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Technologies Involved in the Manufacture of Smart Nonwoven Fabrics

Izabella Krucińska, Ewa Skrzetuska, Beata Surma and Eulalia Gliścińska

Abstract

Many methods can be used to protect humans against hazardous chemicals in the environment such as personal protective equipment and protective clothing. However, what matters most is prevention and early detection of threats. Detecting the presence of hazardous chemicals such as organic liquids and the vapours they give off is possible using sensors. Effective chemosensory properties are revealed by conductive polymers and carbon particles, where the electrical resistance of chemicals changes. Still open to debate is finding the optimum means of applying chemical sensors that would provide high sensitivity, durability, reliability, and resistance but at the same time would not be expensive. The authors propose introducing chemical sensors in the form of nonwoven fabrics produced by the melt-blown method and by electrospinning. The analysis takes account of melt-blown nonwoven fabric based on polylactide (PLA)-containing carbon nanotubes, nonwoven fabric made by electrospinning based on polyethylene oxide–containing carbon nanotubes and carbon nonwoven fabric from polyacrylonitrile submicron precursor fibres formed by electrospinning. Assessment of the effectiveness of the sensors to liquid vapours including methanol, acetone, benzene and toluene (concentration 200 ppm) has been carried out. The resulting nonwoven sensors are characterized by good electrical conductivity and altered electrical resistance as a result of the presence of vapours.

Keywords: Melt-blown method, electrospinning, vapour sensors, textile sensors, carbon nanotubes, submicrofibre-activated carbon

1. Introduction

Significant progress in the manufacture of composite materials has recently given rise to new opportunities for the use of nonwoven fabrics. The functionalization of composite materials involves the introduction of electrically conductive nanoadditives. It allows acquiring original polymer materials for possible use in smart products. There has been in recent years a growing...
interest in technologies aimed at imparting specific properties to textile products (i.e. generating so-called “smart” nonwoven fabrics such as fabrics capable of changing their properties under the influence of external stimuli). Techniques used to produce nanocomposites or select nano and polymeric materials may be of use in the construction of various types of sensors. Smart textiles – also called “active”, “interactive” and “adaptive” textiles – can be produced using such solutions.

Smart textiles can be functionalized by incorporating active materials into fibre, or by modifying the surface of textiles to give them specific characteristics. Active materials can be stimulated by a number of factors such as stressing, temperature, humidity, ultraviolet radiation and chemical substances. Smart textiles react to these stimuli by changing various parameters such as dimension state, change in resistance or in the distribution of stresses [1–9]. The use of nanotechnology in the functionalization of materials made by classical textile techniques allows certain unique properties, such as sensory properties or electrical conductivity, to be achieved. Introducing different types of nanoparticles to fibres can drastically alter the properties of materials [10, 11]. Ongoing work is currently aimed not only at obtaining new polymers, but also at effectively modifying them with nanoadditives and finding new solutions in processing techniques, so as to obtain polymeric materials that can be used in the construction of sensors. Sensors are usually components of a larger system, often defined as devices that receive and respond to a signal or stimulus. Their task is to capture information from the environment or to test an object by recognizing and recording it. Sensors should enable fast, simple and continuous measurements of the value being measured. It is important that the impact of using sensors does not being about changes in the tested objects [12–15].

Innovative solutions of noncontact sensors, material processing and design have an important input in development of smart textiles. Such materials combine a number of features of sensors such as electronic data processing and the ability to send information to other devices (e.g. alarm systems, data loggers, and monitoring devices). This has resulted in a sharp increase in interest in specialized products for medicine, filtration and protective services. Sensors used in textiles such as clothes, carpets, upholstery, furniture, wallpaper and paint have the potential to radically change lifestyles, enabling monitoring and action at a distance [16–21]. Some electroactive polymers may be useful in the production of fibre sensors as a result of their intrinsic dielectric or conductive properties, light weight, flexibility and relatively low price [7–9, 22, 23]. This paper focusses on a new area of research undertaken by the authors, one that deals with transferring properties of electrical conductivity to nonwoven fabrics by incorporating carbon nanoparticles into their structure.

This work involves using carbon nanotubes to impart sensory properties. Melt-blown and electrospinning were the methods selected to form fibres. The characteristic properties of carbon nanotubes – such as thermal conductivity, electrical conductivity, high modulus, high strength and resistance to chemicals – make them widely used in nanotechnologies. The electrical properties of carbon nanotubes are typical of two-dimensional structures, and electrical conductivity varies depending on the structure of nanotubes (single or multi-walled) and chirality. The electrical conductivity of nanotubes is also sensitive to the influence of external factors such as electric fields, magnetic fields, mechanical properties, state of the
environment (temperature, vapour content of selected chemicals). Mechanical properties are characterized by high mechanical strength, elasticity, susceptibility to deformation as a result of bending, torsion or flexibility (e.g. during stretching the length of nanotubes may increase by up to 40% without changing their structure [24]). The peculiar properties of nanotubes are widely used in many fields of nanotechnology: for example, when creating nanocomposites using nanotubes as reinforcing material and functionalizing composites, when creating nanocontainers to store gases (like hydrogen) [24], when removing dioxins prior to medical waste incineration and from chemical products [24]. Nanotubes play important roles in environmental protection. However, the greatest hope for the peculiar electrical properties of nanotubes (e.g. in microelectronics [25]) lies in their potential to exceed the limits of silicon technology.

The electrical sensory properties of carbon nanotubes were used in this work to functionalize nonwoven fabrics produced using modern techniques. Melt blowing and electrospinning are often used to produce filter materials to protect against toxic molecules. Therefore, the manufacture of nonwoven fabrics that are sensitive to vapours for use in filtration materials represents an innovative approach to receiving signals about the concentration of toxic vapours in the air. A new generation of smart half-masks that protect the respiratory tracts of users can be developed using such fabrics.

2. Materials and methodology

2.1. Producing a nonwoven fabric of polylactide (PLA) using melt blowing and carbon nanotubes

The most suitable materials to produce nonwoven fabrics via melt blowing are those whose melt flow index is high. Most thermoplastic polymers can be used in this technique. However, as a result of very good processing properties and low price the most commonly used is polypropylene. Polycarbonate, polyester, polyamide and polystyrene are also frequently used to make nonwoven fabrics. When selecting an appropriate polymer for the construction of a chemical vapour sensor both the Hildebrandt and the Flory–Huggins theories should be followed [7, 26], especially when a compound is influenced by a solvent (swelling, dissolution). This happens when the solubility parameters of the polymer and solvent used are similar. The Flory–Huggins solubility parameter has been presented in previous work [7].

The polymeric sensor produced by melt blowing was assumed to have been manufactured from PLA to which multi-walled carbon nanotubes (MWCNT) were then introduced. Preliminary experiments made it possible to establish a percolation threshold for nonwovens produced by melt blowing. A conductive nonwoven containing 2% MWCNT was found to be adequate to produce a 4060D PLA polymer (98% PLA 4060D/2% MWCNT) [7]. Increasing the content of MWCNT to 4% was found to cause a linear increase in the conductivity of nonwovens, but a decline in the strength of the product.

Nonwoven fabrics made of PLA and MWCNT were produced in two stages. First, the polymer PLA 4060D (NatureWorks) had 4% MWCNT (Nanocyl® 7000, Nanocyl SA, Belgium) added
to it. A ready-made nanocomposite (PLA/4% MWCNT) was then mixed with pure PLA 4060D to obtain the final composition PLA/2% MWCNT. The two-step process was designed to ensure carbon nanotubes were uniformly distributed in the structure of the product and that the formation of undesirable agglomerates was reduced. The nanotubes were 90% pure, 9.5 nm in diameter and 1.5 μm in length. The polymer selected had a molar mass of up to 87 000 Da and a D-isomer content of 12% [7].

2.2. Producing a nonwoven fabric of polyethylene oxide using electrospinning and carbon nanotubes

Polyethylene oxide (PEO) with the addition of MWCNT was selected for the production of nonwovens using the electrospinning polymer solution technique [8]. The polymer had a molar mass of 400 000 Da. To produce nonwovens with this technique, a solution of PEO in distilled water at a concentration of 5 wt.% was prepared to which a homogeneous suspension of the MWCNT containing 3% by volume carbon nanotubes with respect to the polymer volume was added. Mixing the nanotube suspension was carried out using an ultrasonic homogenizer at 150 W and a frequency of 30–40 kHz. The nanotube suspension was then added to the polymer solution and mixed in an ultrasonic homogenizer at 150 W and a frequency of 3–40 kHz at a temperature of 20°C for 0.2 hours, followed by 24 hours in a magnetic stirrer. Electrospinning consisted of an electrostatic field made up of the polymer composition prepared. The electrostatic field was the result of the potential difference between the capillary feed polymer and a collecting drum. A supply voltage of 15 kV was applied to the capillary by a generator while the receiving drum was grounded. The distance between the capillary and the drum was 20 cm [8].

2.3. Carbon nonwoven fabric produced by polyacrylonitrile electrospinning

Another option presented in this paper is nonwoven fabrics made from submicron carbon fibres. The first step taken to produce carbon structures was to prepare a nonwoven precursor. The precursor was obtained by electrospinning fibres from a solution of polyacrylonitrile (PAN). A 15% spinning solution of PAN powder was prepared to obtain the nonwoven precursor. The solution was produced by Zoltek Zrt. (Hungary) in dimethyl sulfoxide (DMSO) manufactured by POCH (Gliwice, Poland). The intrinsic viscosity of the PAN was equal to 1.3 ± 0.02 dL/g [23, 27]. Electrospinning was performed on a large-size laboratory device large-size laboratory line for producing nonwovens from the solution electrospinning technique that had 32 capillaries at 22 ± 10°C and a relative humidity (RH) of 38% under normal atmospheric pressure [23]. Process parameters were: generator voltage 15 kV, distance between the feeding capillary and collecting drum 15 cm, capillary diameter 0.9 mm [23].

The precursor nonwoven fabric was first subjected to thermal stabilization, which consists in heating to a temperature of 200°C and thermosetting for 6 hours. It was then oxidized by heating to a temperature of 220°C and thermosetting for another 6 hours. The heating cycles were performed in a stream of air. After washing the nonwoven fabric in carbon dioxide, it was subjected to pyrolysis, which involved heating to a temperature of 600°C in an atmosphere of inert gas and annealing at the final temperature. The nonwoven fabric was then subjected
to chemical activation by impregnation with a solution of potassium hydroxide using a vacuum method, and kept under reduced pressure which was slowly increased to atmospheric pressure. This was followed by soaking the nonwoven fabric in an aqueous solution of potassium hydroxide, removing the excess hydroxide solution, leaving the nonwoven fabric at room temperature, drying to a constant weight and annealing in a stream of inert gas. Finally, the nonwoven fabric was cooled and extracted using an aqueous solution of hydrochloric acid and then distilled or deionized water [28].

2.4. Methods used for nonwoven fabric assessment

The cross-sectional shape and thickness of fibres comprising the nonwoven fabric were examined using a JEOL JSM-5200LV scanning electron microscope (SEM). Image processing and measurements were carried out using LUCIA G image analysis software. The results are shown in Table 1 and Figure 1.

The electrical conductivity of the nonwoven fabric produced was calculated by measuring surface resistance according to EN 1149-1:2008 – Protective clothing. The electrostatic properties of the nonwoven fabric were calculated using the surface resistivity test method. An electrometric direct method using a Keithley 610C solid-state electrometer was employed in the study. The voltage source was an RFT-4218 DC power supply with a voltage range of 0–3000 V. The electrodes and the test sample were placed in a Faraday cage. Constant conditions for conditioning and testing were: temperature 23°C, RH = 25%. The results are shown in Table 2.

Sensory tests for the presence of solvent vapours were carried out using a laboratory measurement system. Such a system allows for measurements of the humidity and temperature of the atmosphere prevailing in the system and the creation and introduction of a given concentration of liquid vapours to the measuring system. The sensory sensitivity of the nonwoven fabric produced was investigated with measuring apparatus constructed at the Department of Material, Commodity Sciences and Textile Metrology (Lodz University of Technology, Poland). This was equipped with a tank serving as a gas chamber, a pump for mixing gas fumes, and a measuring chamber containing the measuring electrodes connected to a Keithley multimeter. The gas chamber was used to evaporate the appropriate amount of solvent. The mass of solvent to be evaporated in the gas chamber to achieve a concentration of X ppm was calculated according to equations (1–2) [7]:

\[
Y = \left( \frac{X \times M}{22.4} \right)
\]

(1)

\[
m = Y \times V
\]

(2)

where \(Y\) is the density of solvent vapours (mg/m^3), \(X\) is parts per million (1/10^6 ppm), \(M\) is molecular weight (kg/kmol), \(m\) is mass of solvent to be evaporated (mg), \(V\) is volume of gas chamber (0.024 m^3).
The gas chamber houses a thermometer and humidity sensor that ensure tests are conducted under identical climate conditions (temperature 23°C and RH of 25%). After evaporation of the solvent in the gas chamber, the vapour is pumped to the measuring chamber in which a test sample 2 cm × 4 cm in size is placed on the measurement electrodes. The sensory properties of the nonwoven fabric were tested for vapours of various solvents, and changes in resistance were recorded. The liquids used were typed according to EN 14605+A1:2009. The sensory properties were also investigated for vapours of both polar and nonpolar organic liquids at a concentration of 200 ppm.

The sensory properties of samples for toxic vapour substances were characterized by defining a sensory factor $S$. This was defined by formula (3) [7, 29]:

$$ S = \left| \frac{R_{rel}}{R_{init}} \right| \times 100\% $$  

where

$$ R_{rel} = \frac{R_i - R_0}{R_0} $$

$R_{rel}$ is relative changes in electrical resistance, $R_0$ is initial sample resistance ($\Omega$), $R_i$ is final resistance of the sample ($\Omega$) [7, 29].

3. Results and discussion

Table 1 shows the thickness of fibres forming the nonwoven fabrics.

<table>
<thead>
<tr>
<th>Type of nonwoven fabric</th>
<th>Production technique</th>
<th>Thickness of fibre (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>98% PLA 4060D/2% MWCNT</td>
<td>Melt blowing</td>
<td>17.75</td>
</tr>
<tr>
<td>97% PEO/3% MWCNT</td>
<td>Electrospinning</td>
<td>0.24</td>
</tr>
<tr>
<td>Carbon (precursor 15% PAN/85% DMSO)</td>
<td>Electrospinning carbonization</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Table 1. Thickness of fibres forming the nonwoven fabrics [7, 8, 23]

Figure 1 shows the structure of the nonwoven fabrics and the shape of constituent fibres.

The results show that fibres in the nonwoven fabric prepared by electrospinning a polymer solution of PEO have the lowest diameter. However, microscopic observation shows that the addition of carbon nanotubes has caused many beads, making the structure nonuniform. The carbon nonwoven fabric made of PAN has the highest fibre thickness uniformity. The melt-blown nonwoven fabric shows a high spread in fibre thickness – there are both fine fibres with
a diameter of approx. 5 μm and coarse fibres with a diameter of approx. 80 μm. Table 2 shows the results of the electrical conductivity test of the nonwoven fabrics.

<table>
<thead>
<tr>
<th>Type of nonwoven fabric</th>
<th>Production technique</th>
<th>Surface resistivity (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>98% PLA 4060D/2% MWCNT</td>
<td>Melt blowing</td>
<td>5.63 * 10⁷</td>
</tr>
<tr>
<td>97% PEO/3% MWCNT</td>
<td>Electrospinning</td>
<td>1.67 * 10⁴</td>
</tr>
<tr>
<td>Carbon (precursor 15% PAN/85% DMSO)</td>
<td>Electrospinning carbonization</td>
<td>4.89 * 10⁵</td>
</tr>
</tbody>
</table>

Table 2. Electrical surface resistivity of the nonwoven fabrics

Table 2 shows that the best conductivity was observed for the PEO nonwoven fabric made by electrospinning the polymer solution, while the worst conductivity was observed for the PLA nonwoven fabric with carbon nanotubes formed using the melt-blown technique. According to EN 1149-1:2008, homogeneous materials are characterized by electrostatic properties when they show a surface resistivity of less than 2.5 × 10⁸ Ω. In other words, all three nonwoven fabrics have electrostatic properties.

Table 3 summarizes sensory test results for the presence of polar and nonpolar solvent vapours. The sensitivity threshold of solvent vapours was based on data about the toxic effects they have on the human body. The data suggest the minimum concentration of solvent vapours having a toxic effect on the human body is 200 ppm for toluene, 300 ppm for methanol and 500 ppm for benzene and acetone [7]. Research into all three types of nonwoven fabrics was carried out at 200 ppm.

Table 3 shows average test results calculated from sensory measurements of the three nonwoven fabrics. Figures 2–5 illustrate changes in relative electrical resistance calculated by formula (4) in terms of the influence of different solvent vapours.
Sensory phenomena occurred in all three types of nonwoven fabrics. Comparison of the nonwoven fabrics presented in Table 3 shows that the nonwoven fabric manufactured by electrospinning a polymer solution containing nanotubes (97% PEO/3% MWCNT) has the higher sensitivity to vapour sensing of all the solvents (at 200 ppm concentration) then the nonwoven fabric constructed with carbon fibres carbonized from a nonwoven precursor (15% PAN/85% DMSO). This may result from the characteristics of polymer and carbon fibres. Fibre thickness may also be significant. Reducing fibre thickness increases specific surface area, which allows greater surface diffusion of solvent molecules to fibres. Furthermore, PEO/MWCNT-penetrating molecules are known to bring about further separation of nanotubes in percolation paths that were originally formed by nanotubes separating as a result of stretching.

Results from the nonwoven fabric made of 98% PLA 4060D/2% MWCNT show that sensor response to methanol vapours is relatively low (15%), while responses to benzene, acetone and toluene vapours reach 60%, 40% and 35%, respectively. Relative changes in electrical resistance \( R_{\text{rel}} \) coincide with the Flory–Huggins parameter \( \kappa_{\text{PLA/benzene}} < \kappa_{\text{PLA/acetone}} < \kappa_{\text{PLA/toluene}} < \kappa_{\text{PLA/methanol}} \).

Looked at from a technological viewpoint, this research demonstrates that all of the process parameters evaluated affect the properties of the manufactured products. Comparison of the response plots of produced nonwoven fabrics with chemical stimuli shows that the melt-blown nonwoven fabric made of polymer (98% PLA 4060D/2% MWCNT) respond differently than the nonwoven fabric made of polymer solution (97% PEO/3% MWCNT) and the carbon nonwoven fabric made of the precursor formed using a 15% PAN/85% DMSO solution.

Analysis has shown that differences in both the intensity and directivity of sensory properties are likely caused by the use of different technological parameters. This phenomenon may result from the structural arrangement of macromolecules and nanotubes affecting the formation of electroconductive tracks directed along the fibre axis. Too large a distance between one nanotube and another may cause a rapid increase in resistance. Finding the optimum draw ratio imposed during nonwoven fabric formation can lead to better positioning of them in the conductive network formed by well-oriented MWCNT. This implies that dispersed nanotubes can be combined or separated for such nano and submicron-composite structures.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Sensory factor (%)</th>
<th>Sensory factor (%)</th>
<th>Sensory factor (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>98% PLA 4060D/2% MWCNT</td>
<td>97% PEO/3% MWCNT</td>
<td>Carbon (precursor 15% PAN/85% DMSO)</td>
</tr>
<tr>
<td>Melt blowing</td>
<td>15</td>
<td>98</td>
<td>18</td>
</tr>
<tr>
<td>Electrospinning</td>
<td>40</td>
<td>67</td>
<td>19</td>
</tr>
<tr>
<td>Electrospinning + carbonization</td>
<td>35</td>
<td>106</td>
<td>14</td>
</tr>
<tr>
<td>Methanol</td>
<td>60</td>
<td>102</td>
<td>13</td>
</tr>
<tr>
<td>Acetone</td>
<td>40</td>
<td>67</td>
<td>19</td>
</tr>
<tr>
<td>Toluene</td>
<td>35</td>
<td>106</td>
<td>14</td>
</tr>
<tr>
<td>Benzene</td>
<td>60</td>
<td>102</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 3. Sensory test results for the presence of solvent vapours in the three nonwoven fabrics [7, 23]
Figure 2. Changes in relative electrical resistance of nonwoven fabrics subjected to methanol vapours at 200 ppm: a) 98% PLA 4060D/2% MWCNT, b) 97% PEO/3% MWCNT, c) carbon (precursor 15% PAN/85% DMSO)

Figure 3. Changes in relative electrical resistance of nonwoven fabrics subjected to acetone vapours at 200 ppm: a) 98% PLA 4060D/2% MWCNT, b) 97% PEO/3% MWCNT, c) carbon (precursor 15% PAN/85% DMSO)
Figure 4. Changes in relative electrical resistance of nonwoven fabrics subject to toluene vapours at 200 ppm: a) 98% PLA 4060D/2% MWCNT, b) 97% PEO/3% MWCNT, c) carbon (precursor 15% PAN/85% DMSO)

Figure 5. Changes in relative electrical resistance of nonwoven fabrics subject to benzene vapours at 200 ppm: a) 98% PLA 4060D/2% MWCNT, b) 97% PEO/3% MWCNT, c) carbon (precursor 15% PAN/85% DMSO)
4. Conclusions

This paper has shown the possibility of using nonwoven fabrics as sensors to detect organic vapours. The results show that electrospinning and melt blowing for nonwoven fabric formation comprising a composite system made of a polymer matrix reinforced with MWCNT (98% PLA 4060D/2% MWCNT, 97% PEO/3% MWCNT) can be used to produce nonwoven fabrics whose resistance changes under the influence of solvent vapours. This is equally true of submicron carbon fibres made from a precursor using a 15% PAN/85% DMSO solution. All three nonwoven fabrics revealed an electrical response on contact with methanol, acetone, benzene and toluene vapours at a concentration of 200 ppm. Samples in direct contact with vapours show high sensitivity and very short response times, no longer than 20 seconds after exposure.

Nonwoven sensors show good electrical conductivity and, in the presence of vapours, they change their resistance. Such sensors are very light as a result of their high porosity. This also provides them with high sensory capacity. They show high sensitivity for substances that are widely used in industry and/or are highly toxic. What is more, sensors produced in this way can be easily shaped and adapted to the surface on which they are to be placed.

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