Production and Properties of Nanofiber Nonwovens for Industrial Applications

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HIROSE PAPER MFG. CO. LTD.
1. Production of nanofibers by “Electro Bubble Spinning Method”

2. Properties of nanofibers overlaid nonwovens

3. Properties of polymer/silica composite nanofibers

4. Industrial applications for nanofiber nonwovens
Why has electrospinning not been widely used for the production of nanofiber?

1. Inefficient nozzle based electrospinning is still predominant
2. High maintenance due to the clogging of nozzles
3. Nonuniformity of nanofiber layer thickness
4. High production cost
Electro Bubble Spinning (EBS)

Principle of EBS

\[ P = 4 \times \gamma \times \cos \theta / D \]

- \( \gamma \): surface tension of the polymer solution
- \( \theta \): contact angle of a porous material and a polymer solution
- \( D \): bubble point diameter of the porous materials

(Japanese Patent 3918179)
Comparison of fiber diameter of nanofiber and conventional fiber

PVA nanofiber
AFD = 125 ± 36 nm

Short fiber (vinylon)

16 μm
Improvement of nanofiber production

Speed up of production line $\rightarrow$ more spinning units

Advantages of EBS
1. High production throughput
2. Low variation in basis weight of nanofiber
3. Easy maintenance
4. Excellent cost performance
Nanofiber Production Line based on the EBS method

Line length : 20M
Spinning area : 16M
Width of the Web : 1,600mm
### Production Speed

<table>
<thead>
<tr>
<th></th>
<th>AV.</th>
<th>SD</th>
<th>CV(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight of nanofiber (g/m²)</td>
<td>5.75</td>
<td>0.27</td>
<td>4.7</td>
</tr>
<tr>
<td>Average fiber diameter (μm)</td>
<td>0.1520</td>
<td>0.0087</td>
<td>5.7</td>
</tr>
<tr>
<td>Bubble point diameter (nm)</td>
<td>284</td>
<td>9</td>
<td>3.2</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
<td>198</td>
<td>7</td>
<td>3.5</td>
</tr>
</tbody>
</table>

![Graph showing relationship between Basis Weight of nanofiber (g/m²) and Production Speed (m/min.)](graph.png)
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Composites of 2 and 3 layers can be produced.
Nanofiber overlaid nonwoven (Top View)

Wet-laid nonwoven (PE/PP fiber)
PVA nanofiber

X500  50μm
Nanofiber overlaid nonwoven (Side View)
Pore size can be controlled by the amount of nanofiber overlaid.
Pore size reduced from ~100μm down to 200nm.
Air permeability of nanofiber web is 1/10 of microfiber web at same pore diameter (10μm)
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Production of Composite Nanofibers

Composite Nanofiber

Ceramics nanoparticle

Polymer solution

Silica content in solid of spinning solution (wt%)

Silica content in nanofiber (wt%)

$y = 0.9887X$

Graph showing the relationship between silica content in the solid of the spinning solution and in the nanofiber.
Composite Nanofibers of PVA/ceramics

PVA/SiO$_2$(100nm) composite nanofiber

PVA/SiO$_2$(500nm) composite nanofiber

PVA/Al$_2$O$_3$(4.7 μm) composite nanofiber
<table>
<thead>
<tr>
<th></th>
<th>As spun</th>
<th>200°C×1Hr</th>
<th>300°C×1Hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA nanofiber</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>[Image]</td>
<td>[Image]</td>
<td></td>
</tr>
<tr>
<td>PVA/SiO&lt;sub&gt;2&lt;/sub&gt; nanofiber</td>
<td>Bublbe Pore : 0.449μm, Mean Flow Pore : 0.2768μm</td>
<td>Bubble Pore : 0.456μm, Mean Flow Pore : 0.2841μm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Image]</td>
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</table>
## Heat resistance of PVDF/SiO\textsubscript{2} nanofiber

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<tbody>
<tr>
<td><strong>PVDF nanofiber</strong></td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td><strong>PVDF/SiO\textsubscript{2} nanofiber</strong></td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
<tr>
<td>Bubble Pore</td>
<td>0.805μm</td>
<td>0.706μm</td>
<td>—</td>
</tr>
<tr>
<td>Mean Flow Pore</td>
<td>0.473μm</td>
<td>0.414μm</td>
<td>—</td>
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</table>
### Morphology changes of PVDF/SiO$_2$ nanofibers

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<tr>
<td>PVDF nanofiber</td>
<td><img src="as_spun_PVDF.png" alt="Image" /></td>
<td><img src="200C_PVDF.png" alt="Image" /></td>
<td><img src="300C_PVDF.png" alt="Image" /></td>
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<tr>
<td>PVDF/SiO$_2$ nanofiber</td>
<td><img src="as_spun_PVDF_SiO2.png" alt="Image" /></td>
<td><img src="200C_PVDF_SiO2.png" alt="Image" /></td>
<td><img src="300C_PVDF_SiO2.png" alt="Image" /></td>
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- Melted
- Maintaining nanofiber structure
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Control of Diameter of PVA nanofiber

222±79nm

597±324nm

448±216nm

1,711±724nm
Cross Section View of Multi-layered Nanofiber Web
PVA nanofiber with nanosilica shows improved heat resistance

Separator of three-layer structure

PVA/SiO$_2$ nanofiber

Wet-laid nonwoven (polyolefin)
Overcharging test started from fully charged (4.15V) condition
Charging current: 15A (0.5C) constant current
Upper limit charging voltage: 10V

PVA nanofiber separator → Ignited by thermal runaway after overcharging of battery

PVA /silica containing nanofiber separator → No runaway happened during overcharging
Nail penetration test started from fully charged (4.15V) condition. A 5mm SUS nail was struck into battery perpendicularly to laminated electrode.

Thermal runaway does not occur on the battery with PVA/silica containing nanofiber separator.

Nominal capacity: 30 Ah
Potential Applications of HIROSE nanofibers

<table>
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<th>Technical Background</th>
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<tr>
<td>High performance/high safety Li-Ion Battery Separator</td>
<td>Ultrathin wet-laid nonwovens Polymer/Ceramic composite nanofiber</td>
</tr>
<tr>
<td>High Performance Filter Media (Air, Liquid)</td>
<td>Nanofiber diameter control technology</td>
</tr>
<tr>
<td>Apparel, Tissue Engineering, etc.</td>
<td>High throughput spinning technology (low cost)</td>
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Thank you for your attention
Contact information

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