SELF-ACTUATING FIBRE REINFORCED EPOXY COMPOSITES

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SUMMARY

The aim of this study has been to develop glass fibre reinforced hydrogel electro-active polymers. In particular, a study has been made of the role and function of distributed fibrous electrodes to optimise the magnitude and rate of self-actuation. As a part of this work a characterisation study on the epoxy hydrogel has also been carried out.

Keywords: Composites, active, hydrogels

BACKGROUND

Electroactive polymers (EAPs) cover several different material types that have a mechanical response to various stimuli. A recent review by Bar-Cohen and Zhang [1] discussed the different materials and stimuli associated with various EAPs. From the wide range of materials available, this study has chosen to focus on a type of ionic EAP, an epoxy based hydrogel.

Previous work on epoxy based hydrogels by Yoshioka and Calvert [2] has demonstrated useful actuation potential and mechanical performance of these electroactive polymers as they undergo a swelling/deswelling resulting from ion diffusion under the action of changes in surrounding pH or applied potential [3]. The load-bearing performance and geometric constraint of epoxy based hydrogels (to maximise actuation potential) has been further investigated via the addition of E-glass fibre reinforcement [4] to create a composite material. The constraining effect can be best explained via Figure 1, where a hydrogel sample is seen to expand approximately isotropically, whereas the addition of a woven glass fibre cloth reinforcement imparts a high degree of anisotropy, in this case a major expansion in the through-thickness direction, the glass fibre reinforcement restricting expansion in the plane.

In this previous study the EAP volume change was generated through immersion in an acidic (low pH) solution, however, in an actuating application the required change of pH could be generated locally via a potential difference across attached electrodes. The electroactivity of epoxy hydrogels relies on ionic diffusion and thereby their response rate is dependant on the ion diffusion path [5]. Typical hydrogels tend to respond slowly to any stimulus as the mechanism relies on diffusion of ions, either H+ or OH-, through the bulk polymer. A potential method to accelerate this diffusion process is to embed distributed electrodes within the material to enable localised generation of ions throughout the volume of the bulk polymer. To this end, carbon fibre (CF) tows (12k Toray) were investigated as embedded electrodes, as such an arrangement offers the additional advantage of providing further structural reinforcement. Previous work in the

field has examined the embedment of metallic electrodes within hydrogels [6] and the use of deposited platinum on active PAN fibres [7].

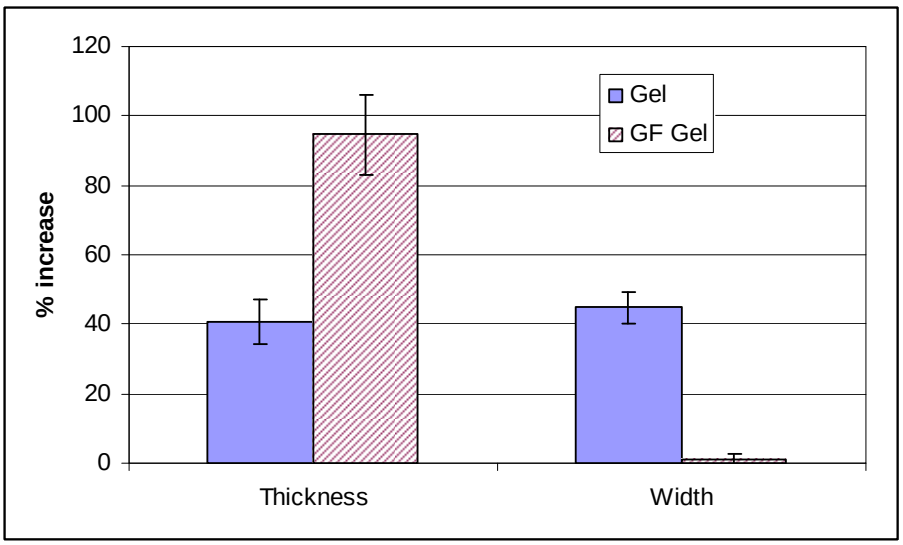

Figure 1 - Effect of pH3 solution on the unreinforced and glass fibre reinforced gel in terms of samples thickness and width.

SPECIMEN PREPARATION

The epoxy hydrogel system chosen was similar to that used by Yoshioka and Calvert [2], based on ethylene glycol diglycidyl ether (EGDGE) and an amine of trimethylolpropane tris[poly(propylene glycol), amine terminated] ether. A 2:1 mix ratio of amine to epoxide groups was utilised as this ratio has been previously shown to offer the largest actuation potential. However, following initial trials the hydrogel formula was altered to overcome manufacturing difficulties. The main changes being the removal of sucrose as an additive, a reduction in the proportion of fumed silica and cure of the material at ambient temperature. Thus, the final formulation used for all subsequent studies was as follows:

Table 1 - Epoxy hydrogel formula

Component	Amount (wt%)
EGDGE	18%
Amine	30%
Distilled water	45%
Fumed silica	7%

For hydrogel only specimens the formula was mixed prior to casting in silicone moulds and allowed to cure overnight. For the fibre reinforced hydrogel specimens, two layers of eight harness woven satin E-glass cloth (296 gsm CS Interglas) of 0.4 mm thickness were used as the reinforcement. In addition, for each specimen, three carbon fibre tows (12k, Toray) were placed in between two layers of the glass cloth prior to impregnation with the epoxy hydrogel resin, Figure 2.

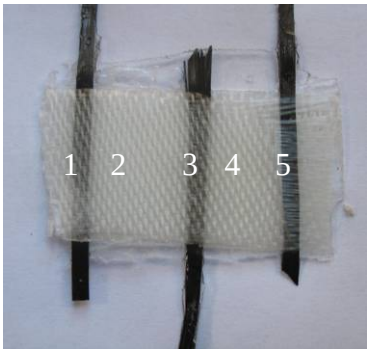

Figure 2 - Embedded carbon fibre tows within glass fibre reinforced epoxy hydrogel composite.

EQUILIBRIUM WATER CONTENT

An important parameter in the characterisation of hydrogels is the equilibrium water content (EWC), a measure of the water within the system under equilibrium conditions. One group of six hydrogel samples were made according to the formulation shown in Table 1, with another group of six samples made without the addition of fumed silica. Following sample preparation they were immersed in distilled water at ambient temperature for three days to ensure complete saturation. These samples were then weighed prior to being vacuum dried at ambient temperature for a further three days before being reweighed. The results are shown in Table 2, from which it can be seen that the presence of the fumed silica marginally reduces the water uptake.

Table 2 - Equilibrium Water Content for epoxy hydrogel.

	Average % EWC	Std dev
Without Silica	78.8	0.228
With Silica	75.1	0.033

If the values in Table 2 are compared to those obtained by Yoshioka and Calvert [2] it can be noted that the hydrogel formulation used in this study has a higher water content due to the removal of sucrose and a reduced fumed silica content. This should facilitate a greater actuation potential as more H^+ ions can be transferred in and out of the polymer molecular structure.

DMA TEST METHOD

Due to the gel-like nature of the epoxy material it was decided that Dynamic Mechanical Analysis (DMA) was the most appropriate method to characterise the mechanical properties of the hydrogel. DMA testing applies an oscillating load to a sample of material and the resulting displacement of the sample is measured, this can be carried out at a range of frequencies and temperatures depending on the information required. This testing gives an indicative measurement of the innate mechanical properties of the material.

Effect of silica addition

Fumed silica (SiO_2) is a particulate additive which can effect the rheological and mechanical properties of polymers. Yoshioka and Calvert [2] sought an increase in viscosity that the silica imparts for their specific manufacturing process. In the study discussed herein, the epoxy hydrogel samples are cast rather than deposited, thus this viscosity increase is not required. Furthermore, since the silica was known to influence the physical and mechanical properties of the host polymer it was decided to assess this effect using DMA testing.

Two groups of hydrogel samples (4.5 mm x 5.5 mm x 3 mm) were manufactured according to the formulation shown in Table 1, with and without the fumed silica. These samples were tested in the DMA using a frequency range of 10-100Hz with a static load of -2N and a dynamic load of 0.1N at ambient temperature. The results from this testing are shown in Figure 3, from which it can be seen that the addition of the fumed silica approximately doubles the measured dynamic Young's modulus. From a mechanical properties perspective, the silica is a welcome addition to the hydrogel. These measurements were made in the as-manufactured condition prior to exposure of the hydrogel to an aqueous solution where it is expected that the modulus will decrease as the gel absorbs water. A higher weight fraction of silica was also investigated; however, this led to the epoxy resin being too viscous for practical use.

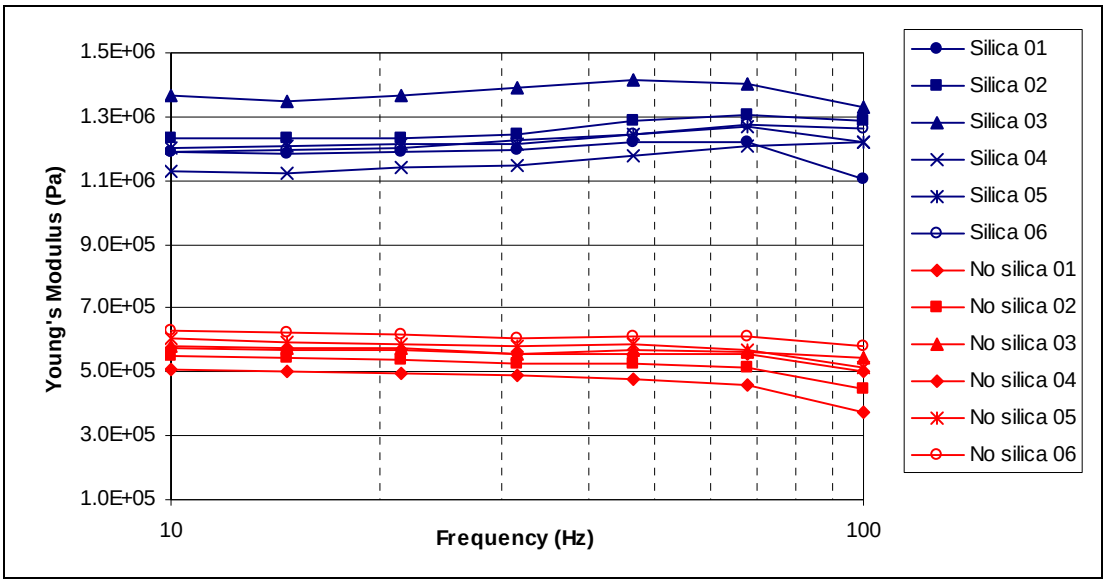

Figure 3 - Results from DMA testing for epoxy hydrogel with and without silica addition.

Effects of Environmental Conditions

As mentioned in the previous section, hydrogels are expected to exhibit a change in stiffness as their water (H+ ion) content is altered. To quantify this level of change a set of specimens were manufactured and exposed to different pH solutions as follows:

- as manufactured
- distilled water saturated (pH8)

- 0.01M NaCl aqueous saturated (pH8)
- pH12 saturated and
- pH2 saturated.

'Saturated' means that the samples were conditioned at ambient temperature for 12 hours in the respective solutions. 0.01M NaCl aqueous solution is the electrolyte that will be used in the electrical activation testing of the materials; pH12 and pH2 are the likely extremes of the pH scale that the material will see during electrical activation at +10V and -10V respectively.

Samples of 4.5 mm x 5.5 mm x 3 mm were again manufactured according to the formulation in Table 1. These samples were tested in the DMA using a frequency range of 1-100Hz with a static load of -2N and a dynamic load of 0.1N at ambient temperature. Figure 4 shows the results over the entire frequency range for one sample sequentially exposed to the different conditions. It can be seen that there is an almost 50% reduction in Young's modulus for all cases in comparison with the as-manufactured condition, with slight variation between the saturated solution conditions.

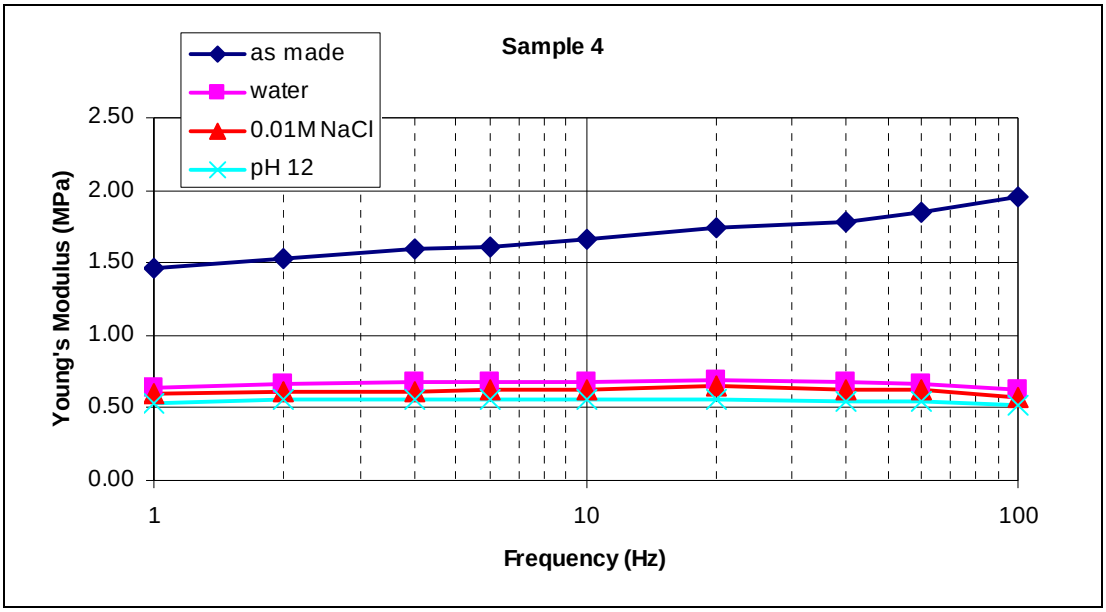

Figure 4 - Results for a sample exposed to different solutions.

It is not possible to average the results over the entire frequency range due to some strain rate dependency of the epoxy, therefore, Table 3 shows the average modulus achieved at a frequency of 10Hz for all the samples. This confirms the substantial change in modulus from as-manufactured to a saturated condition and only small variation between the different saturated states.

Table 3 - Average modulus results of the epoxy hydrogel at 10Hz.

	As manu-factured	water saturated	0.01M NaCl saturated	pH2 saturated	pH12 saturated
Average Young's Modulus (MPa)	1.86	0.78	0.71	0.58	0.57
Std dev	0.258	0.058	0.047	0.062	0.040

The average dynamic Young's modulus of the epoxy hydrogel is approximately 0.6 MPa which compares well with the values of 0.47 MPa in basic conditions and 0.57 MPa in acidic conditions, obtained by Yoshioka and Calvert [2]. The difference is attributed to the different epoxy formulation and test methodology used i.e. axial tensile versus DMA testing.

Some of the small discrepancy between the results from the different saturated states is attributed to specimen dimensional changes. The specimens expand under acidic (pH2) conditions and contract under basic (pH12) conditions as the H+ ions are transported in and out of the hydrogel. Load level is a controlling parameter in the DMA testing. Thus, the stress and strain measured are a function of specimen dimensions, which can effect the derived dynamic modulus values. Table 4 gives an indication of the volumetric change that the specimens undergo during exposure to different pH solutions. The large difference in volume between the pH2 and pH12 conditions is the effect that is exploited for actuation.

Table 4 - Volume change compared to as-manufactured condition.

Immersion Solution	water saturated	0.01M NaCl saturated	pH2 saturated	pH12 saturated
Average volume change (%)	141%	173%	754%	109%
Std dev	16.6	15.3	6.8	1.5

ELECTRODE CONFIGURATION

Initial Actuation Testing

Figure 5 shows a schematic assembly of a self-actuating fibre reinforced composite based on an epoxy hydrogel matrix, indicating the orientation in which displacement and force have been measured. To establish the feasibility of using CF tows as distributed electrodes, a specimen was placed within a 0.01M NaCl aqueous electrolyte solution (pH8) and 5V applied as shown in Figure 5. The sample thickness was measured at five locations (shown in Figure 2) before and after application of the potential difference, Figure 6. It can be seen that an anode (positive voltage) generates a local expansion and a cathode generates a local contraction of the hydrogel. The areas between the electrodes are largely unaffected. This demonstrates the potential for using embedded CF tows as distributed electrodes in creating a self-actuating composite.

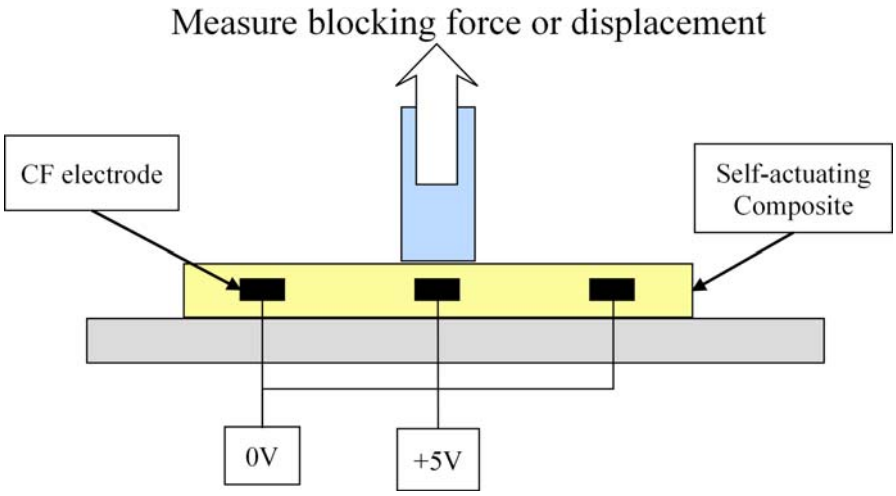

Figure 5 - Schematic of self actuating composite in operation

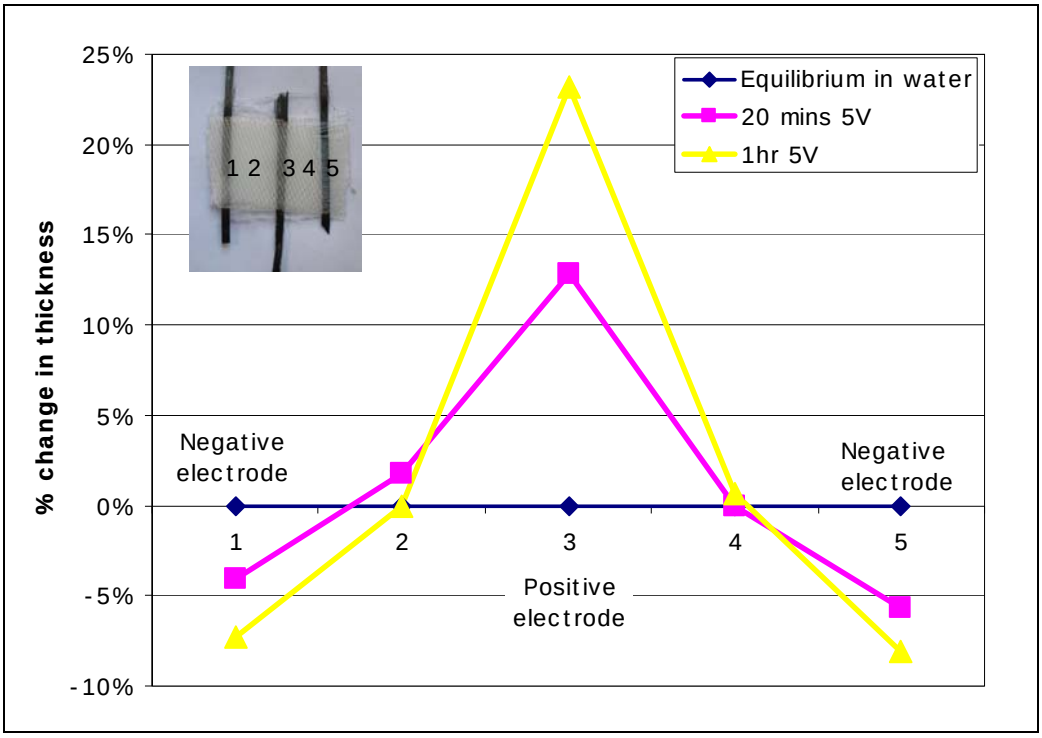

Figure 6 - Thickness change due to an applied voltage ±5V.

Displacement

To assess the limiting displacement of the composite self-actuator (Figure 5), the DMA was programmed to measure the displacement required to maintain a zero force. Thus, a specimen (1.25mm thickness) was placed in the DMA following immersion within a 0.01M NaCl solution and the position controller set to a zero force start point. After being allowed to settle for 3 minutes, a voltage of +5V was applied and the resulting change in displacement was recorded, Figure 7. In this case an 80% increase in thickness was observed.

Figure 8 shows the effect on actuation response of the same specimen under cyclically reversing electrical potential. Although the specimen responds by a contraction in volume, it is not of the same magnitude as the expansion. In fact, the response seems to indicate some form of creep response as the forward (+5V) potential cumulatively increase overall displacement. It is currently undetermined as to the precise reason for this asymmetry in response; however, work is ongoing to determine its cause. Recent work published by Guenther *et al*.[8] also report non-linear responses from hydrogels and highlights the complex nature of this field through experimental and analytical methods.

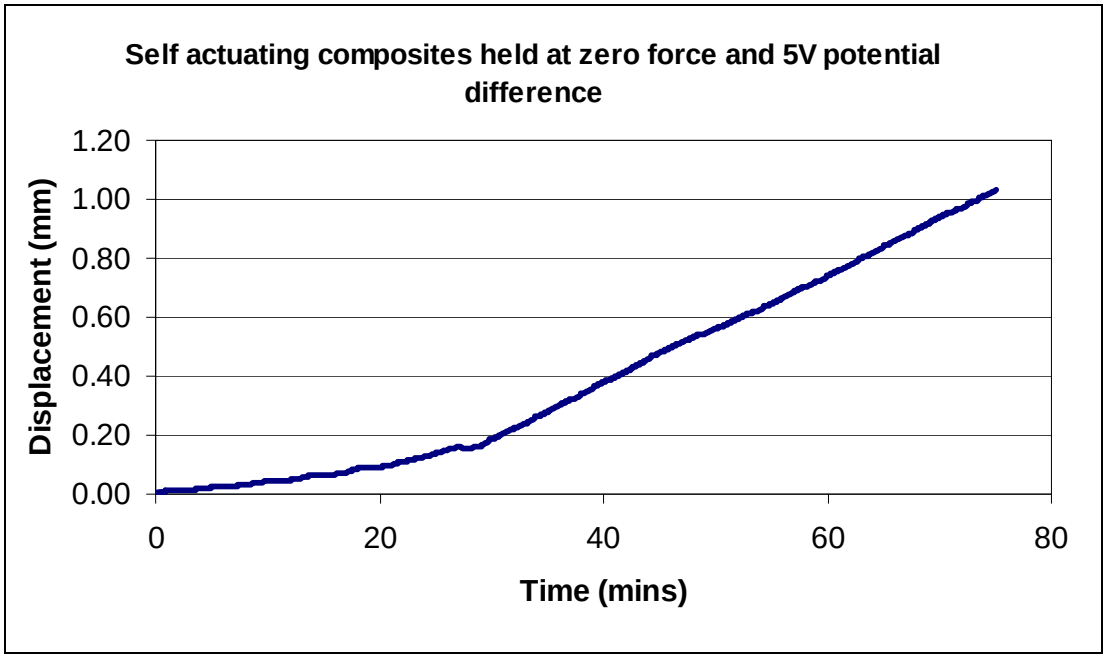

Figure 7 - Displacement response of a self actuating composite.

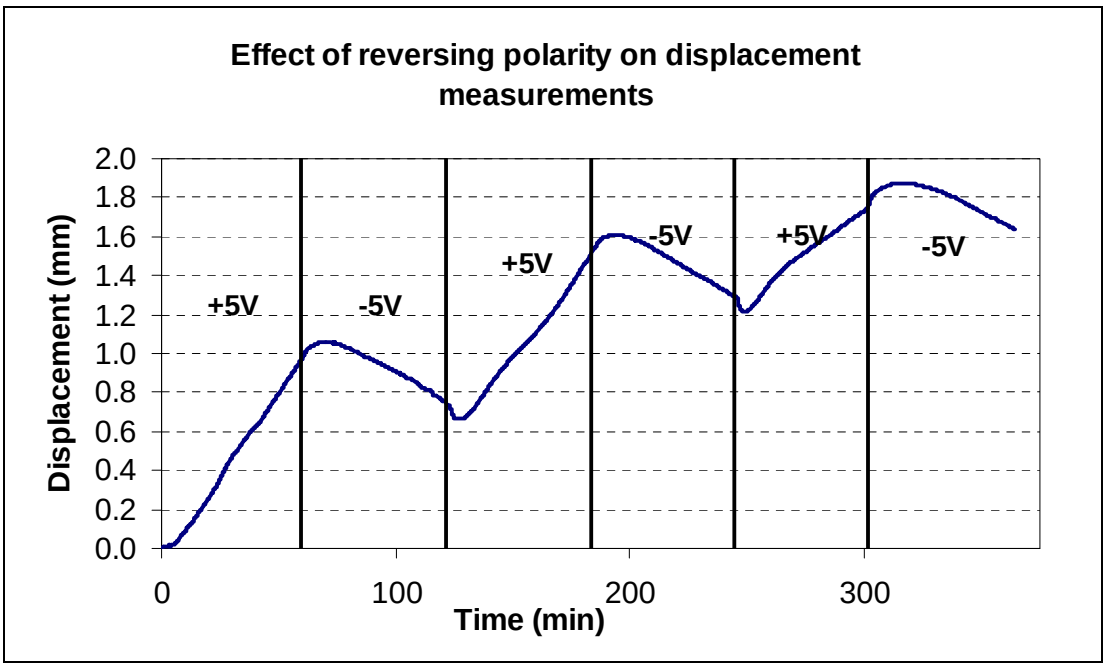

Figure 8 – Reversal of applied p.d. polarity on displacement

Load Measurements

An active composite with CF electrodes, Figure 2, with a thickness of 1.15 mm was placed within an Instron 3343 test machine (1kN load cell) to establish the total force that can be generated when actuated by application of a potential difference under a blocking load. The specimen was immersed in a 0.01M NaCl electrolyte solution (pH8) and whilst remaining submerged, was positioned as shown in Figure 5, such that a carbon fibre tow electrode (marked 3 in Figure 2) was directly below the axis of the load cell. A compressive preload of 3N was applied to the specimen to ensure positive contact with the test machine grips. This arrangement was allowed to settle for approximately 3 minutes prior to application of +5V with CF tow 3 (Figure 2) acting as the anode and CF tows 1 and 5 (Figure 2) acting as the cathodes. After 30 minutes the potential difference was reversed. Cross-head movement was prevented throughout the testing after application of the initial 3N preload. Instron software was used to record changes in load, Figure 9.

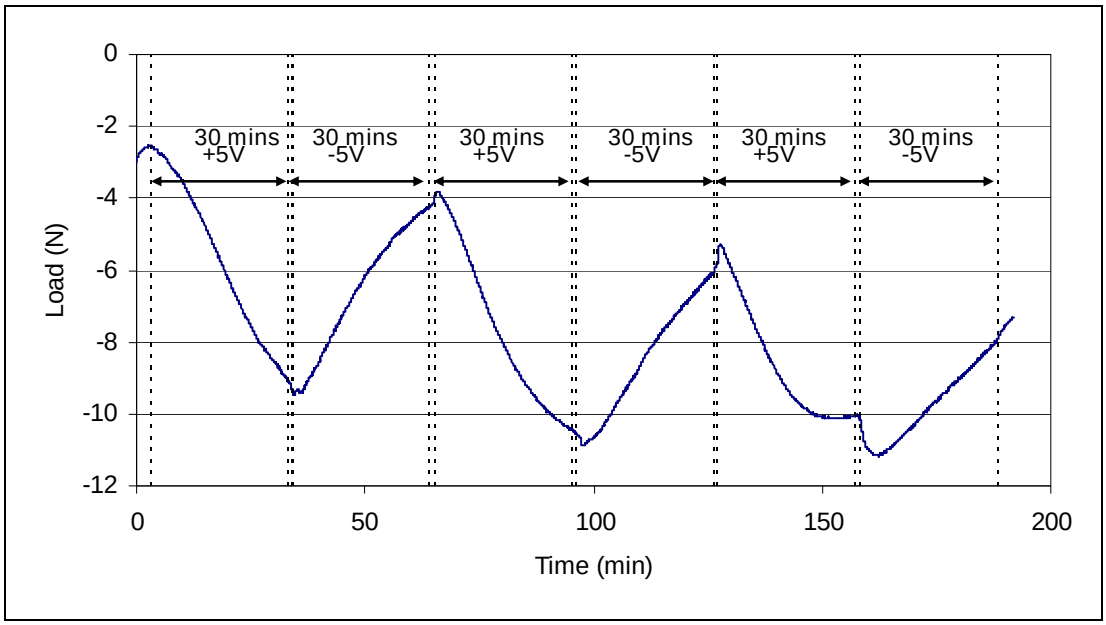

Figure 9 - The effect of cyclically reversing applied potential on the total force generated by an active hydrogel fibre reinforced composite.

DISCUSSION

The main aim of this work was to characterise the actuation potential of an electroactive epoxy hydrogel as the matrix within a self-actuating fibre reinforced composite. A secondary aim was to investigate the utilisation of a carbon fibre tow as an embedded electrode within the composite to maximise rate and magnitude of actuation displacement. As can be seen from Figures 8 and 9 the application of potential difference between CF electrodes is capable of generating sufficient localised pH changes in the electrolyte to initiate localised expansion and contraction. Also, control of the rate of actuation using this approach seems promising, with 1 mm thickness specimens having been shown to increase in thickness by 100% or generate a peak load of approximately 8N within 30 minutes of actuation. Relative to the work by Yoshioka

and Calvert [2] this is a fairly rapid response as in their studies a 130 μm film was shown to require approximately 25 minutes to double in thickness.

This study has highlighted several issues for further investigation. Firstly, the progressive drift or creep observed in both the load and displacement measurements during the reversal in potential needs to be understood and inhibited if possible. Secondly, an improved understanding of the change in Young's modulus as a function of local pH is required, as this will directly affect any actuator response in a real application. Finally, due to the large volume change associated with the actuation of this type of epoxy hydrogel, any constraint or packaging of a composite actuator will be critical in to ensuring the load/displacement generation is maximised whilst providing containment of any necessary electrolyte.

POTENTIAL APPLICATIONS

One of advantage of the proposed use of distributed CF tows as embedded electrodes is the ability to tailor their precise arrangement to control the nature of the actuation via volumetric change. For example, using standard composite manufacturing techniques, CF tows can be easily incorporated, Figure 10, to provide very localised actuation. This may find application in manipulating texture or topography of aerodynamic surfaces.

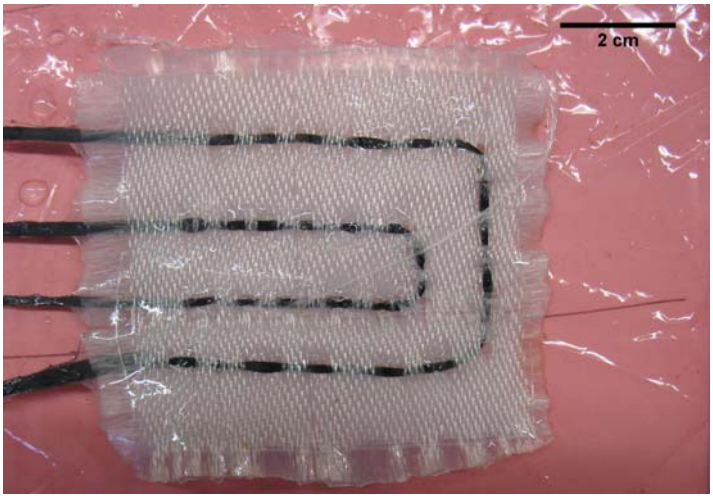

Figure 10 - Example of the electrode pattern that can be achieved when using CF tows.

ACKNOWLEDGEMENTS

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