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Modelling and Analysis of pH Responsive Hydrogels for the Development of Biomimetic Photo-Actuating Structures

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ABSTRACT

Photo-actuating structures inspired by the chemical sensing and signal transmission observed in sun-tracking leaves have recently been proposed by Dicker *et al.* The proposed light tracking structures are complex, multicomponent material systems, principally composed of a reversible photoacid or base, combined with a pH responsive hydrogel actuator. New modelling and characterization approaches for pH responsive hydrogels are presented in order to facilitate the development of the proposed structures. The model employs Donnan equilibrium for the prediction of hydrogel swelling in systems where the pH change is a variable resulting from the equilibrium interaction of all free and fixed (hydrogel) species. The model allows for the fast analysis of a variety of combinations of material parameters, allowing for the design space for the proposed photo-actuating structures to be quickly established. In addition, experimental examination of the swelling of a polyether-based polyurethane and poly(acrylic acid) interpenetrating network hydrogel is presented. The experiment involves simultaneously performing a titration of the hydrogel, and undertaking digital image correlation (DIC) to determine the hydrogel's state of swelling. DIC allows for the recording of the hydrogel's state of swelling with previously unattained levels of resolution. Experimental results provide both model material properties, and a means for model validation.

INTRODUCTION

Photo-actuating structures inspired by the chemical sensing and signal transmission observed in sun-tracking leaves [1,2] have recently been proposed by Dicker *et al.* [3,4] (Figure 1). These structures are designed to actuate such that a desired orientation be maintained between the structure and a light source. Within the structure sensing occurs from the light exposure of a reversible photoacid [5] or base [6], whilst actuation results from the swelling of a pH responsive hydrogel. The two components are separated, with a control signal being sent from one location to the other by the diffusion of ions, and the resulting pH change. By carefully designing the system geometry such that light exposure is a function of the device's orientation (through angled shades), and by linking through solution appropriate sensing and actuating elements, it is anticipated that precise and stable control can be imparted to the structure. It is believed that such a structure will share the properties of robustness and efficiency often found in Nature, and find application in the tracking of photovoltaic panels for increased energy yield.

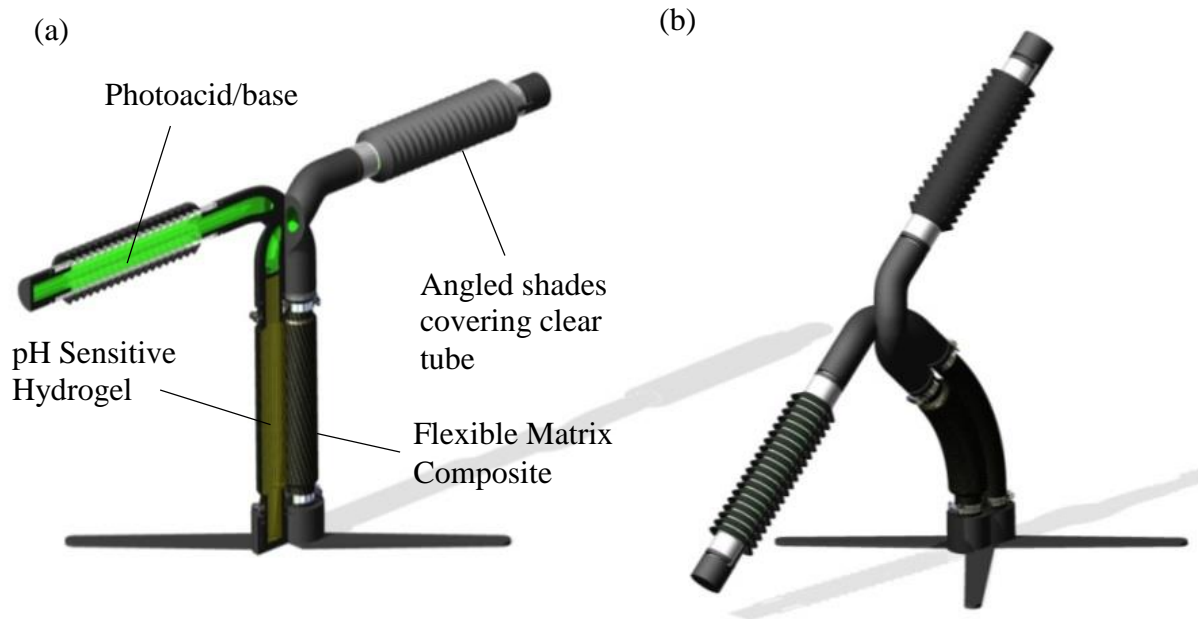


Figure 1 A concept for a simple twin vein analogue of a sun tracking leaf (a) Un-actuated device with quarter section removed to reveal internal structure. (b) Full device in actuated state showing orientation towards a light source. The device geometry acts to link the sensing element (photoacid/base) with the actuation element (pH sensitive Hydrogel). The shading of the tubes containing the photoacid/base, and the nature of the chemical response results in the generation of a control signal that is both proportion to the error in orientation, and dependent upon both the history and rate of this signal (photo reaction). This results in a closed-loop chemical control system, akin to an electronic proportional-integral-derivative (PID) controller commonly used in engineering systems [1].

THEORY AND EXPERIMENT

Despite the large body of work on the modelling and prediction of pH induced hydrogel swelling, to the best of the author's knowledge, all of the published equilibrium methods are based on the assumption that the concentration of hydrogen ions (pH) in the solution domain be known and fixed. This is a reasonable assumption for most systems, where the composition of this domain can be controlled by the addition of further acids or bases. This consideration allows the composition to be held constant as a boundary condition in the analysis, and allows for both the protonation state of the hydrogel, and the unknown free species concentrations in the hydrogel domain to be solved with either a finite element method, or an analytical expression based upon Donnan equilibrium.

However, this assumption of known hydrogen ion concentration in the external domain is no longer valid for the systems proposed in this work. In these systems, the pH is changed through a rather modest shift in the dissociation constant of a low solubility photoacid or base, as such, the resulting pH in the external domain is a function of the equilibrium interaction of all free and fixed (hydrogel) species in both domains. To account for this, a homogenized solution approach is taken to predict the final composition of the combined system. Donnan equilibrium,

considering conservation of mass and electro-neutrality [7] is then iteratively calculated to arrive at a final compositions for each domain, and the resulting degree of swelling for the actuated hydrogel. The model description and computation flow is detailed in Figure 2.

This method relies on three assumptions, the first is that a homogenized approach can predict the final protonation state of the hydrogel. The second is that Donnan equilibrium holds for the system being studied, and finally that the material behavior is linear elastic. As a result, the predictions yielded are unlikely to be of high accuracy, but provide an indication of the feasibility of the photoacid-hydrogel system proposed, whilst also providing indications of trends for optimization of hydrogel actuation, which can later be examined by experiments.

The photoacid investigated with the developed model is the protonated merocyanine developed by Shi *et al.* [5]. Upon irradiation with visible light (419 nm and 570 nm) this molecule changes from a weak acid with $pK_a = 7.8$, to a strong acid with $pK_a = 2.5$. This reversible process has a long lived excited state compared to other photoacids, having a half-life of approximately 70 seconds. Although the shift in pK_a is modest, it does span the expected transition pK_a of a large number of hydrogels, those based on carboxylic acid, with pK_a of approximately 4.3.

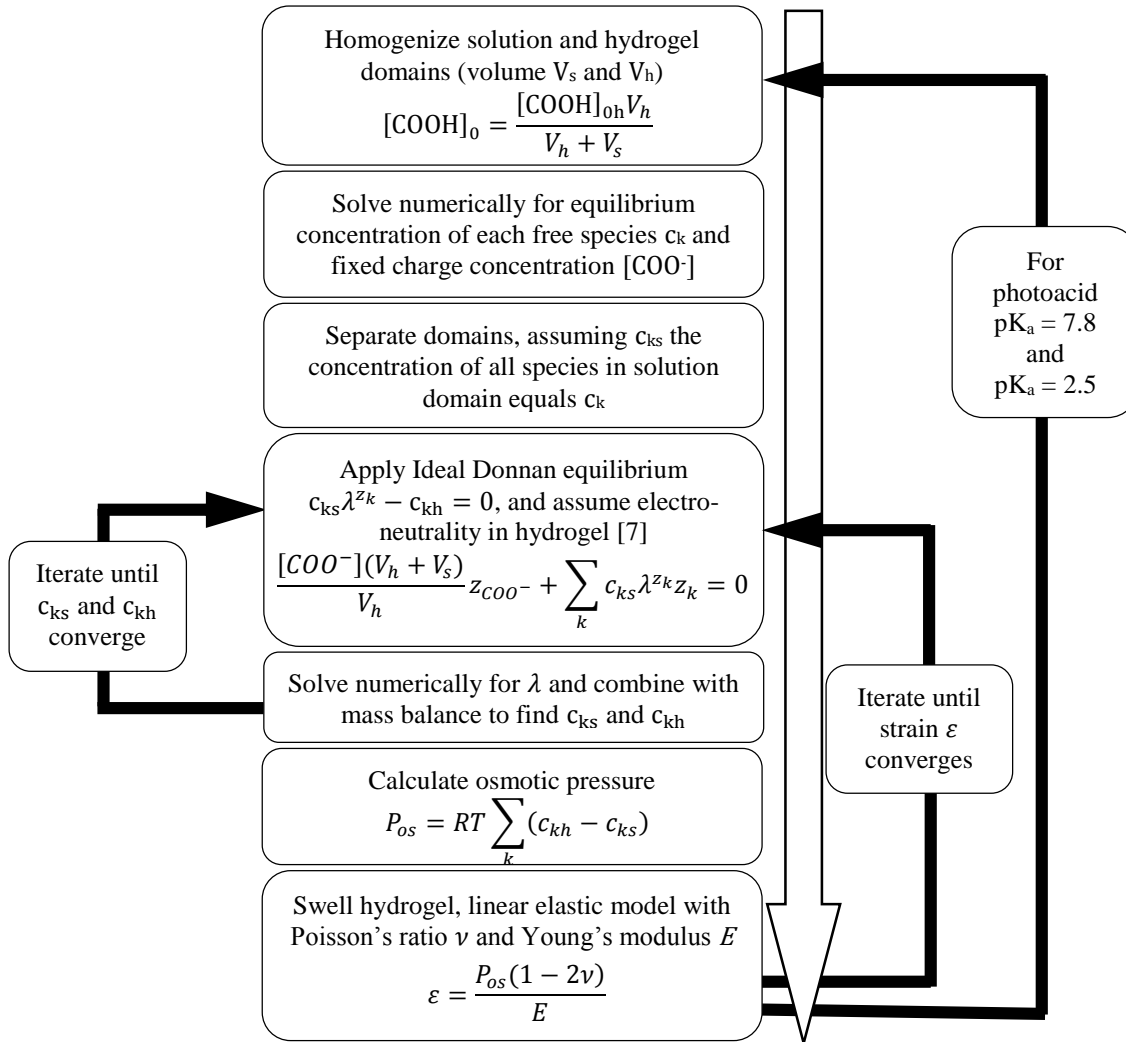


Figure 2 Model description, in the form of a computational flow diagram.

This work also examines experimental hydrogel swelling resulting from limited shifts in pH around the hydrogel's transition pK_a . The investigation involves simultaneously performing a titration of the hydrogel (measuring degree of protonation), whilst visually determining the hydrogel's state of swelling with digital image correlation (DIC). This low cost experimental setup (Figure 3) allows for the separation of the chemical and mechanical contributions to actuation performance, and the determination of the model inputs of hydrogel pK_a and fixed charge density $[COOH]_0$.

DIC is an optical non-contact method for measuring full field displacements and strains. The DIC code used in this experiment is the open source Matlab code of Jones [8,9]. The code is modified for automated, near real-time operation during the experiment. In this manner, the experimental control software (Matlab), is able to check if both the pH and, critically the swelling, has converged before progressing with the next titration injection, ensuring equilibrium results are obtained. The images are recorded in greyscale, and taken with a low specification camera (Canon 450D), fitted with a 100 mm macro lens, limiting geometric distortions. A similar setup has been employed to examine the Poisson's ratio of soft materials by Pritchard *et al.* [10].

The hydrogel examined is the polyether-based polyurethane and poly(acrylic acid) interpenetrating network hydrogel developed by Naficy *et al.* [11]. The clear films (0.15 mm x 45 mm x 10 mm), are covered in a random speckle pattern with a marker pen for the purposes of the DIC, and sat on a white acrylic sample bed to ensure contrast with the markings (Figure 3a).

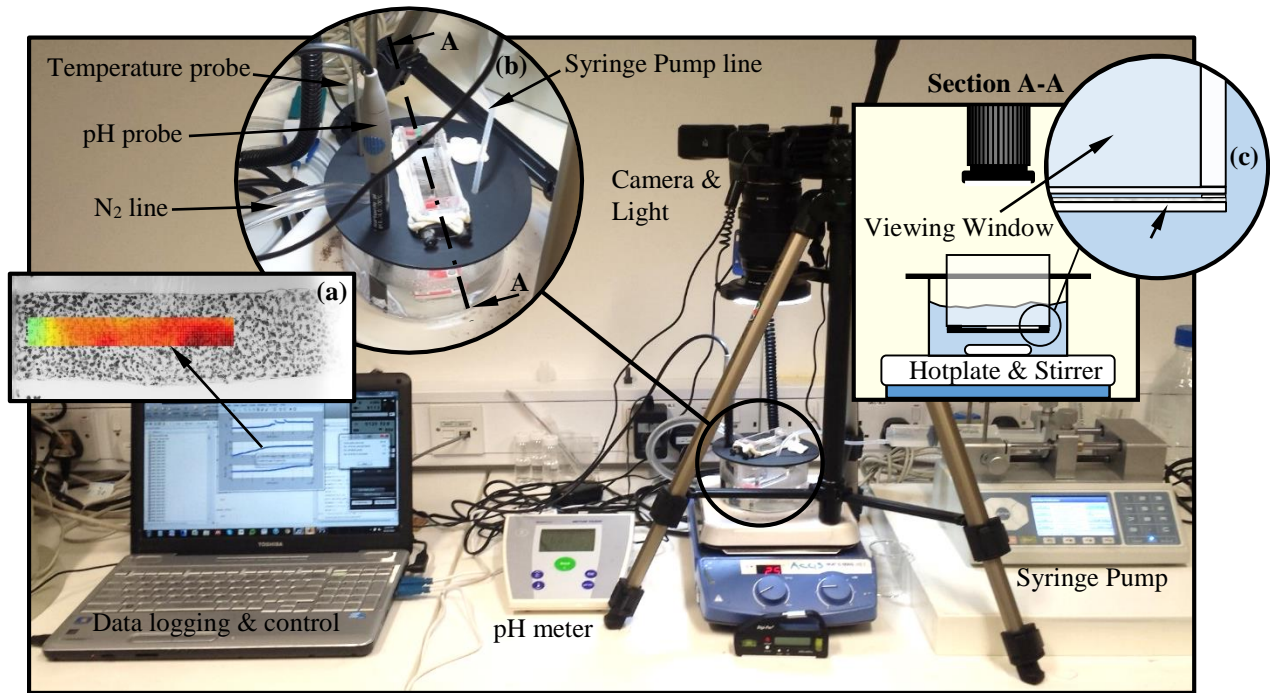


Figure 3 Experimental setup, highlighting the instruments involved in the simultaneous titration and DIC. (a) Camera image with overlay of DIC calculated equivalent strain, calculated as $\epsilon_{eqv} = \sqrt{[\epsilon_x^2 + \epsilon_y^2 - \epsilon_x\epsilon_y + 3\epsilon_{xy}^2]}$ note the effect of end clamping on the strain at the left of the image, strain in this image spans from ~10% to 18%. (b) Titration cell. (Section A-A) acrylic viewing window and sample holder, cuts through solution surface distortions. (c) Detail of sample location, note solution gap above sample.

A selection of results from both the characterization experiment and parametric analysis employing the developed model are included as Figure 4 and Figure 5.

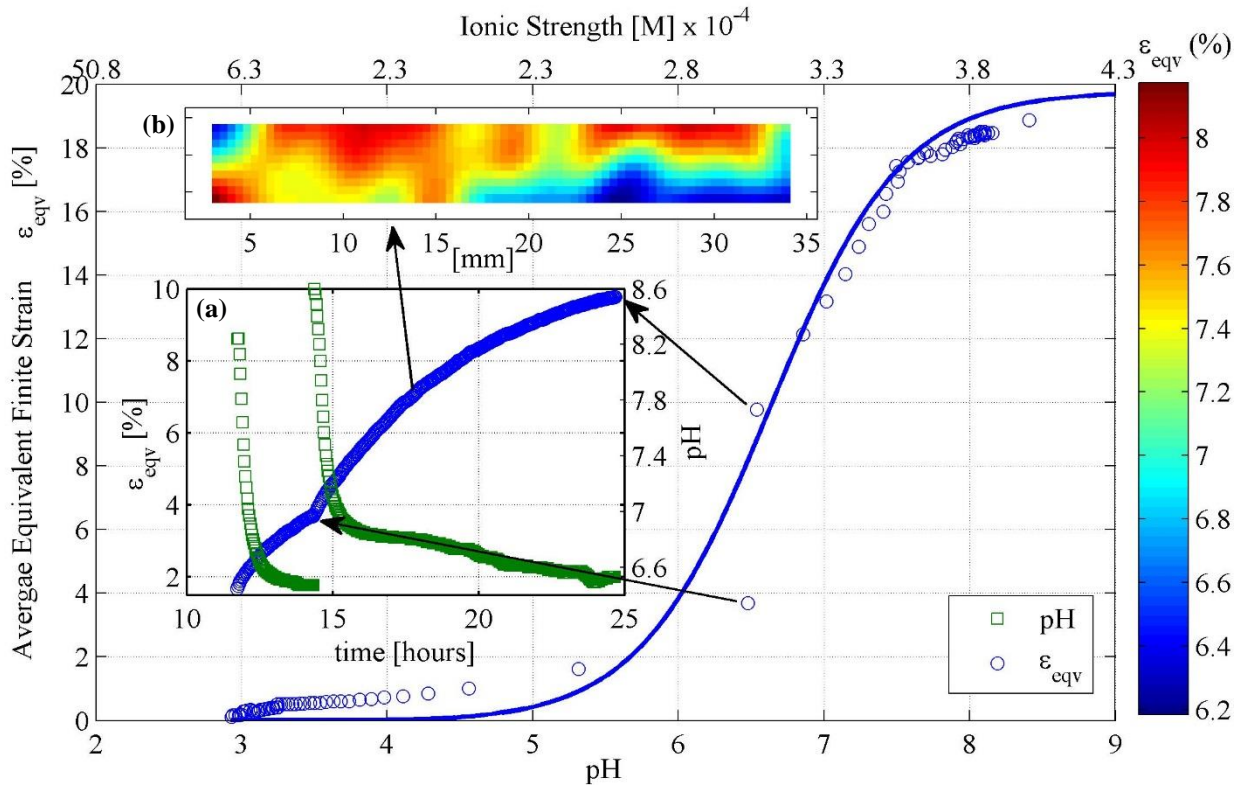


Figure 4 Characterization result showing the three layers of detail that underlie the equilibrium swelling results (a) Swelling kinetics, shows convergence of both strain and pH, and (b) Equivalent strain field in sample region of interest. The solid line is the model prediction, although a close correlation is observed, it is found that the result is sensitive to Poisson's ratio, a value not measured. It is set to $\nu=0.45$ in this analysis.

CONCLUSIONS

The effectiveness of the developed model to assess the suitability of a characterized hydrogel (Figure 4, circle markers) for a proposed photoacid system is demonstrated in Figure 5. Significant further work is required to test the validity of the developed model for a wider range of hydrogel systems. However, preliminary results suggest it is more than suitable for the intended use as a design aid for hydrogel systems (Figure 4, solid line model prediction).

The introduction of near real time DIC as a characterization tool unlocks the ability to examine hydrogel swelling with previously unobtainable resolution, both in terms of equilibrium and kinetic data. The low cost of the setup enables the technique to be accessible to all researchers of actuating soft material. Furthermore, although full field strain data is of little interest when undertaking free swelling of isotropic materials, it can provide critical insights into material performance and properties, for example Poisson's ratio, for systems with a applied load, or material anisotropy. Future work includes control experiments to ensure the DIC speckle pattern is not affecting the system, a quantification of experimental error, and the characterization of repeated hydrogel swelling.

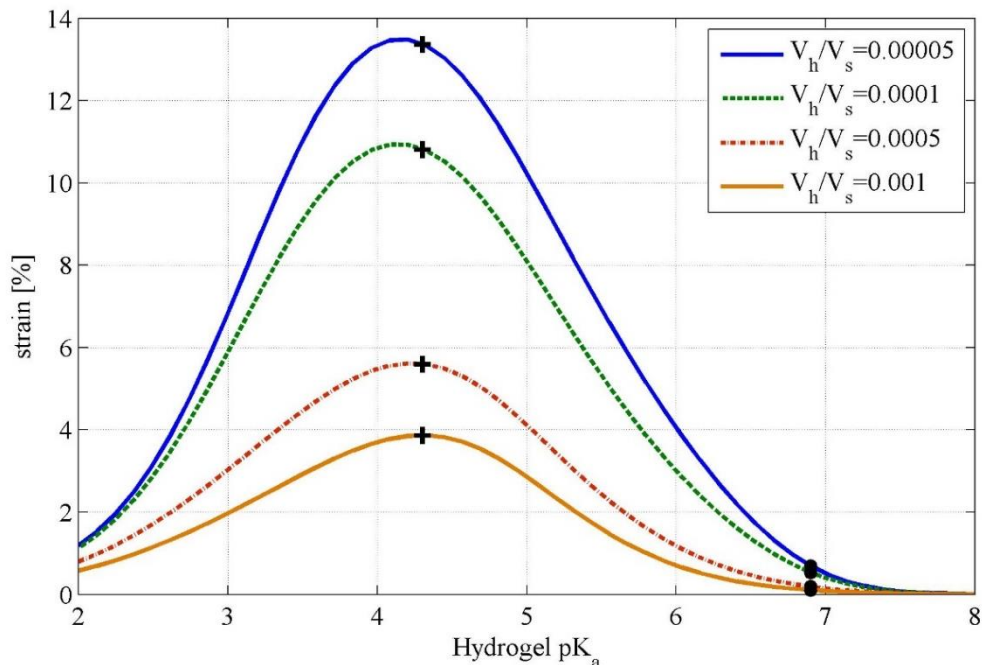


Figure 5 An example of the type of parametric analysis that the model quickly enables. Here the effect of a change in the hydrogels transition point (pK_a), for photoacid systems with a variety of initial hydrogel volume (V_h) to solution volume (V_s) ratios is examined. Even for small volume ratios that limit the buffering effect of the hydrogel on the low solubility photoacid, the system is only viable for a limited range of hydrogel pK_a . Although this range includes the expected pK_a value for carboxylic acid based gels (~ 4.3 cross markers), the value found in the characterization experiment was 6.9. At this value, the system is not viable, as indicated by the circle markers.

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REFERENCES

- [1] A. Schwartz and D. Koller, *Plant Physiol.* **80**, 778 (1986).
- [2] F.J.F. Fisher, D.L. Ehret, and J. Hollingdale, *Botany* **65**, 2109 (1987).
- [3] M. Dicker, J.M. Rossiter, I.P. Bond, and P.M. Weaver, *Bioinspir. Biomim.* **9**, 036015 (2014).
- [4] M. Dicker, P.M. Weaver, J.M. Rossiter, and I.P. Bond, *Smart Mat. Struct.* **23**, 095021 (2014).
- [5] Z. Shi, P. Peng, D. Strohecker, and Y. Liao, *J. Am. Chem. Soc.* **133**, 14699 (2011).
- [6] M. Irie, *J. Am. Chem. Soc.* **105**, 2078 (1983).
- [7] J. Ricka and T. Tanaka, *Macromolecules* **17**, 2916 (1984).
- [8] E.M.C. Jones, (2013). <http://www.mathworks.com/matlabcentral/fileexchange/43073-improved-digital-image-correlation--dic->
- [9] E.M.C. Jones, M.N. Silberstein, S.R. White, and N.R. Sottos, *Exp. Mech.* **54**, 971 (2014).
- [10] R.H. Pritchard, P. Lava, D. Debruyne, and E.M. Terentjev, *Soft Matter* **9**, 6037 (2013).
- [11] S. Naficy, G.M. Spinks, and G.G. Wallace, *ACS Appl. Mater. Interfaces* **6**, 4109 (2014).