Surface Wettability of Polyvinyl Butyral Nanofibrous Membranes

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Abstract: This study explores the mutual correlation between structures of electrospun fibrous membranes prepared from polyvinyl butyral (PVB) and the wettability of the same. The final morphology of the fibres ( wrinkled, smooth, ribbon-like and porous) was investigated by dissolving the PVB in various solvents and solvent mixtures. It was found that some concentrations of PVB in certain solvents and their mixtures exerted an influence on the diameter of the given fibre and water contact angle. The nanofibrous membranes were produced via electrospinning, and characterized by scanning electron microscopy (SEM) and measurement of contact angle. Discussion is included on comparison of the wettability of the PVB films and nanofibres.

Keywords: Electrospinning, Nanofibres, Polyvinyl butyral, Contact angle, Wettability.

1. INTRODUCTION

The wetting behaviour of a liquid on a solid surface is highly crucial to the surface properties of said materials and to application in industrial daily life. A wide range of utilizations demand materials with a hydrophobic surface, for example, self-cleaning materials\textsuperscript{[1]}, water repellent membranes\textsuperscript{[2]} and separators for lithium-ion batteries\textsuperscript{[3]}. Researchers had a look to nature and subsequently demonstrated that combinations of at least two different (micrometre and nanometre) length scales are necessary to create a synthetic hydrophobic surface\textsuperscript{[4–6]}.

A promising method for producing a textured surface with controlled wettability is electrospinning, wherein specific micro- and nanostructures are constructed on the surface. This permits creation of fibres of ultrafine diameter (100–400 nm) with enriched beads (0.5–2 µm) on them, thereby constituting a non-woven layer with a surface of hierarchical roughness. Additionally, employing the electrospinning technique affords researchers a wide set of parameters that effectively control the roughness of the surface; e.g., bead or bead-on-string structures, and ribbon-like, porous or circular fibres\textsuperscript{[7]}. The most important factors to affect the morphology of fibres include the following parameters pertaining to: i. polymers and solvents (molecular weight of the polymer, the evaporation of solvents); ii. solutions (surface tension, electrical conductivity, viscosity); iii. Processes (humidity, applied voltage, tip-to-collector distance). Furthermore, supplementation with additives—such as fumed silica—allows for improvement in wetting properties\textsuperscript{[8–10]}.

Herein, the authors compare the wettability of films and fibres created from PVB dissolved in various solvents or solvent mixtures. Hierarchically structured hydrophobic membranes were produced through the process of preparing fibres that were wrinkled, smooth, ribbon-like or porous and associated beads.

2. EXPERIMENTAL

Materials

Used polymer, namely PVB (Mowital B 60H; \(M_w = 60,000\) g/mol) was kindly provided by Kuraray Specialities Europe. The PVB was composed of vinyl butyral, vinyl alcohol and vinyl acetate, in this case 75–81 %, 18–21 % and 1–4 %, respectively. The PVB was dissolved in various solvents, namely ethanol (99.0% Brenntag GmbH, Germany) and methanol (99.5% Brenntag GmbH, Germany), and in two mixtures of solvents—tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) at the volume ratios 9:1 and 8:2 (THF – 99.0% BASF Ludwigshafen, Germany; DMSO – 99.0% Grüssing GmbH, Germany). The
concentration of polymer in the solvents was fixed at 6, 8 and 10 wt.%. All solutions were magnetically stirred (on a Rotilabo® MH 20 device; Carl Roth, Germany) at 250 rpm at 20.0±1.0 °C for 48 hrs.

Methods

The electrical conductivity of the solutions was measured on a digital conductometer (a CG 855; Schott Instruments, Germany), which had been equipped with a platinum electrode. Concurrently, temperature (25.0±0.5 °C) was monitored on a K204 digital thermometer data logger (Voltcraft, Germany).

Additionally, the surface tension of the solutions was gauged on a K12 tensiometer with built-in processor (Kruess GmbH, Germany). Measurements were taken with a platinum probe for 180 s at 24.0±0.5 °C.

Rotational rheological measurements were performed on a Physica MCR 501 device (Anton Paar, Austria) equipped with concentric cylinders (26.6/28.9 mm inner/outer diameters) at a constant temperature of 25.0 °C; the shear rate ranged from 0.01 to 300 s⁻¹.

The nanofibrous membranes were spun on a laboratory device consisting of a high voltage power supply (Spellman SL70PN150, USA), a carbon steel stick (10 mm in diameter) and a motionless flat metal collector. The electrospinning process was carried out at a voltage of 20 kV with the tip-to-collector distance fixed at 100 mm under room conditions (temperature 24.0±1.0 °C; relative humidity 41.0±1.0 % and 65.0±1.0 %). The drop of the polymer solution placed on the tip equalled approx. 0.2 ml. Characterization of the fibrous membrane was conducted by SEM on a Vega 3 high resolution device (Tescan, Czech Republic). Mean fibre diameter was determined in Adobe Creative Suite software, wherein 300 measurements were taken from 3 different SEM images.

The authors prepared PVB films by dispensing the solutions into glass Petri dishes and leaving the same under conditions of room temperature until the solvents had evaporated.

The wetting properties of the PVB nanofibrous membranes were discerned via drop shape analysis on a DSA30 unit (Kruess GmbH, Germany) equipped with a CCD camera. The volume of the water droplets was 2 µl, while the temperature was 23.3±0.5 °C. The contact angle was obtained immediately upon the instant the given droplet made contact with the nanofibrous membrane. In total, thirty droplets (10 droplets in 3 lines – marked by letters (A–J) and numbers (1–3) in forthcoming Figure 5) were measured for each sample. The distance between each droplet equalled 7 mm in line and 6 mm between the lines.

3. RESULTS AND DISCUSSION

Surface Tension, Electrical Conductivity and Viscosity

Parameters that significantly influence both the electrospinning process and the morphology of electrospun fibres include surface tension, electrical conductivity and the rheological properties of the polymer solution, as summarized in a reference [11]. Table 1 details the two such properties of the PVB

<table>
<thead>
<tr>
<th>Polymer Solutions</th>
<th>Concentration [wt.%]</th>
<th>Surface Tension [mN/m]</th>
<th>Electrical Conductivity [µS/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
<td>24.31±0.09</td>
<td>29.9</td>
</tr>
<tr>
<td>PVB/Methanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>24.68±0.04</td>
<td>32.6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>24.93±0.07</td>
<td>37.3</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>22.86±0.02</td>
<td>9.2</td>
</tr>
<tr>
<td>PVB/Ethanol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>23.06±0.05</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>23.19±0.03</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>29.94±0.02</td>
<td>2.4</td>
</tr>
<tr>
<td>PVB/THF:DMSO (9:1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>31.50±0.20</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>32.20±0.20</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>31.65±0.18</td>
<td>7.8</td>
</tr>
<tr>
<td>PVB/THF:DMSO (8:2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>32.60±0.20</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>33.70±0.30</td>
<td>9.0</td>
</tr>
</tbody>
</table>
solutions. The authors found that surface tension and electrical conductivity increased upon higher concentration of PVB in the solutions. Note that reducing the surface tension of the polymer solution (e.g., by using different solvents or adding surfactants) allows finer fibres to be produced. In terms of solvents, the PVB dissolved in methanol and ethanol showed lower values for surface tension. The literature describes how higher electrical conductivity favours the performance of electrospinning and decreases fibre diameter [12]. Herein, the PVB dissolved in methanol exhibited the highest values for electrical conductivity.

The rheological properties of the PVB solutions are directly related to concentration, molecular weight and given solvent. In order to compare the viscosity of the PVB solutions, the value of relative viscosity \( \eta_{rel} \) was calculated with the following equation:

\[
\eta_{rel} = \frac{\eta}{\eta_0}
\]

where \( \eta \) is the shear viscosity of solutions, and \( \eta_0 \) is the shear viscosity of neat solvents or mixture of solvents.

Figure 1 shows the results for relative viscosity plotted as a function of concentration. As expected, viscosity dramatically increased upon higher concentration of the PVB in the solvent. This might occur due to a greater number of molecular chain entanglements arising through the greater content of PVB [13, 14].

![Graph showing dependence of relative viscosity on concentration of PVB.](image)

**Figure 1:** Dependence of the relative viscosity of the solutions on the concentration of PVB.

**Characterization of Fibres**

The authors obtained PVB layers with different fibre morphologies, including bead-on-string and uniform fibres which also varied in diameter, by applying particular concentrations and solvents. The so-called bead-on-string formation pertains to the morphology of beads and fibres in the structure, and is attainable when the concentration of the solution is sufficiently low (6 wt.%). When the concentration of the solution reaches a certain value, beads disappear and only uniform fibres are presented (8–10 wt.%); notably, fibre diameter also increases. Figure 2 details SEM images of the PVB fibres with different morphology. Moreover, the employed solvents changed the structure of the fibres. Dissolving PVB in methanol led to round-shaped fibres with a wrinkled surface, while those resulting from the PVB/ethanol solutions were mostly ribbon-like in shape. The THF:DMSO mixture of solvents at various ratios exerted a significant effect on the porosity of the fibres [14]. Porous fibres were produced from PVB/THF:DMSO at the volume ratio of 8:2 and the relative humidity of 65%.

Fibre diameter increased in parallel with a higher concentration of PVB in the solutions, as shown in Figure 3. This was a consequence of the greater viscosity of the solution, which hindered the drawing of fibres during the electrospinning process. The fibres prepared from the mixture of solvents exhibited larger diameters (up to 1,000 nm), caused by a combination of low electrical conductivity and high surface tension.

Several types of PVB nonwoven layers— with different fibre diameters and surface morphologies— were obtained for the wettability measurements, as detailed in Table 2. Round, wrinkled fibres fabricated from the PVB/methanol solutions exhibited a high contact angle, independently on their diameters or the beads occurrence. The aforementioned ribbon-like fibre structure was produced from the PVB/ethanol solutions. The finest fibres were created from a solution at 6 wt.% concentration which was demonstrated in the highest water contact angle (139°) due to consisting of a hierarchical structure of beads and very thin fibres.

The fibres spun from the PVB/THF:DMSO (9:1) solution had smoother surfaces than the porous fibres created in PVB/THF:DMSO (8:2) solution with different volume ratios. Notably, smooth fibres that varied in diameter (ranging from 231 to 878 nm) exhibited the exact same contact angle of 129°. However, a more complex effect was exerted by the diameters of the porous fibres (268, 760 and 1,021 nm) on contact angle (124, 139 and 135°). Consequently, enhancing hydrophobicity of said porous fibres brought about higher contact angles for the same compared to smooth fibres.
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For the purpose of comparison, PVB films were also prepared and investigated. As it was found smooth, solvent-cast PVB films exhibited better wettability (lower contact angles) than the nanofibrous structure of the membranes (Table 3).

The surfaces of the nanofibrous membranes were inhomogeneous due to irregularities in collecting nanofibres on the collector during the electrospinning process. Thus, nanofibrous membranes with variable roughness, which is reflected in their wetting properties at various positions, were obtained. Therefore, mapping diagrams covering a larger area were created to determine more accurately the contact angles of the nanofibrous membranes (see Figure 4). The rougher layer corresponded to higher values for contact angle. Moreover, the droplet could be held by the fluff of fibres sticking out from the nanofibrous membranes, which indicated nearly superhydrophobic properties, as shown for fibres spun from PVB/THF:DMSO (8:2).

In contrast to the relatively inhomogeneous nanofibrous membranes with lower wettability, the films demonstrated homogeneous high wettability, although the identical solutions had been employed in their preparation. Figure 5 displays the wetting behaviour of the PVB films.
Table 2: PVB Fibre Diameters and their Contact Angles

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Concentration [wt.%]</th>
<th>Fibre diameter [nm]</th>
<th>Contact angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVB/Methanol</td>
<td>6</td>
<td>187±65</td>
<td>137±5</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>343±127</td>
<td>134±7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>486±147</td>
<td>138±6</td>
</tr>
<tr>
<td>PVB/Ethanol</td>
<td>6</td>
<td>173±72</td>
<td>139±2</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>290±95</td>
<td>137±3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>543±194</td>
<td>138±3</td>
</tr>
<tr>
<td>PVB/THF:DMSO (9:1)</td>
<td>6</td>
<td>231±66</td>
<td>129±4</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>612±149</td>
<td>129±5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>878±257</td>
<td>129±3</td>
</tr>
<tr>
<td>PVB/THF:DMSO (8:2)</td>
<td>6</td>
<td>268±103</td>
<td>124±10</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>760±476</td>
<td>139±5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1,021±407</td>
<td>135±7</td>
</tr>
</tbody>
</table>

Table 3: Contact Angles of the PVB Films

<table>
<thead>
<tr>
<th>Samples</th>
<th>Concentration [wt.%]</th>
<th>Contact Angle [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVB/Methanol</td>
<td>8</td>
<td>79±4</td>
</tr>
<tr>
<td>PVB/Ethanol</td>
<td>8</td>
<td>76±4</td>
</tr>
<tr>
<td>PVB/THF:DMSO (9:1)</td>
<td>8</td>
<td>71±4</td>
</tr>
<tr>
<td>PVB/THF:DMSO (8:2)</td>
<td>8</td>
<td>77±3</td>
</tr>
</tbody>
</table>

Figure 4: Mapped surfaces of nanofibrous membranes prepared from 8 wt.%.: a) PVB/Ethanol, b) PVB/Methanol, c) PVB/THF:DMSO (9:1) and d) PVB/THF:DMSO (8:2) solutions.
CONCLUSION

Based on the experimental results presented herein, it is possible to produce different fibre morphologies through the various solvents and concentration of polymer utilized in the electrospinning process. The authors reported hierarchically structured hydrophobic layers formed of beads and wrinkled, smooth, ribbon-like or porous fibres. All the structures of the prepared fibres exhibited higher water contact angles (124–139°) than the PVB films (71–79°).

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