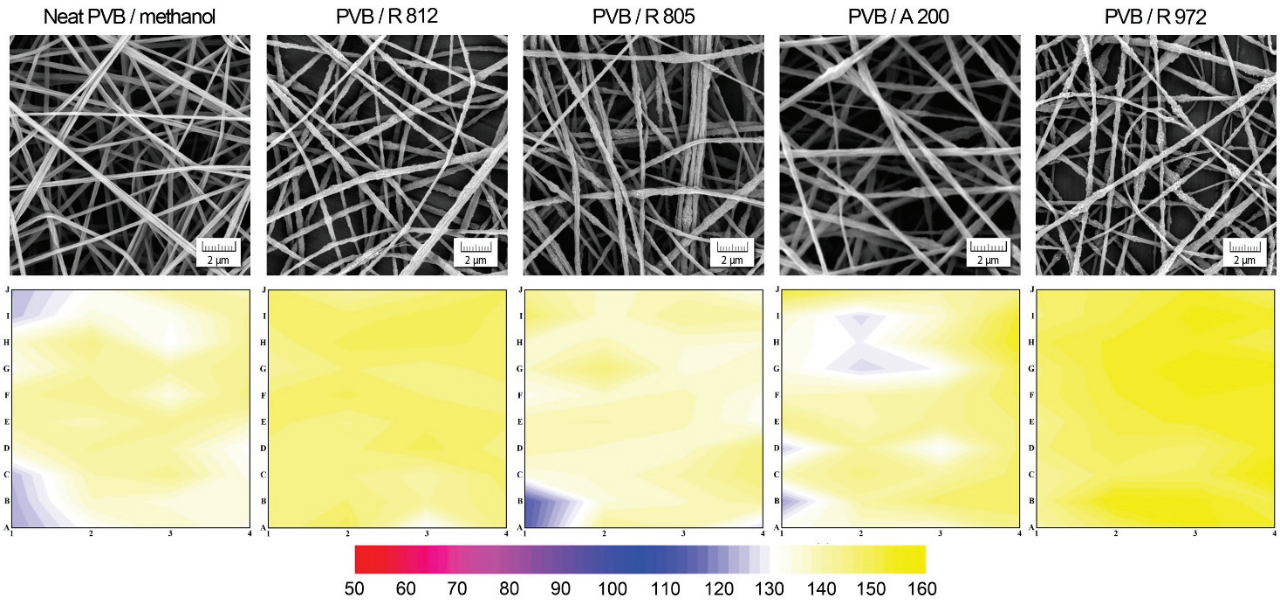

Figure 2 The SEM images and mapping of contact angles of PVB/silica fibres produced from methanol solutions

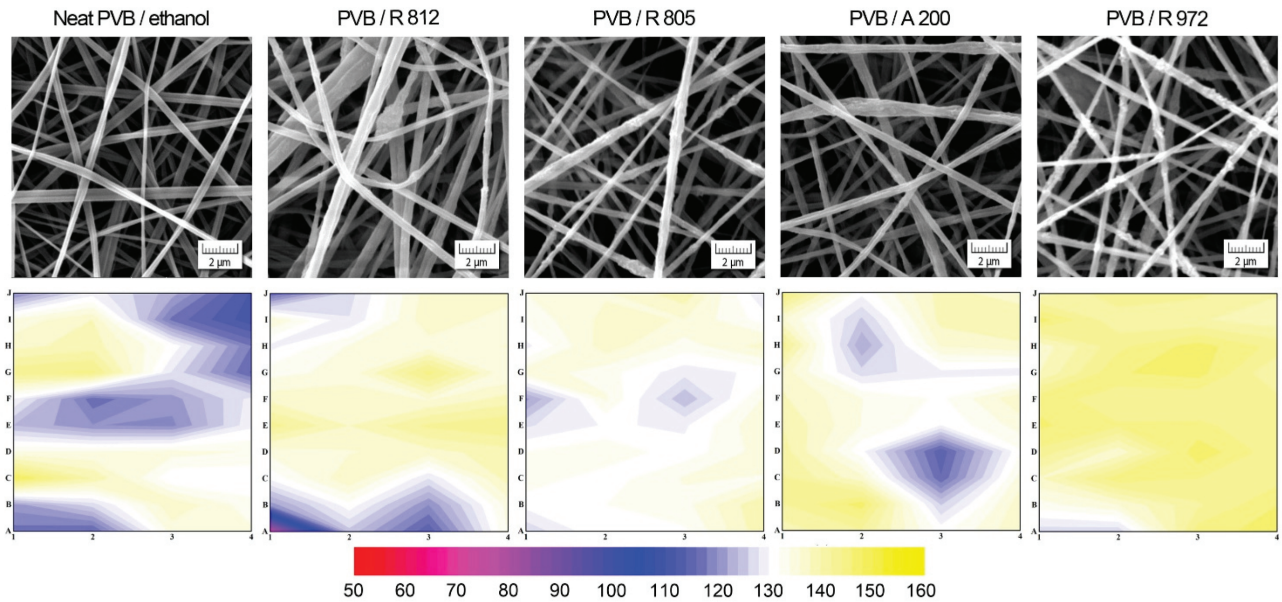

Figure 3 The SEM images and mapping of contact angles of PVB/silica fibres produced from ethanol solutions

The surface roughness of electrospun nanofibres increases the contact angles in comparison to the cast films. The values obtained are listed in **Table 3** and the mapping of CA is shown in **Figure 4**. The wettability of cast films exhibited rather hydrophilic behaviour, it means the CA is lower than 90°. The silica R 972 with the highest particle size incorporated into the PVB film shows again the highest CA compared to the others.

Table 3 The contact angles [°] of PVB films

	PVB in methanol	PVB in ethanol
Neat PVB	77 ± 4	82 ± 4
PVB / R 812	80 ± 5	75 ± 3
PVB / R 805	72 ± 4	80 ± 6
PVB / A 200	77 ± 2	81 ± 5
PVB / R 972	81 ± 2	79 ± 3

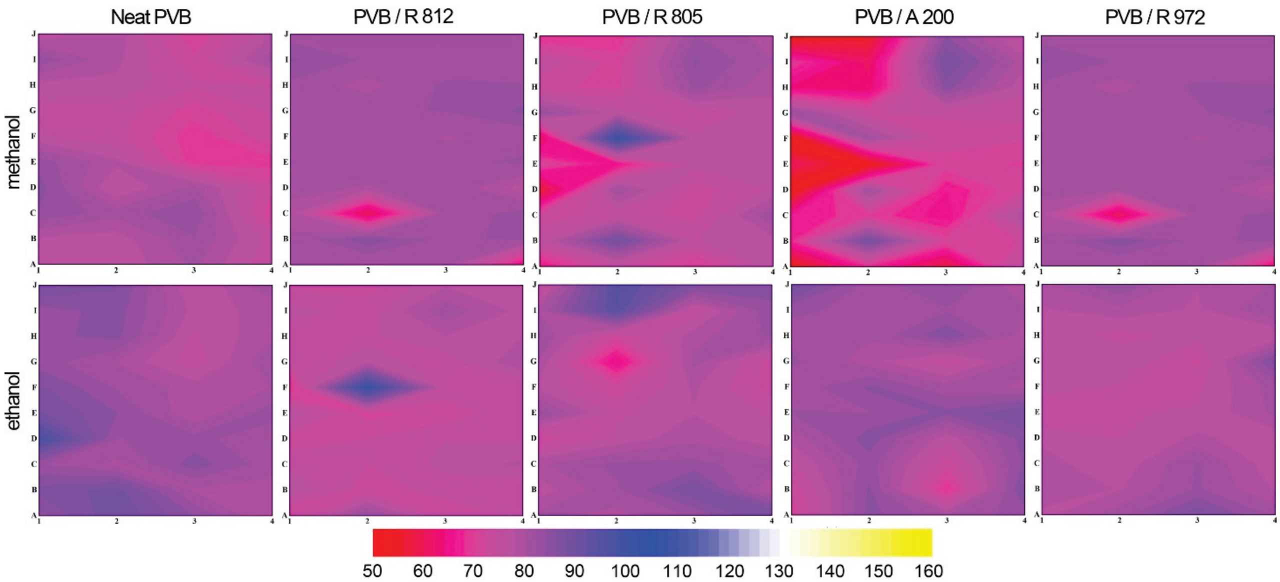

Figure 4 Mapping of contact angles of neat PVB and PVB/silica films

4. CONCLUSION

The circular and flat nanofibres with diameters ranging on average from 291 to 363 nm and 414 to 536 nm were successfully prepared from PVB dissolved in methanol and ethanol, respectively, containing fumed silica nanoparticles. It was shown that in contrast to the films, the nanofibrous webs exhibit nearly or totally superhydrophobic behaviour. In summary, the used solvents and the sizes of silica changed surface covering of the nanofibres with the more favourite results if methanol is used. In each case adding the fumed silica R 972 with highest size (16 nm) to PVB solution favours an increase of the contact angle of prepared nanofibrous webs or cast films.

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