Printed epoxy-based hydrogel chemical sensors

Paul Calvert, Prabir Patra and Deepak Duggal; U. Mass Dartmouth; N. Dartmouth MA 02747 USA

Abstract

Most hydrogel actuators and sensors are made via acrylate polymerizations. Because these chain reactions are inhibited by oxygen, it is difficult to print thin films or dots with good control. Epoxy curing chemistry is much less sensitive to experimental conditions. We have previously shown that hydrogels formed from reaction between water-soluble amines and epoxides can be readily printed. If the gel is filled with conducting carbon at a level close to the percolation threshold, the resistance changes as water is taken up or removed from the gel. In particular, a pH decrease results in ionization of amine groups and drives swelling of the gel. By incorporating an enzyme, such as glucose oxidase, that releases hydrogen ions when its substrate is present, a resistance change can be used to measure glucose concentrations. These gels also respond to stress with a change in resistance. By making the gel the anode or cathode of an electrolytic cell, they can also be formed as actuators that expand or contract as the pH changes locally.

Epoxy chemistry has been little explored for gels. It is very versatile and could be used to make a wide range of gel composites with one or more phases, varying water contents, varying functional groups and a range of electrical conductivity.

1. Introduction

We are interested in printing chemical sensors onto textiles for applications in liquid sensing, including real time analysis of sweat. Our biomimetic concept is that combinations of multiple small printed sensors may be used to give information about a system even though any one sensor shows sensitivity to a variety of chemicals and is history dependent and non-linear. This is by analogy to the sensing systems of insects where similar deficiencies are balanced by arrays of sensors with overlapping sensitivities.

We are focussing on resistive sensors because of the simplicity of measuring resistance and envisage sensor arrays on fabric connected by printed metal lines to a single sensing unit, which is tuned to detect changes in resistance. After an exploration of printed conducting polymer sensors, we have selected a matrix system of carbon-filled epoxy hydrogels. The carbon volume fraction is at the percolation threshold such that the gel is somewhat conducting. Changes in volume as the gel expands or contracts in response to the concentration of analyte will result in decrease or increase in resistance as the spacing between carbon particles changes.

The hydrogels chosen are based on water-soluble diepoxides and polyfunctional amines [1]. The epoxy-amine reaction is not sensitive to oxygen as is the polymerization of the normal unsaturated monomers used for hydrogels, such as acrylates. This allows us to produce reproducible structures in thin films.

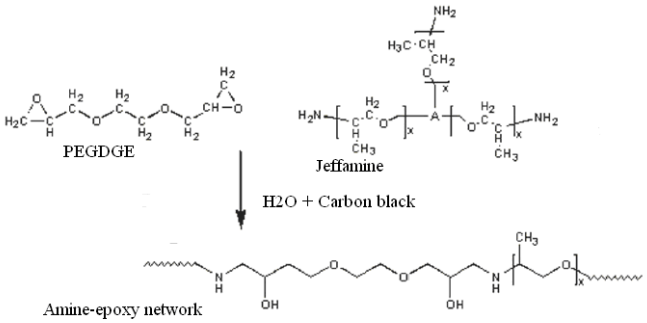
In this paper we describe the sensing of glucose using epoxy hydrogels containing bound, entrapped glucose oxidase enzyme. In the presence of glucose the enzymatic oxidation of glucose produces acid and the acid would be expected to result in ionization of the amine functionalized gel and so cause it to swell. This principle could be applied to a wide range of enzymes and substrates as long as a product affects the gel volume.

2. Experimental

2.1 Gel preparation

Gels based on water-soluble aliphatic polyamines and polyetheramines reacted with aqueous solutions of polyethyleneglycol diglycidylether (PEGDGE) were prepared. Carbon black 10 wt% was added to make the gels conductive close to the percolation threshold. Amine-cured epoxy networks are mostly formed from the epoxide-amine addition reaction which is shown in figure 1 below. The $-CH_3$ group closest to the NH_2 group in the T-Jeffamine will produce a steric interference to slow the reaction rate of the secondary amines as compared to the unreacted primary amines. Hence most of the remaining amine hydrogens on the final network will be secondary amines.

Figure 1: Gel formation



By varying the ratio of amine to epoxide, the gel has varying residual amine concentrations which give rise to strong swelling in acidic solutions where the amine becomes ionized as $-NH_3^+$. Molar ratio of epoxide in PEGDGE to amine hydrogens in Jeffamine was adjusted to make different gels which are shown in the table 1 below.

Jeffamine T-403 has six reactive amine hydrogens and PEGDGE has two epoxy groups.

	PEGDGE	JEFFAMINE	WATER	Ratio of reactive Amine: Epoxy	Carbon black
Gel 1	1.5mmol	1.26mmol	1.4g	2.52	0.28g
Gel 2	1.7mmol	0.6mmol	1.2g	1.05	0.24g
Gel 3	1.7mmol	2.09 mmol	1.84g	6.79	0.37g
Gel 4	2.6mmol	2.2mmol	2.4g	2.53	0.48g
Gel 5	1.6mmol	1.4mmol	1.48g	2.62	0.30g
Gel 6	1.6mmol	2.2mmol	1.84g	4.12	0.37g

Table 1 Gel compositions with different epoxy-amine ratios

2.2 Determination of equilibrium water contents

The equilibrium water contents (EWCs) of gels was defined as the ratio of water weight to total gel weight.

The cylindrical gels were put in a container having distilled water for 12 hours. They were then taken out of the container and weighed after removing the surface water using a filter paper. Dehydration of the gel was achieved in the vacuum chamber at room temperature. The water content of the above described gels was calculated and is shown below in table. Gel no. 3 and 6 were too sticky due to high amine content or lower cross linking density and so were not investigated further.

	Gel 1	Gel 2	Gel 4	Gel 5
Water content%	62.5	48.6	64.4	66.1

Table 2: Equilibrium water content of the gels.

3. RESULTS AND DISCUSSION

3.1 Glucose sensor

Hydrogels were formed with and without immobilized glucose oxidase and were put on a printed circuit board coupled across copper conductive lines.

Glucose oxidase is an enzyme that catalyses β-D-glucose to gluconic acid and hydrogen peroxide, using molecular oxygen as the electron acceptor. The gluconic acid produced during the reaction lowers the pH of the solution and a decrease in swelling behavior was expected. This change in swelling is quantified in terms of resistance measurement occurring due to the change in carbon-carbon particle distance.

The gel was allowed to swell in distilled water and the increase in resistance follows the swelling as shown in figure 2. Gel with bound enzyme swelled less strongly than gel with attached enzyme. Figure 3 shows the effect of submerging these gels in dilute glucose solution. The enzyme-bound gel shows a steady decrease in resistance while the untreated gel does not change. Unexpectedly, the resistance change on glucose treatment is a decrease rather than the increase that was expected to result from acid release. Separate experiments do show that the gel swells and the resistance does increase on immersion in acid.

One of the potential applications of this sensor is to measure glucose level in blood or sweat. Because sweat

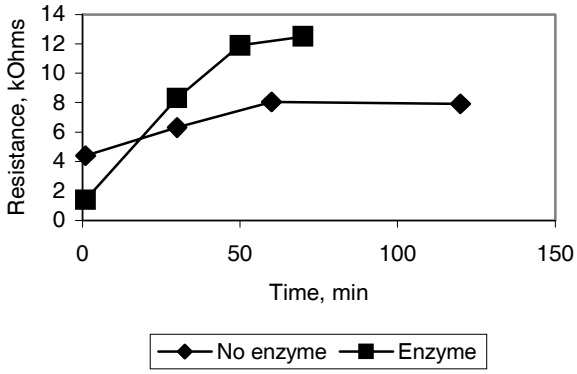


Figure 2: Gel resistance on swelling in water

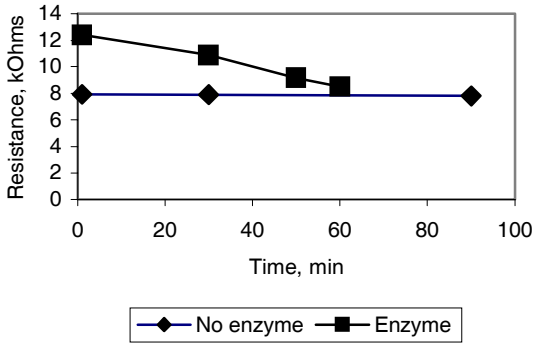


Figure 3: Response of gel, with and without enzyme to glucose in solution in water.

contains electrolytes like sodium chloride and sodium bicarbonate, the tests were repeated in salt solution. Gels were immersed in a bath containing glucose (5mmol) and NaCl (0.11mol) dissolved in distilled water. The results of swelling gels in saline are shown in figure 4. It is not obvious why the enzyme-bound gel shows little swelling. After equilibration, the gels are moved into glucose-containing saline solutions and the resistance decrease in the enzyme-treated gel as shown in figures 5 and 6.

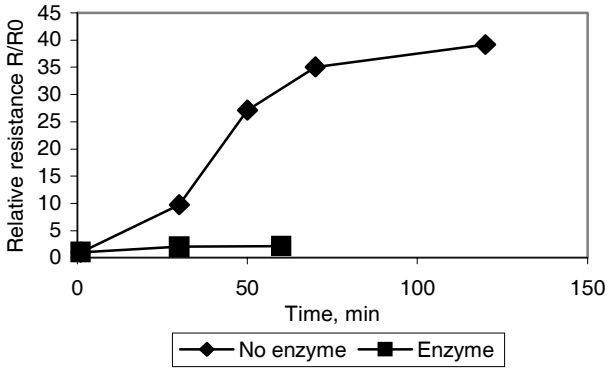


Figure 4: Swelling response of gel in saline (NaCl) solution

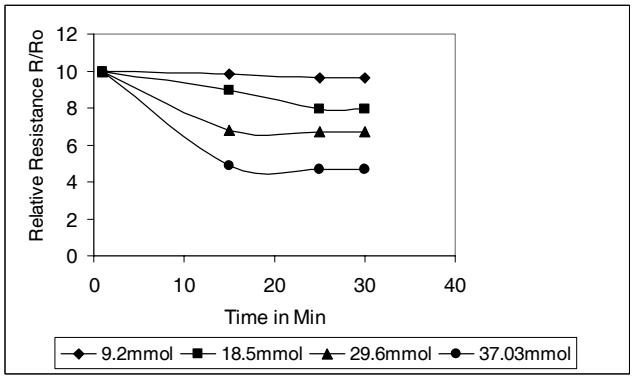


Figure 5: Response to glucose solutions of different concentrations

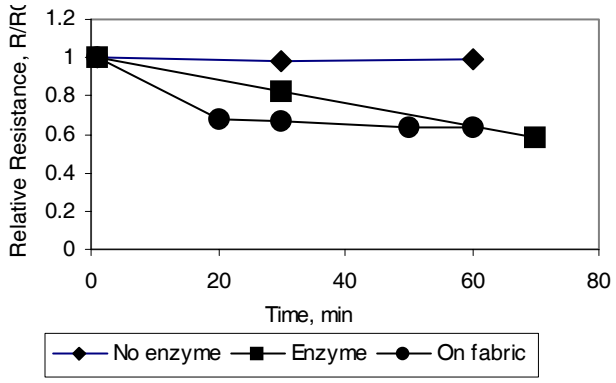


Figure 6: Response of gels to glucose in saline solution

3.2 Wearable glucose sensor

The enzyme-bound gel was deposited on a piece of fabric and was allowed to cure for 2 hours. Two Silver conductive lines were drawn on the fabric so as to make desired electrical connections between the gel and Keithley 196 multimeter. A schematic of the hydrogel based chemical sensor is shown in figure 7 below.

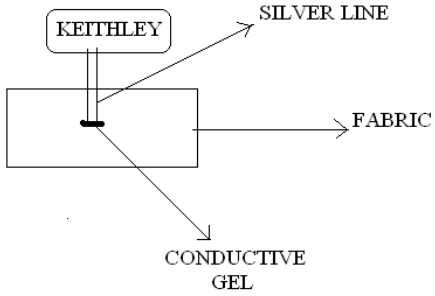


Figure 7: Hydrogel based wearable glucose sensor

The response of this textile-based sensor to glucose is also shown in figure 6. The response is similar to the gel on a printed circuit board, but faster.

4. CONCLUSIONS

We have shown that printed conducting hydrogel sensors can be used to detect glucose at the 5mM level in water and in saline. To the best of our knowledge this does represent a new family of sensors that can be readily use on soft materials such as fabric.

5. ACKNOWLEDGEMENT

We would like to thank the National Textile center for supporting this research.

6. REFERENCES

1. Y. Yoshioka and P. Calvert, "Epoxy-based electroactive polymer gels", *Experimental Mechanics* 42,404-408, (2002).

Biography

Paul Calvert is department chair and Prabir Patra is research fellow and Deepak Duggal is a graduate student in the Department of Materials and Textiles at University of Massachusetts Dartmouth.