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# Structural Parameters of Functional Membranes for Integration in Smart Wearable Materials

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**Abstract**

*Smart clothes can be described as textiles that change their behavior under some external factors (stimulants). The response of the smart cloth can be passive (just as a sensor) or active (where a combination of sensing and another reaction takes place). The materials involved in these textiles are crucial for many applications, especially for health related applications where the "wearables" can provide instantaneous monitoring and aid to people with certain disabilities. This work consists of two main parts: First it investigates the different materials used in smart clothing for monitoring the vital activities of the human body (e.g. the breathing rates) with an emphasis on piezoresistive structures as they work sensing elements for mechanical strains. Second this work presents the production of functional membrane samples based on synthesized pyrrolinone ester hydrazone dye with a preliminary investigation of their chemical and geometrical parameters, especially their sensitivity for monitoring the presence of ammonia to function as a smart textile based colorimetric chemosensor.*

**Key words:** *colorimetric chemosensor, electrospun membranes, functional dyes, piezoresistive sensors, smart clothing.*

## Introduction

The terms "smart" and "intelligent" textiles are commonly used interchangeably in the literature to refer to those textiles with the unique ability to change their behavior under specific conditions where the textile material senses and responds to its environmental stimulant [1]. This change in behaviour is connected with external stimuli (which might be mechanical, chemical, thermal, optical, magnetic, electric, etc.), and can be seen as a change in the colour, shape, orientation of the structure, or polarity. In the literature, "passive smart textiles" are used to refer to "functional" textiles. However, the functionality of these materials is added by means of the material, composition, construction and/or finishing [1]. The main difference between "smart" and "functional" textiles is that "functional textiles" do not need specific activation or stimulus as they are activated (functional) all the time.

Smart textiles can be categorized according to different points of view, such as: methods of manufacturing [2], applications [3] and stimulus that activates the change. In this work smart materials will be categorized according to the stimulant whether it is mechanical, chemical, thermal or optical. Electronic-textiles (e-textiles) form another class of clothes that are traditionally called smart textiles, although they might not necessarily react to external stimulants in the same way as materials categorized accord-

ing to the definition above. On the other hand, e-textiles integrate electronic components into the fibrous structure of textiles to obtain an added functionality that cannot be performed by the textile alone. This integration, historically, evolved under three stages, as shown in *Figure 1*, where firstly the textile structure was utilised as a platform that carries the different elements (e.g. power source, output display and external connecting wire). Later the textile became part of an electric circuit using conductive yarns to connect the other elements and replace the external wires. Finally there is a tremendous research that tries to achieve integration to deeper levels by having, for example, fibrous power sources (e.g. polymeric solar cells) as well as fibrous output devices and conductive fibres for the connection. The output devices in this third category might not necessarily work as traditional displays but it can indicate its output by performing a different function such as a change in colour. This last stage of integration represents its ultimate goal, where all the elements of the "circuits" are represented in fibrous form based on smart materials that react to external stimulants, such as the piezoelectric, thermochromic, shape memory and mechanophoric [1].

The application of smart textiles varies in many fields, and there is growing research interest in their application in the medical field. E-textiles are commonly used in rehabilitation with a continuous logging for physiological data,
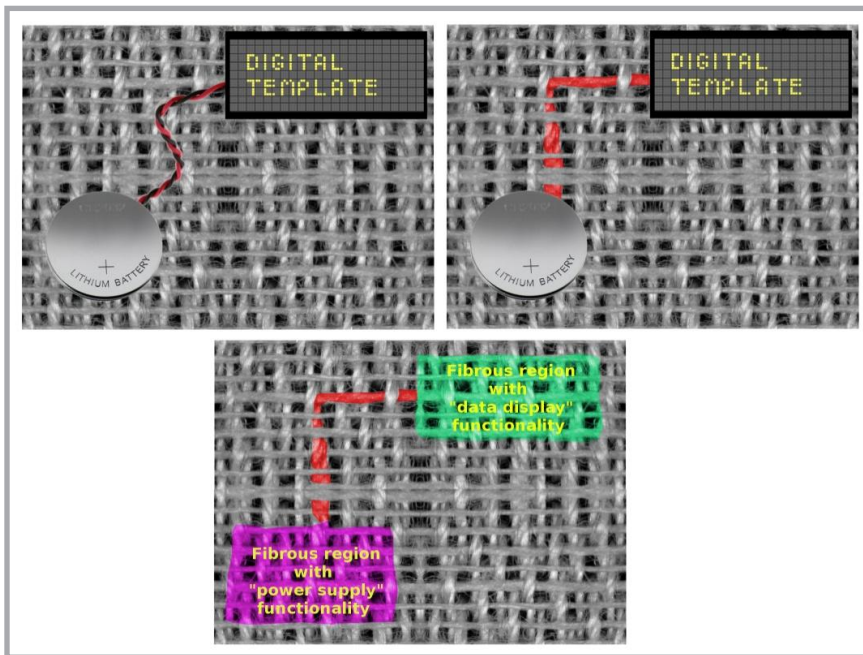
**Figure 1.** *Historical progress of integrating electronics within textile structures.*
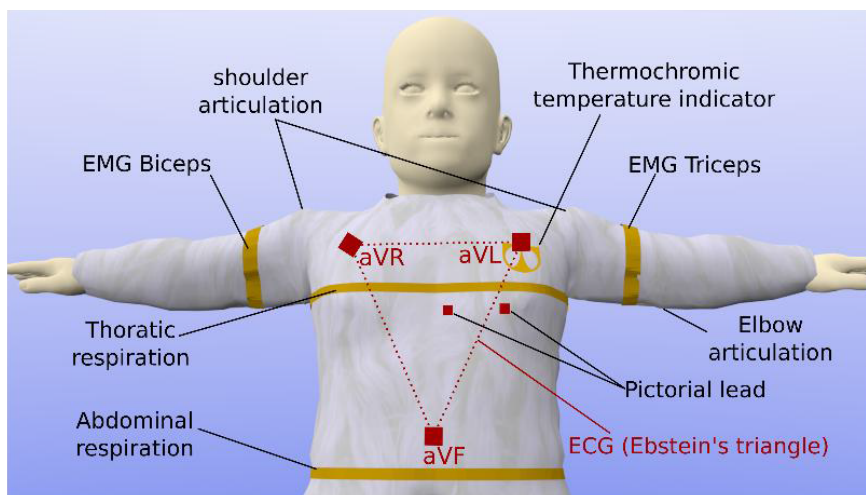


**Figure 2.** *Wearable unit with multiple sensing elements for continuous monitoring of physiological and movement data. The coloured sections also might include thermochromic indicators.*

where the sensors are integrated in the structure and are expected to monitor personal activity during daily life and ensuring the early detection of abnormal conditions. An example of such a wearable units is shown in *Figure 2*, with multiple embedded sensors for recording electrocardiographic (ECG), electromyographic (EMG), respiration and movement data, as well as with colour change indicators that consist of thermochromic structures.

### Smart textiles and breathing monitoring

Breathing monitoring is one of the important issues, especially for new-born babies, where some unexpected diseases can lead to sudden death; e.g. "sudden infant death syndrome" (SIDS). This syndrome usually affects children up to one year old and researchers still have no clear description of its reasons, although some external factors are considered as suspected causes for this sudden death (smoking of mother during pregnancy, baby sleeping on its abdomen, overheating of baby,... etc., although these causes are not confirmed as main reasons).

Many experimental procedures are implemented for breathing monitoring, and a major connection between all these methods is the use of sensors that react

to mechanical deformation. By use of piezoelectric and piezoresistive sensors for this application [4, 5], the recorded electrical signal demonstrates a change with the mechanical deformation during breathing (e.g. chest or abdominal expansion), which affects the cross-sectional area of the conductive element. A similar mechanism that affects transmitted light through optical fibres is also implemented in this application [6]. A third common category of materials used for this breathing monitoring includes capacitor based sensors, where mechanical deformation affects the capacitance of the structures used [7-9].

Piezoelectric sensors are made of special materials that are able to create an electrical signal under the application of force. This mechanical force (implied in the name by the Greek part *piezo*) affects the crystalline structure and its symmetry, where in the condition of no applied force, protons and electrons are mixed together and distributed in a symmetric manner in the atomic crystal, which leads to an overall neutral charge. On the other hand, the application of the force affects the symmetry of the structure, where the positive and negative charges start to prefer one side of the crystal over the other, leading to polarity in the crystal. Collecting the developed charges can be used as an indicator of mechanical change, and the signal collected can be used as a sensor for breathing. On the other hand, piezoresistive materials allow a change in electric resistance during the application of mechanical deformations. The application of a mechanical force results in a change in the material's cross-sectional area, which directly affects the resistivity of the material to the electric current. Since piezoresistive sensors will be sensitive to the thoracic circumference variations that occur during respiration [10], they are widely used in breathing monitoring due to the change in electrical resistance with each stretching and compressing cycle. Usually these sensors use conductive structures [5] or layers [4] to conduct an electric signal. Unlike piezoelectric materials, piezoresistive materials are not able to generate electric signals themselves, but an electric source has to be added to the measuring circuit.

Capacitor based breathing monitoring systems capitalize on the dependence of capacitance on the material of the capacitor's plates as well as on the distance between the plates, and the material fill-

ing this space. The application of a mechanical force results in a change in the distance between the capacitor's plates, hence a change in the capacitance within the electric circuit and a variation in the passing current.

The design of smart clothes with sensing components should consider many factors, for instance, since the fabric structure affects the sensitivity of measurement, it is more frequent to use elastic materials that are able to deform during mechanical loading (i.e. during breathing). Knitted fabrics [4, 5] as well as woven structures [8] are applicable for breathing monitoring; however, knitted structures show more conformity to deformations than woven fabrics [11]. Because the monitoring of breathing should be continuous for extended periods, the comfort and fit of the garment are very important issues that should be considered at the design stage. Also placing the sensors is crucial as they should fit at specific locations with maximum proximity to the chest and abdomen positions [7, 8, 11]. Experimental testing of these systems usually apply different loading scenarios to mimic the variation of breathing rates, rhythms and strength [4].

### Chemosensors

The colorimetric chemosensors have become of special interest in detecting the presence of ions and pH change as well as in the monitoring of toxic species, as they change their colour according to the existence of stimulants [12-18]. The growing priority of these materials is increasing due to their great need in health care, environmental conservation, and for human prosperity in the 21st century. Many techniques are used for detecting pH changes, such as microelectrodes [19], acid-base indicator titration, and potentiometric titration [20]. The most common problematic point in these techniques is their complication of processing or high cost of application. Thus colorimetric chemosensors provide a reliable alternative because of their simplicity in monitoring ions or pH change with the naked eyes without any complicated instruments. Moreover these sensors are also cheap and have high sensitivity levels [21-22], which have proved to be useful in many applications and prevented danger in various fields [23-24].

### Functional membranes

For better sensing elements, the sensor should be exposed to a high degree of
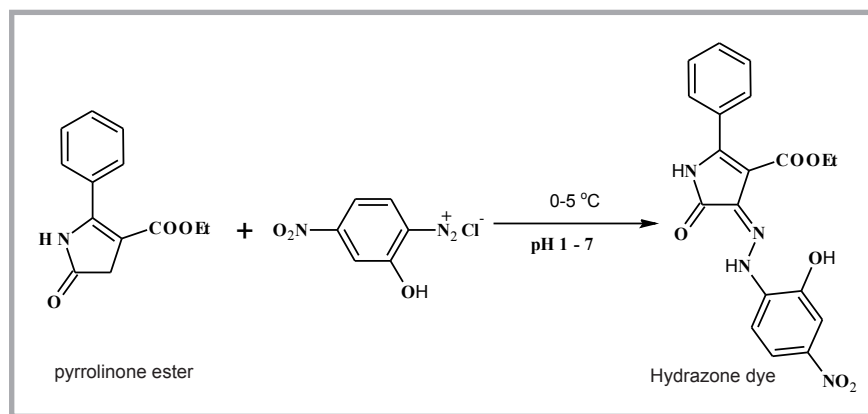


*Figure 3. Synthesis of hydrazone functional dye used.*

the stimulant applied, which is known in electrical circuit terminology as a high signal to noise ratio (SNR). This high degree of exposure can be achieved over a bigger surface of contact between the smart material (i.e. sensor) and external stimulant (e.g. temperature). Fortunately nano-scale structures allow a bigger surface to volume ratio when compared to micro or macro-scales of the same material. Polymeric solutions can be processed through electrospinning to form fibres that have diameters in the nanometer range (about 100 nm). In the electro-spinning process, the polymer solution is exposed to a high voltage electric field that creates competition between the internal forces within the solution (e.g. surface tension) and external electric forces (e.g. polar forces). Once the external forces exceed a certain limit, droplets of the polymer solution start to attenuate and fly to the counter electrode, allowing the solvent to evaporate during the flight time, and the solid fibres formed can be collected. The nanofibres produced usually have mean diameters below 500 nm and are deposited randomly on the collector to form a membrane. Mixing a functional compound with the polymer in its solution before solidification allows the production of functional membranes that adopt the characteristics of polymer and the functionality of the compound, as demonstrated in the following sections.

### ■ Experimental

A functional dye that showed sensitivity to the pH of its environment was synthesized and used in this study. The functional hydrazone dye was prepared via a procedure that depends on diazo-coupling on pyrrolinone ester intermediate.

### Synthesis of hydrazone dye

The synthesis of the hydrazone dye was based on a diazo-coupling reaction prepared by the formation of diazonium salt and coupling with pyrrolinone ester, as demonstrated in *Figure 3*. The synthesis procedure was reported in our previous work [25-26], and it can be briefly described here: it is started by dissolving 2-amino-5-nitrophenol (0.01 mol) in concentrated HCl (35%, 4 ml) and 30 ml of water through stirring. Then the mixture is cooled (external cooling) to a temperature between 0-5 °C, and 10 ml of 1M $NaNO_2$ is added dropwise for a period of 30 minutes. The mixture is stirred for another 40 minutes at 0-5 °C, and iodid-starch paper is used to check the excess of nitrous, which is destroyed by adding traces of sulphamic acid. When the reaction is completed, a solution of the diazonium compound is used for the next coupling reaction.

Pyrrolinone ester intermediate (0.01 mol) is dissolved in 100 ml of ethanol during reflux, then the mixture is externally cooled to 0 °C, and the solution of diazonium salt is added dropwise. The reaction mixture is stirred in the temperature range 0-5 °C for 4 hours, then gradually warmed to room temperature and left overnight under stirring. Precipitated dye was filtered off and washed with methanol and water. Final products were recrystallised, characterised by elemental analysis, mass spectrometry and melting points. These results we published earlier [25].

### Functional nano-membrane preparation

Hydrazone dye was used at different concentrations (0.5, 1, 1.5 and 2 wt%) as a colorant for polymer solutions, which were electrospun later to form
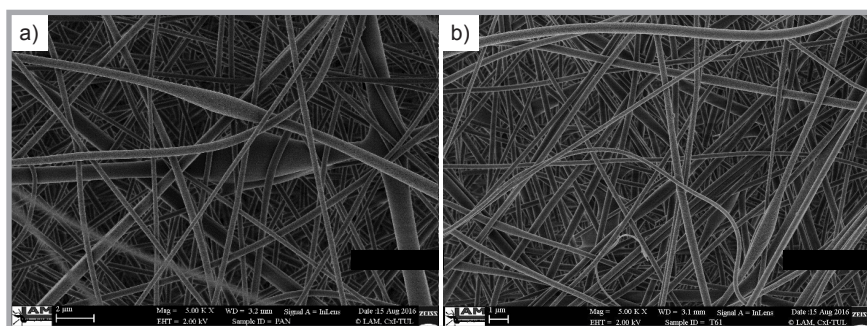
**Figure 4.** *SEM images for different membrane samples: a) Pure PAN sample, b) PAN + the functional dye.*
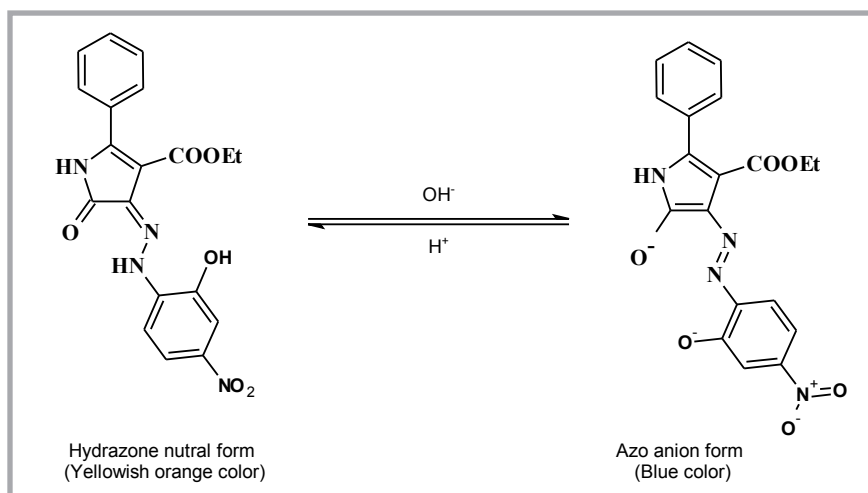


**Figure 5.** *Effect of pH change on the hydrazone dye structure in the solution.*

nano-fibre membranes. The polymer used in this study was polyacrylonitrile (PAN) with an average molecular weight of 150 kDa (Sigma Aldrich). The polymer was dissolved 10wt% with functional dye in N,N-dimethylformamide (DMF), and the solution underwentcontinuous stirring for a few hours, then left overnight with shaking.

The polymer solution was spun using a Nanospider electrospinning machine (Elmarco, NS IWS500U, Liberec, Czech Republic) with interchangeable electrode systems. The spinning distance was 133 mm with a substrate speed of 0.015-1.95 m/min, running at a voltage of 46.4 kV, and with an air flow of 80-170 m³/h. The spinning electrode width was 500 mm with an effective width for the nanofiber layer of 300 mm.

**Scanning electron microscopy (SEM)**

The surface topology of the samples and their elemental compositions were carried out using Carl Zeiss (MERLIN, ULTRA plus) scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). The membrane samples produced were mounted on an aluminum stub using carbon double-sided tape, and then sputter-coated with gold before use in the SEM.

**Ammonia detection**

The coloured nano-membranes prepared were used for monitoring the ammonia gas by immersing a small sample of the membrane in a series of ammonia solutions with different concentrations (2.5, 5, 10, 15, 20 & 25%), and studying the change of colour of the membrane.

The relative colour strength (K/S) and CIELAB coordinates (L*a*b*) of the dyed membranes were also measured using a Hunterlab's UltraScan PRO spectrophotometer (USA) under illuminant D65, 10° standard observer. The K/S values of the dyed membranes were measured by the light reflectance technique using the Kubelka-Munk *Equation (1)* [27], and the reflectance (R) of the dyed membrane was identified according to:

$$K / S = \frac{(1-R)^2}{2R} \qquad (1)$$

where,
R – decimal fraction of the reflection of the dyed fabric, K – absorption coefficient and S – scattering coefficient.

## ■ Results and discussion

The preparation of the functional dye used in this study was done according to our previous route reported [26], as shown in *Figure 4*. The synthetic procedure was based on two different steps: diazonium salt formation from amine, and coupling with pyrrolinone ester intermediate to form a red powder. The dye prepared was fully characterized using different spectroscopic analysis, which established the chemical structure and melting point of the dye prepared as being in agreement with the data previously reported.

The electrospinning process took place as described above and different membranes were produced. Pure PAN membrane without any additives was used as a control sample for comparison with the other functional membranes (PAN+ func-

**Table 1.** *Colour data and effect of ammonia concentration on colour parameters.*

| Sample | L* | a* | b* | C* | h | ΔE | k/s | λ_max |
|---|---|---|---|---|---|---|---|---|
| Control membrane Sample (2% dye) | 70.10 | 37.34 | 63.00 | 73.24 | 59.35 | – | 7.45 | 460 |
| 2.5% ammonia | 43.42 | 36.56 | 42.01 | 55.69 | 48.97 | 31.68 | 18.20 | 465 |
| 5% ammonia | 34.04 | 30.34 | 25.53 | 39.65 | 40.07 | 43.96 | 18.28 | 460 |
| 10% ammonia | 33.99 | 28.46 | 25.25 | 38.05 | 41.58 | 44.56 | 18.20 | 465 |
| 15% ammonia | 34.25 | 29.48 | 25.32 | 38.86 | 40.66 | 44.05 | 17.95 | 465 |
| 20% ammonia | 29.11 | 23.83 | 17.57 | 29.61 | 36.39 | 51.17 | 18.73 | 460 |
| 25% ammonia | 26.34 | 19.93 | 12.26 | 23.40 | 31.59 | 55.46 | 19,90 | 465 |

tional dye) that were produced at different concentrations of the dye. *Figure 5* shows micrographs of the samples at a similar magnification level, and by analysing the SEM images of these samples the fibre diameter distribution was calculated. A Matlab software algorithm was developed to analyse the membrane's pictures, and the fibre diameter was computed and found to be 150-250 nm for the different samples. The topology of the fibres demonstrate smooth surfaces, which implies compatibility and good mixing between the dye and polymer within the solution. Investigating the surface of the functional membranes at their macroscopic level demonstrated an even distribution of the colors with a uniform appearance. The dye also did not show any leakage from the membrane during the washing and wet handling of the samples.

The sensitivity of the functional membranes to their medium's pH was tested using different concentrations of ammonia solutions. The control sample (i.e. pure PAN) did not show any change in colour after exposure to the ammonia, while the functional membrane samples demonstrated a clear shift in colour from yellowish orange to a dark brown colour, as shown in *Figure 6*, and as can be quantitatively seen in *Table 1*. This change can be attributed to the presence of hydrazone dye, which is characterised by the formation of an anion azo form in alkaline medium. This anion form was easily formed due to the effect of the nitro groups, which exist in conjunction with the hydrazone, as shown in *Figure 5*.

In the case of a pH change using different ammonia concentrations, the colour of the membrane was significantly changed to a deep brown shade. The change in colour was also observed to be reversible, as samples that were exposed to ammonia and then treated in an acidic medium (or washed in a neutral medium) returned back to their original yellowish color, as shown in *Figure 6*.

Colour data was also studied for the colored membrane with 2% hydrazone dye, which was immersed in solutions of different ammonia concentration (2.5, 5, 10, 15, 20 and 25 %). The data summarised in *Table 1* shows a big change in the colour of the original samples due to the effect of ammonia. The value of L*, a* and b*
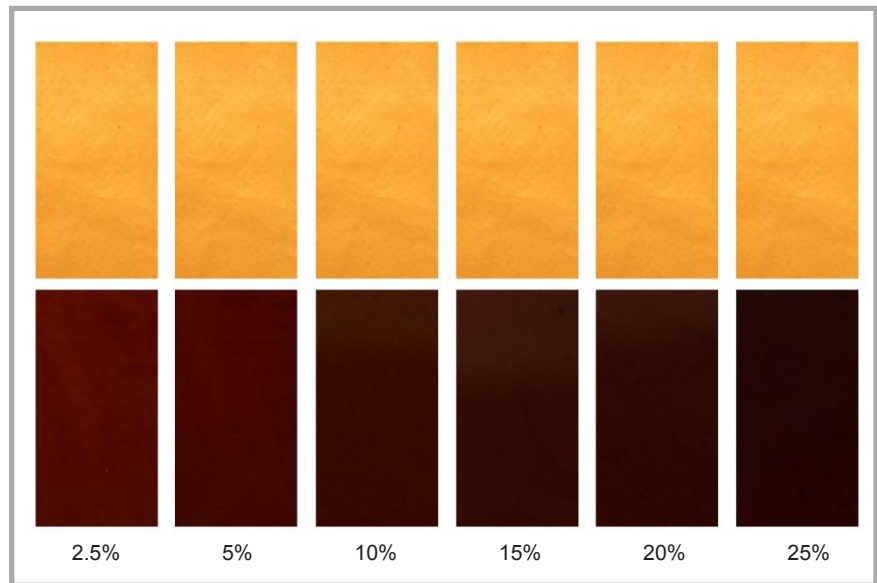


**Figure 6.** *Effect of ammonia solution on the change in membrane colour. The upper row in the figure represents the control sample (without ammonia) and the lower represents the sample's color after immersion in solutions with the concentrations indicated.*

decreased rapidly by increasing the ammonia concentration, which was proven by the depth of the colour, from yellowish orange to a dark brown colour. The shift in colour can be quantitatively identified by the value ΔE listed in *Table 1*, which shows an increased shift from the standard sample (without ammonia) as the ammonia concentration increases.

### ■ Conslusions

A brief survey on smart materials and their potential applications in clothing for recording the vital activities of the body was introduced in this work. Peizoresistive and chemosensor materials were discussed as common materials implemented in breathing and pH monitoring, respectively. Moreover a functional dye was used to introduce pH sensing characteristics to nano-fibrous membranes of polyacrylonitrile. The preliminary results for the sensitivity of functional membranes to ammonia were reported in this work, and the membranes produced have potential application in visual detection of hazardous gases in industrial environments by integrating them in work clothing or air filters. A future work to extend this research is to carry out a further quantitative study on the kinetics of colour change, as well as on the use of modified structures of functional dye with different polymeric materials to meet the performance requirements of other environmental applications.

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