WEARABLE MICRO-FLUIDIC pH SWEAT SENSING DEVICE BASED ON COLORIMETRIC IMAGING TECHNIQUES

Vincenzo F. Curto[1], Cormac Fay[1], Shirley Coyle[1], Robert Byrne[1], Dermot Diamond[1], Fernando Benito-Lopez[1*]

[1]*CLARITY: Centre for Sensor Web Technologies, National Centre for Sensor Research, Dublin City University, Dublin 9, IRELAND*

ABSTRACT

In this paper a wearable electronic-free micro-fluidic device for the continuous monitoring of pH in sweat during exercise is described. The sensing capability is based on ionogels, ionic liquid hydrogels, containing pH sensitive dyes capable of reporting pH activity in the range from 3 to 10. Previously, we reported a flexible micro-fluidic barcode capable of measuring the pH of sweat in real time [1]. Here we have improved the device in terms of wearability, physical robustness, chemistry of the sensor and its optical response by using a mobile phone for data collection and a more accurate algorithm for colorimetric image analysis.

KEYWORDS: Wearable, HSV Colour Space, Colorimetric detection, sweat pH

INTRODUCTION

Sweat is a body fluid naturally produced during physical exercise and emotional stress, and it is essentially a filtrate of blood plasma containing many substances such as sodium, chloride, and lactate [2]. Through the analysis of its composition it is possible to obtain useful information regarding the physiological condition of the body, providing information about the health and well-being of the individual, especially during sport activities.

Autonomous wearable sensors to monitor sport activities should consist of reliable systems capable of monitoring physical and/or bio-chemical conditions in real time. Important requirements such as low cost, flexibility, long term stability and minimal discomfort to the wearer are essential characteristics that these sensors need to satisfy. Here we preset a wearable micro-fluidic device based on ionogels to monitor pH of sweat. Accurate pH values can be obtained by colorimetric image analysis of the colour changes in the sensing area.

EXPERIMENTAL

The flexible and wearable micro-fluidic platform consists of four independent reservoirs made on poly(methyl methacrylate) (PMMA) and pressure-sensitive adhesive (PSA). A base layer of PMMA 125 μm thick followed by one layer of PSA (80 μm) and another of PMMA (125 μm) were cut using the CO_2 laser forming four rectangular reservoirs of 2 mm × 6 mm, in which the ionogels were polymerised. The ionogel is a solid, flexible and easily patterned material generated by UV-photopolymerisation from the tetrabutylphosponium dicyanamide (dca) ionic liquid and a hydrogel polymer (*N*-isopropylacrylamide and *N,N'*- methylene-bis(acrylamide)), Figure 1-left. After polymerisation four different pH sensitive dyes are incorporated in the polymer matrix by drop casting. Due to ion-pair interactions between the various pH indicators and the ionic liquid that forms the ionogel structure, there is no leaching of pH dyes, enabling long analysis times without compromising the sensitivity of the system [3]. After polymerisation and incorporation of the dyes the system was sealed by a lid consisting of two layers, PSA (80 μm) and PMMA (50 μm), glued to the previous three layers (Figure 1-right).
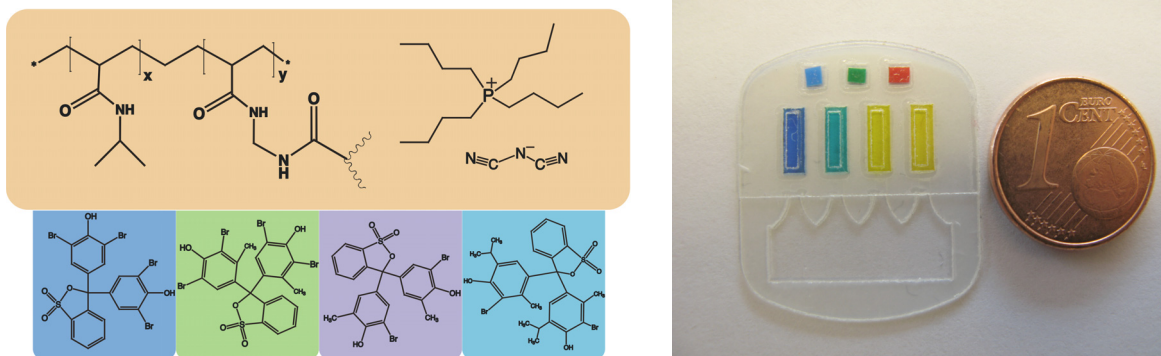

Figure 1: (left) Chemical structures of the hydrogel and the tetra-butyl phosphonium dca ionic liquid (top) and the four chemical structures of the pH sensitive dyes (bottom). From left to right: Bromophenyl Blue (BPB), Bromocresol Green (BCG), Bromocresol Purple (BCP) and Bromothymol Blue (BTB). (right) Wearable micro-fluidic device.

Bench experiments were carried out using artificial sweat (according to ISO 3160-2). Each ionogel was exposed to a solution of known pH from 3 to 10 with a step of 0.5 for a period of time of five minutes and after drying the sensing area a digital picture was taken. After transferring the images in the computer hard driver, the analysis in colour change of the ionogel barcode was performed by means of the OpenCV computer vision library.

Firstly, a copy of the original image was created and then converted into the HSV colour space. Next, a configuration of noise reduction techniques were applied including gaussian blurring, median and mean filtering in order to aid the segmentation stage. After this, a connected component analysis process was applied to the Hue (H) channel of the image which resulted in neighboring pixels of similar colour being grouped together into separate image regions *i.e.* each pixel was assigned a grey level (0-255) relating to a single connected region. Following this, the regions were ranked according to their area size and presented visually to a user where seed points were selected relating to the 4 gels and 3 reference patches; the order of selection was used to identify each gel and patch. A binary erosion process followed for each region in order to remove possible boundary pixels. Finally, each identified region was applied to the original image where the average Hue value of the respective regions was taken to represent the colour state of the gels and patches at that time. Once plotted, a sigmoidal fit of the data points for each gel was achieved using Boltzmann's regression model.

RESULTS AND DISCUSSION

With the aim of improving the wearability of the device, there were eliminated sharp corner and the circular configuration reduces the discomfort for the wearer (Figure 1-right). In figure 2 is shown the micro-fluidic device placed on the arm of an athlete through a transparent and flexible plaster to achieve a better contact between the sensing areas and the skin. pH changes in sweat during exercise can be easily monitored by harvesting digital pictures of the ionogel barcodes over time.

Figure 2: Wearable micro-fluidic device located on the arm using a high adhesive transparent sweat patch. The camera of a mobile is using to take pictures of the sensing area of the device. The mobile application will be used for real time pH monitoring of sweat during exercise.

Improvements of the long term stability was gained avoiding the delamination of swollen ionogel from the micro-fluidic device during measurements. It is prevented by covalent immobilisation of the ionogel on the surface of the poly(methyl methacrylate) substrate. The PMMA is first surface activated using water-vapor plasma, ensuring a good hydroxylation of the surface [4]. Then, an alkenyl terminated self-assembled monolayer (SAM) is deposited using the silane-coupling agent 7-octenyltrichlorosylane, see the scheme in Figure 3-left. Figure 3-right shows a fully swollen, drop shaped ionogel covalently bonded to PMMA after storage in ethanol for 5 hours.
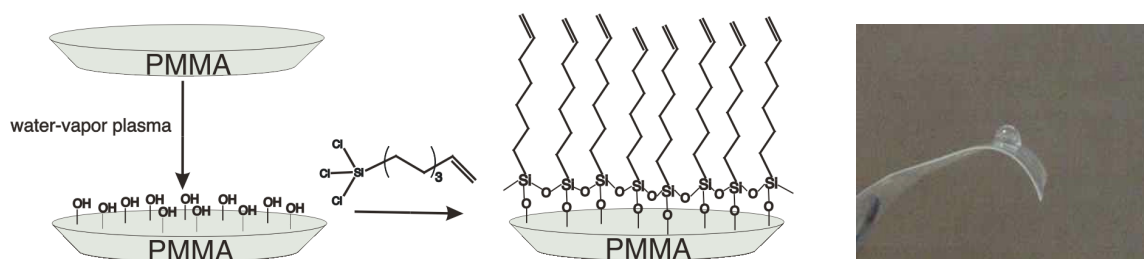

Figure 3: (left)Schematic representation of the PMMA chemical surface modification. (right) Picture of the swollen grafted ionogel on PMMA.

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The main achievement of this work compared with the system previously reported [1] is the colorimetric techniques for the estimation of pH. The images are processed using a combination of segmentation, labeling and colour space conversion algorithms programmed using the OpenCV computer vision library (see experimental paragraph). Figure 4 depicts calibration response curves of each respective pH dye from pH 3 to pH 10 when analysed using the Hue component of the HSV colour space. Each pH dye shows excellent correlation to a sigmoidal regression model i.e. with an R^2 value of greater than 0.995.
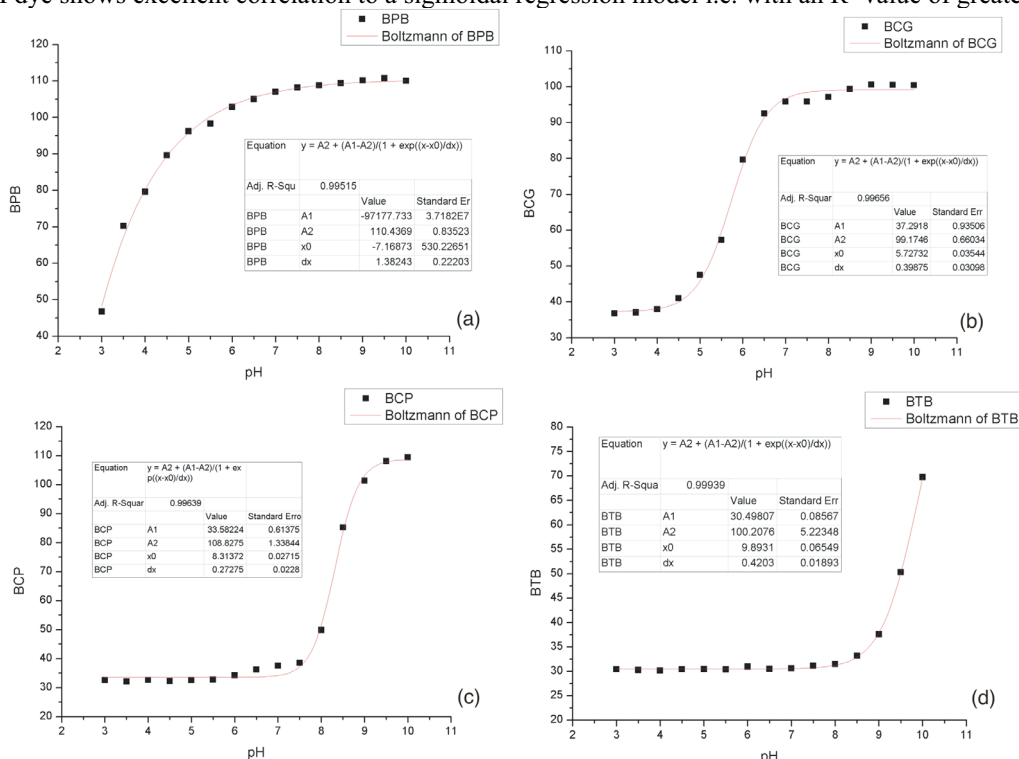

Figure 4: Calibration curves of the camera's response to colorimetric changes of pH dyes:(a)BPB, (b)BCG, (c)BCP, (d)BTB.

CONCLUSION

In this work we have presented significant improvements in a electronic-free micro-fluidic device capable of measuring the pH of sweat, potentially during a period of physical exercise. The micro-fluidic device was developed using low cost and flexible materials, integrating novel ionogel and pH sensitive dyes as sensing material. Robustness and wearability of the platform were improved by covalent attaching of the ionogel on PMMA and given a more ergonomic shape, respectively. Improvements in the colorimetric detection technique was gained through the implementation of an algorithm using the Hue value of the HSV color space, obtaining calibration curves with a R^2 value grater than 0.995 by a Boltzmann's regression model.

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CONTACT

*F. Benito-Lopez, tel: +353-1-7007603; fernando.lopez@dcu.ie