Ionic Liquid/SAN Nanofibers as Chemiresistor

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SAN/BMIPF$_6$ nanofibers were fabricated by an electrospinning process and used as chemiresistors for sensing alcohol vapours. A hydrophobic and air-stable ionic liquid, BMIPF$_6$, was used to impart electrical conductivity to insulating SAN nanofibers. The effects of BMIPF$_6$ addition on the morphology of the nanofibers were explained in terms of surface tension, viscosity and conductivity. After exposing the SAN/BMIPF$_6$ nanofibers collected on an interdigitated electrode to alcohol vapours (ethanol, 1-propanol and 1-butanol), the resistance of the nanofibers decreased due to adsorption of alcohol molecules. The electrospun SAN/BMIPF$_6$ nanofibers sensor exhibited good sensitivity and reproducibility.

Key Words : Ionic liquid, Styrene-Acrylonitrile copolymer, Electrospinning, Nanofibers, Sensor

Introduction

Recently, nanomaterials have attracted a great deal of attention because of their unique optical, electronic, magnetic, catalytic and sensing properties.\(^1\)\(^2\) In addition, many methods in nanomaterial fabrication have been proposed, such as salt-assisted microemulsion polymerization, chemical vapour deposition (CVD), electropolymerization, friction transfer deposition and electrospinning.\(^13\) Among the techniques of fabricating micro and nanoscaled materials, electrospinning is a simple method. Electrospinning can be used to fabricate nanofibers with a one-dimensional structure.\(^6\) The one-dimensional structure of electro-spun nanofibers has a higher surface area to volume ratio than a two-dimensional structure. Consequently, electrospun nanofibers have potential applications as a high sensitive vapour sensor where a large surface area is required.\(^7\) Up to now, electrospun nanofibers have been used as the sensing materials for NH$_3$, optical sensors, humidity, camphosulfonic acid (HCSA), hydrogen peroxide, and glucose.\(^8\)\(^11\)

High performance chemical vapour sensors have been in demand in a range of fields including space exploration, industrial production, environmental monitoring, and homeland securities.\(^12\) Good and efficient chemical vapour sensors require several fundamental preconditions: (1) high sensitivity and selectivity, (2) rapid response time and recovery time, (3) low analyst consumption, (4) low operating temperature and temperature independence, and (5) stability in performance. Therefore, many researchers have examined composites composed of conducting materials/polymer as candidates for chemical vapour sensors because composite materials have high sensitivity and reproducibility, good processability, and reasonable cost.\(^13\)

Room temperature ionic liquids (RTILs) have potential applications in a range of fields owing to their unique chemical and physical properties.\(^14\) RTIL, a class of compounds containing organic cations and anions, appear to combine the advantages of the other aforementioned materials for chemical sensing, particularly for gas sensing.\(^15\) In addition, RTILs have been used for the detection of organic vapours owing to their nonvolatile and thermally stable nature in air. As a typical RTIL, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIPF$_6$) has good properties for organic gas sensing. BMIPF$_6$ is a hydrophobic, air-stable and conducting ionic liquid, which possesses unique properties, such as negligible vapour pressure, high thermal stability, and good conductivity.\(^16\) In addition, its unique properties have been used in a variety of applications, such as catalysts, electrolytes, green solvents, and sensors.\(^17\)\(^19\)

In this study, styrene-acrylonitrile copolymer (SAN)/BMIPF$_6$ nanofibers were prepared by electrospinning for alcohol vapour detection for the first time. It is also noted that electrospinning of SAN copolymer has not been reported to date. Styrene-acrylonitrile copolymer (SAN) is widely known for its optical properties, rigidity and resistance for heat and chemicals.\(^20\) In addition, SAN forms a homogeneous solution in BMIPF$_6$ for electrospinning. Electrospun SAN/BMIPF$_6$ nanofibers were fabricated on an interdigitated electrode and exposed to alcohol vapours. The SAN/BMIPF$_6$ nanofibers showed good reversible responses to ethanol, 1-propanol and 1-butanol, respectively.

Experimental

Materials. Styrene acrylonitrile copolymer (SAN) ($M_w = 100000$) was obtained from Kumho Petrochemical, S. Korea. 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIPF$_6$) was supplied by C-tri S. Korea. N,N-dimethylformamide (DMF) was received from OCI S. Korea. Ethanol, 1-propanol and 1-butanol were purchased from Duksan Pure Chemicals, S. Korea.

Fabrication of the SAN/BMIPF$_6$ Nanofibers. Different
weights of BMIPF₆ (the weight ratio of BMIPF₆ to DMF ranged from to 30%) and DMF were added to a 100 mL beaker, and the mixture was dissolved by ultrasonication (500 W, Materials & Sonics Co., USA) for 30 min in a water vessel. After dissolution, 8 g SAN was added to the solution. The mixture was stirred continuously for 12 h at 25 ℃ to obtain a homogeneous solution. Subsequently, the SAN/BMIPF₆ solution was loaded into a syringe connected to a syringe pump (KDS100, KD Scientific, USA). The flow rate of the solution was 0.5 mL/h and the applied voltage was 13 kV (controlled by a high voltage power supply (NanoNC, S. Korea)). The internal diameter of the positively charged metal needle connected to the syringe was 0.25 mm. The distance between the end of the needle and collector was 20 cm. The rotation speed of the collector was 50 rpm. An interdigitated electrode was 20 mm in diameter. The space between the comb fingers of the interdigitated electrode was 150 mm. After collecting the SAN/BMIPF₆ nanofibers onto an interdigitated electrode, they were dried in a vacuum oven for 48 h at room temperature.

**Characterization.** The morphology of the electrospun nanofibers was examined by scanning electron microscopy (SEM, S-4300, Hitachi) operated at 15 kV. Before characterization, the electrospun nanofibers were sputter-coated with platinum. The electrical conductivity, surface tension and viscosity of pure SAN and SAN/BMIPF₆ solution were examined to explain the change in diameter of the electrospun nanofiber. The conductivity of the SAN and SAN/BMIPF₆ solution was measured using a conductivity meter (Walklab Conductivity Meter, Trans Instrument, Singapore). The surface tension of the polymer solution was characterized using a tensiometer (K10ST, Kruss, Germany). The viscosity of the polymer solution was measured using a rotational shear rheometer (MCR 300, Anton Paar Physica, Germany). Fourier transform infrared spectroscopy (FT-IR, VERTEX 80 V, Bruker) was used to confirm the incorporation of BMIPF₆ into the SAN nanofibers. The electrical conductivity of the electrospun nanofibers was measured using a resistivity meter (Hiresta-UP, Mitsubishi Chemical co., Japan). The sensing behavior of the SAN/BMIPF₆ nanofibers were measured at room temperature by hanging the interdigitated electrode covered with electrospun SAN/ BMIPF₆ nanofibers in a conical flask filled with a range of alcohols, such as ethanol, 1-propanol and 1-butanol. The fabricated sensor was exposed to the alcohol vapours. The distance between each organic solvent surface and the interdigitated electrode was fixed to 5 cm. The change in electrical resistance was recorded using a digital multimeter (Agilent 34411A, USA) connected to a computer.

**Results and Discussion**

Morphology of the Electrospun SAN/BMIPF₆ Nanofibers. Figure 1 shows SEM images of the pure SAN nanofibers and SAN/BMIPF₆ nanofibers containing 5, 10, 15, 20 and 30 wt % BMIPF₆ in DMF. In Figure 1(a), the pure SAN nanofibers consisted of a beaded and fibrilar structure. On the other hand, the SAN/BMIPF₆ nanofibers (Figure 1(b), (c), (d), and (e)) had only a fibrilar structure. The morphology of the collected nonwoven nanofibers is affected by the surface tension, viscosity and density of net charges carried by the liquid jet.

Generally, the appearance of beads in nanofibers can be eliminated when the surface tension is decreased by the effect of the last two factors, i.e. viscosity and density of net charges. First, the surface tension is connected to the viscosity of a solution. Second, the addition of salts to increase the net charge density, such as ionic liquid or the use of solvents with lower surface tension affect the elimination of beads. Table 1 lists the viscosity, electrical conductivity and surface tension of the solution for electrospinning. The viscosity of the solution for electrospinning was measured using a rotational rheometer. When the
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Electrospinning process is implemented, the polymer solution flows in the needle, which can be treated as a narrow pipe with a small diameter. Assuming that the SAN/BMIPF₆ solution is a Newtonian fluid, the shear rate can be calculated using the following equation:

\[ \dot{\gamma} = \frac{8\nu}{d} \]

where \( \dot{\gamma} \) is the shear rate in the needle, \( \nu \) is the linear fluid velocity, and \( d \) is the diameter of the pipe. The calculated shear rate was 90.5 sec\(^{-1}\). Therefore, the solution viscosity was measured using an rotational rheometer at a shear rate of 90.5 sec\(^{-1}\).

The addition of BMIPF₆ causes an increase in the viscosity and electrical conductivity of the solution for electrospinning but a decrease in surface tension in the solution for electrospinning (Table 1). Consequently, the decrease in surface tension of the solution causes a change in the morphology of nanofibers.

**Characterization of SAN and SAN/BMIPF₆ Nanofibers.**

Pure SAN and SAN/BMIPF₆ nanofibers were fabricated independently by electrospinning. Figure 2 shows the FT-IR spectra of the electrospun SAN, SAN/BMIPF₆ nanofibers and pure BMIPF₆. Compared to the SAN nanofibers (Figure 2(a)), SAN/BMIPF₆ nanofibers (Figure 2(b)), BMIPF₆ (Figure 3(c)) showed several bands in the range of 400-1600 cm\(^{-1}\).

The FT-IR spectra of all three materials are similar to each other. The FT-IR spectra in Figure 2(a) and (b) show aromatic C-H stretching vibrations at 3010-3100 cm\(^{-1}\) and aliphatic C-H stretching at 2800-2993 cm\(^{-1}\). In addition, the peaks at 2243 cm\(^{-1}\) and 1460 cm\(^{-1}\) indicate C=N stretching and C-H bending, respectively. The peaks at 624, 835, 1170, and 3172 cm\(^{-1}\) in Figure 2(a) and (b) indicate the presence of BMIPF₆ in the SAN/BMIPF₆ nanofibers. The frequency of approximately 835 cm\(^{-1}\) is associated with the combinative vibration of PF₆\(^{-}\) and P-F bond. The vibration of C-H for cyclic BMI\(^{+}\) was observed at 624, 1170 and 3172 cm\(^{-1}\). These FT-IR spectra showed that BMIPF₆ exists in the electrospun SAN/BMIPF₆ composites nanofibers.

**Electrical Resistance of the SAN/BMIPF₆ Nanofibers.**

Figure 3 shows the relationship between the electrical surface resistivity of the SAN/BMIPF₆ electrospun nanofibers and the concentration of BMIPF₆ in the electrospinning solution. With increasing BMIPF₆ concentration, the resistance of the nanofibers decreased from 5.78 × 10\(^{14}\) to 5.04 × 10\(^{8}\) MΩ. In general, ionic liquids are salts in the liquid state and are good intrinsic conducting materials. For example, the conductivity of BMIPF₆ used in this study was approximately 1.4 × 10\(^{-3}\) S/cm at 25 °C. BMIPF₆ is composed of a BMI\(^{+}\) cation and PF₆\(^{-}\) anion, which are charge carriers. The number of charge carrier ions and their mobility in electrospun SAN/BMIPF₆ nanofibers increased with increasing BMIPF₆ concentration. Therefore, the decrease in resistance in the nanofibers was attributed to the addition of BMIPF₆ to the polymer solution.

**Alcohol Vapour Sensing of SAN/BMIPF₆ Nanofibers.**

The response of electrospun SAN/BMIPF₆ nanofibers to the three alcohol vapours (ethanol, 1-propanol, 1-butanol) as a chemiresistor was investigated by measuring the change in electrical resistance. The maximum BMIPF₆ loading (30 wt %) was used to obtain a rapid response time and easily noticeable sensitivity, namely the magnitude of the change in resistance. Electrospinning was impossible over 30 wt % BMIPF₆ due to the high viscosity of the solution.

**Table 1. Electrical conductivity, viscosity and surface tension of SAN/BMIPF₆ solution**

<table>
<thead>
<tr>
<th>BMIPF₆ (wt % to solvent)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical conductivity (s/cm)</td>
<td>-</td>
<td>1.5</td>
<td>2.4</td>
<td>3.3</td>
<td>4.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Viscosity (cP)</td>
<td>690</td>
<td>705</td>
<td>701</td>
<td>699</td>
<td>741</td>
<td>737</td>
</tr>
<tr>
<td>Surface tension (dyne/cm)</td>
<td>14.0</td>
<td>11.0</td>
<td>8.0</td>
<td>4.8</td>
<td>3.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Figure 2. FT-IR spectra of the pure BMIPF₆, electrospun SAN and SAN/BMIPF₆ nanofibers.

Figure 3. Electrical surface resistivity of the SAN/BMIPF₆ nanofibers with respect to the BMIPF₆ to DMF concentration ratio.
Table 2. Properties of alcohols used in the study

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Molar mass (g/mol)</th>
<th>Molar volume (cm³/mol)</th>
<th>δ₂ ^2 (MPa)(^{1/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>46.07</td>
<td>58.5</td>
<td>19.4</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>60.10</td>
<td>75.2</td>
<td>17.4</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>74.12</td>
<td>91.5</td>
<td>15.8</td>
</tr>
</tbody>
</table>

\(\delta = \delta_d + \delta_p + \delta_h\), where \(\delta_d\): solubility parameter, \(\delta_p\): polar term, and \(\delta_h\): hydrogen bond term. \(\delta_h\) denotes the energy from hydrogen bonds between molecules.

The time dependent resistance, \(R_0\) and \(R\), denote the resistance of the initial electrospun nanofibers sensor (at \(t = 0\)) and that exposed to the alcohol vapours at time \(t\). In Figure 4, the resistance of the SAN/BMIPF₆ nanofibers decreased instantly when they were exposed to the three low molecular alcohol vapours. This might be explained by polymer swelling and the number of charge carriers in the electrospun SAN/BMIPF₆ nanofibers. The alcohol vapours adsorbed to the electrospun SAN/BMIPF₆ nanofibers upon exposure. The hydroxyl group in the alcohol molecule is an electron donating group that increases the number of charge carriers in the SAN/BMIPF₆ nanofibers, resulting in increased conductivity. Therefore, the resistance of the electrospun SAN/BMIPF₆ nanofibers decreases when they are exposed to the alcohol vapours.

Figure 4 shows the response of SAN/BMIPF₆ nanofibers to low molecular alcohol vapours. The \(y\)-axis in Figure 4 is the normalized resistance:

\[
\frac{\Delta R}{R_0} \times 100 \% = \left(\frac{R-R_0}{R_0}\right) \times 100 \% \quad (2)
\]

The concentration of each alcohol vapour (ppm) at 25 °C can be calculated using the following equation:

\[
C_{ppm} = C \times \frac{M}{D} \times 10^6 \quad (3)
\]

where \(M\) is the molecular weight of alcohol, \(D\) is the density of alcohol, and \(C\) is the concentration of alcohol vapour at 25 °C in a conical flask. Assuming that each alcohol vapour acts as an ideal gas and is saturated, the concentration of the alcohol vapour \((C)\) can be calculated using the following equation:

\[
P = \frac{n}{V}RT = CRT \quad (4)
\]

The concentrations of ethanol, 1-propanol and 1-butanol vapours were 141, 60 and 22 ppm, respectively (Table 3).

For the three alcohol vapours used for the sensing test at 20 °C, Table 3 lists the properties of the three alcohol vapours. When ethanol molecules were adsorbed on the surface of the electrospun SAN/BMIPF₆ nanofibers, ethanol vapour with the smallest molar volume can diffuse easily into the nanofibers. Moreover, the surface of the electrospun SAN/BMIPF₆ nanofibers contains fluorophosphates anion groups, which can form hydrogen bonds with alcohol vapours. Therefore, ethanol vapours can form the strongest hydrogen bonds with the fluorophosphate anion on the surface of nanofibers owing to its largest \(\delta_h\) value (19.4 (MPa)\(^{1/2}\)). As a result, the number of charge carriers in the electrospun SAN/BMIPF₆ nanofibers increased with increasing amount of adsorption. 1-Butanol showed the smallest change in resistance. 1-Butanol can also form a hydrogen bond with the hexafluorophosphate anion on the surface of the electrospun nanofibers. On the other hand, 1-butanol is more difficult to diffuse in the electrospun nanofibers than ethanol because of its higher molar volume. In addition, 1-butanol has the smallest \(\delta_h\) value (15.8 (MPa)\(^{1/2}\)).

The concentration of each alcohol vapour (ppm) at 25 °C in a conical flask placed in a glove box was calculated using the following equation:

\[
C_{ppm} = C \times \frac{M}{D} \times 10^6 \quad (3)
\]

The concentrations of ethanol, 1-propanol and 1-butanol vapours were 141, 60 and 22 ppm, respectively (Table 3).
phere. This is because a small number of adsorbed alcohol molecules remain on the surface of the nanofibers even after exposure to air because of the hydrogen bonds formed between the nanofibers and alcohol molecules.

**Conclusion**

One-dimensional SAN/BMIPF$_6$ nanofibers were fabricated by electrospinning and used as a chemiresistor to detect alcohol vapours, such as ethanol, 1-propanol and 1-butanol. After BMIPF$_6$ addition, the morphology of the electrospun nanofibers changed from beaded nanofibers to only a fibrilar structure. This is linked to the viscosity, electrical conductivity and surface tension of solution for electrospinning. The addition of BMIPF$_6$ causes an increase in the viscosity and electrical conductivity of the solution for electrospinning as well as a decrease in surface tension in the solution for electrospinning. Consequently, a decrease in the surface tension of the solution causes a change in morphology of the nanofibers. With increasing BMIPF$_6$ concentration, the surface resistivity of the electrospun SAN/BMIPF$_6$ nanofibers decreased from $5.78 \times 10^{14}$ to $5.04 \times 10^8$ Ω·sq$^{-1}$. The electrospun SAN/BMIPF$_6$ nanofibers were fabricated on an interdigitated electrode and exposed to three alcohol vapours (ethanol, 1-propanol, and 1-butanol). The resistance of the SAN/BMIPF$_6$ nanofibers decreased when they were exposed to the three alcohol vapours. Among the alcohol vapours, ethanol vapour produced the highest change in resistance. This phenomenon was explained by the molar volume and strength of hydrogen bonds between the surface of the nanofibers and ethanol. The stable cyclic test showed that an ionic liquid containing the SAN nanofibers can be used for sensing alcohol vapours.

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**References**


![Figure 5. Electrical response of the SAN/BMIPF$_6$ electrospun nanofibers upon cyclic exposure to (a) ethanol, (b) 1-propanol, and (c) 1-butanol vapour.](image-url)