 DOI: 10.1002/masy.201051034

Control of McKibben Polymeric Artificial Muscles by Means of Buffer Solutions

B. Tondu,[*1] *S. Mathé,*[2] *R. Emirkhanian*[1]

Summary: Reversible swelling and de-swelling of pH reactive polymers are mainly made using strong bases and strong acids, typically with pH equal to 0 or 1 and 14 or 13. As a consequence, pH-artificial muscles are triggered off at a pH too high for internal use of such muscles inside the human body. The paper analyses the possibility of using weak base-weak acid buffers to generate the ion circulation necessary for swelling/de-swelling phenomena with a limited pH-range. The paper further reports experiments with ion-exchange resins swelling and de-swelling in response to standard $NaHCO_3/CH_3COOH + CH_3COONa$ weak base-weak acid solutions. The ion exchange resin is placed inside the inner tube of a McKibben-braided structure whose functioning we have discussed elsewhere in connection with its reliability to define a chemo-mechanical artificial muscle with static and dynamic behaviour close to human skeletal muscle. We experimentally show that a 0.25 M buffer solution leads to a maximum isometric force and a contraction time response similar to that obtained with 0.1 M NaOH/HCl strong base-strong acid. As a consequence, our McKibben polymeric artificial muscle is now controlled within a 3.8 pH-range: muscle contraction is triggered at about 8.3 pH, and muscle relaxation at about a 4.5 pH. The dynamic performance of a 170 mm long/7 mm diameter in isotonic mode, with loads between 0.25 kg to 10 kg, is reported.

Keywords: ion-exchange resins; McKibben artificial muscle; pH-muscle

Introduction

Activation of artificial muscles by pH variations is a promising approach in the present-day search for ''new motors'' based on artificial polymer muscle technologies[1] due to its chemical simplicity, its ease of putting into work and its obvious rapidity in the generation of pH steps in comparison, for example, with control by temperature variations. This purely chemical activation mode also appears as an alternative to electrical activation modes by current or tension control. Furthermore, pH value in the body is an important environmental factor and can consequently be viewed as a relevant bio-mimetic agent for artificial muscles aimed at integration into the human body. All pH-muscles are based on the use of pH-sensitive polymers swelling either in basic pH by means of acidic groups such as $-COOH$ or $-SO_3H$, or in acidic pH by means of basic groups such as $-NH_2$. From Kachalski and Kühn's historical experiments,[2,3] to more recent attempts at using thin strips of PVA-PAA[4] or PAN fibres[5–7] or chitosan-based fibres,[8] and even nano PAN fibres,[9] pH-muscle activation is mostly made with 1M acid-base solutions, corresponding to a [0-14] pH range. These extreme pH values are motivated by the maximum protonation and deprotonation that they assure among ionisable reactive polymer functional groups. In a previous

[1] LATTIS (Laboratoire Toulousain des Technologies et de l'Ingénierie des Systèmes), University of Toulouse, Campus de Rangueil, 31077 Toulouse, France
E-mail: bertrand.tondu@insa-toulouse.fr
[2] LISBP (Laboratoire d'Ingénierie des Systèmes Biologiques et des Procédés), University of Toulouse, Campus de Rangueil, 31077 Toulouse, France & UMR5504, CNRS, 314000 Toulouse, France

work we showed how to employ the McKibben-braided structure to construct a compact pH-muscle producing a reversible contraction force with 0.1 M, and even 0.05 M acid-base solutions.[10] However, when lower concentrations – 0.01 M and 0.001 M – are used, the force generated by the artificial muscle dramatically decreases and becomes zero at 0.0001 M concentrations. Other studies also emphasize the use limitation of pH-muscles to very acidic or very basic ranges: for example, PAAM hydrogel actuators have recently appeared to be effective for $pH < 3$ or $pH > 12$.[11] Such pH values are not adapted for future medical applications in which the integration of a pH-muscle inside the human body is imagined. We wish to demonstrate in this paper how the use of standard weak acid-weak basic buffer solutions can be a very simple way of triggering an ion-exchange resin pH-muscle with a limited pH-range. Following section explains the application of buffer solutions to the control of ion-exchange resin pH-muscles; and a in next section we report experimental results obtained with our McKibben-type braided structure both in isometric and isotonic conditions.

Buffer Solutions as a Simple Way of Controlling a pH-Muscle at Low pH-Ranges

PH muscles are generally controlled using strong acid HCl-strong base NaOH. In the case of a pH-sensitive polymer containing acid groups such as the considered ion-exchange resins with COOH functional groups, resin swelling in basic pH is obtained by the exchange inside the aqueous medium of Na^+ ions (from NaOH) with H^+ ions (from COOH functions), and the de-swelling in acid pH by the exchange of H^+ ions (from HCl) with Na^+ ions (from the $RCOO^-Na^+$ functions). When pH varies, the concentrations of Na^+ and H^+ ions also vary. In point of fact, although the term pH-muscle has been adopted for designating this kind of artificial muscle, it clearly appears that their pH-sensitivity is essentially an ion-sensitivity. This means that the true control variable of these artificial muscles is the concentration of reactive ions inside the aqueous medium when pH, in terms of control, is a secondary control variable. By splitting these two control variables, a high concentration of reactive ions in the reactive medium with a moderate pH would be maintained. The standard use of buffer solutions can be thus considered as a very simple and efficient method of reaching this goal. Consequently, we substitute a couple of a weak acid buffer-weak base buffers for the strong acid HCl-strong base NaOH. One of these couples can be $NaHCO_3 - CH_3COOH + CH_3COONa$. Subsequently, we substitute a strong basic ion-exchange equation responsible for the polymer swelling:

$$\begin{aligned} &RCOOH + Na^+OH^- \\ &\rightarrow RCOO^-Na^+ + H_2O \end{aligned} \tag{1}$$

by the following equation in which it is assumed that the weak basic buffer is in excess, *i.e.* $a >> 1$:

$$\begin{aligned} &RCOOH + \underbrace{aNa^+ + aHCO_3^-}_{\text{weak basic buffer in excess}} \\ &\rightarrow RCOO^-Na^+ + (a-1)HCO_3^- \\ &+ (a-1)Na^+ + aH_2CO_3 \end{aligned} \tag{2}$$

and the strong acid ion-exchange equation responsible for the polymer de-swelling:

$$\begin{aligned} &RCOO^-Na^+ + H^+Cl^- \\ &\rightarrow RCOOH + Na^+\,Cl^- \end{aligned} \tag{3}$$

by the following equation:

$$\begin{aligned} &RCO_2^-Na^+ + \underbrace{aCH_3CO_2H + aCH_3CO_2^- + aNA^+}_{\text{weak acid buffer in excess}} \\ &\rightarrow RCO_2H + (a-1)CH_3CO_2H \\ &+ (a+1)Na^+ + (a+1)CH_3CO_2^- \end{aligned} \tag{4}$$

It is important to note that buffered solutions are often used to determine the swelling dependency of a hydrogel onpH.[12–15] However, this is generally made as if the hydrogel candidate was insensitive to the additional ions being added to the medium through the buffer

solutions. Sometimes it appears difficult to understand if pH-sensitivity was determined by dilution of strong acid-base solutions or by buffered solutions (for example, in.[16]) In some other studies, relative in particular to chitosan-based hydrogels, known to be affected by ionic strength, the swelling performances in modyfing pH by dilution or by buffered solution are emphasized. In,[17] for example, it is clearly mentioned that the swelling of a modified chitosan superabsorbant hydrogel is about 50% in an on-off switching experiment from pH = 10 to pH = 3 in buffered solutions, while its swelling ability in an HCl diluted solution of pH = 3 is about 300%. In the case of our artificial muscle, we make the assumption that the high ion-sensitivity of ion-exchange resins is the crucial point for preserving the high swelling ability of this material in buffered solutions.

Application to the Control of a Polymeric McKibben Artificial Muscle

We have detailed in other papers our approach to the McKibben pneumatic artificial muscle[18] and its adaptation to a chemical control approach.[10] Figure 1 synthesizes the experimental set-up used to test such compact pH-muscles.

In the centre we show a typical compact laboratory-developed McKibben muscle: its initial external diameter is around 7 mm and its initial active length (except for metal tips) is around 70 mm for its shortest prototype, to around 170 mm for the longest. The braided sheath is made of nylon; and surrounds a rubber inner tube filled with 580 to 780 μm resin balls. The swelling of these resin balls generates a circumferential stress inside the rubber inner tube that the interwoven braided cords transform into a linear contraction force. The feeding of the artificial muscle in weak base buffer A and weak acid buffer AH, is alternatively realized by a peristatic pump. As sketched on the right-hand side of the Figure, the experimental set-up can be used in two modes: an isometric mode aimed at establishing static performances of the artificial muscle, and an isotonic mode for dynamic performances of the artificial muscle when a load is attached.

Static Characteristics in Isometric Conditions

The pH-muscle isometric test is performed at a zero contraction ratio, *i.e.* at initial active length of the muscle in order to

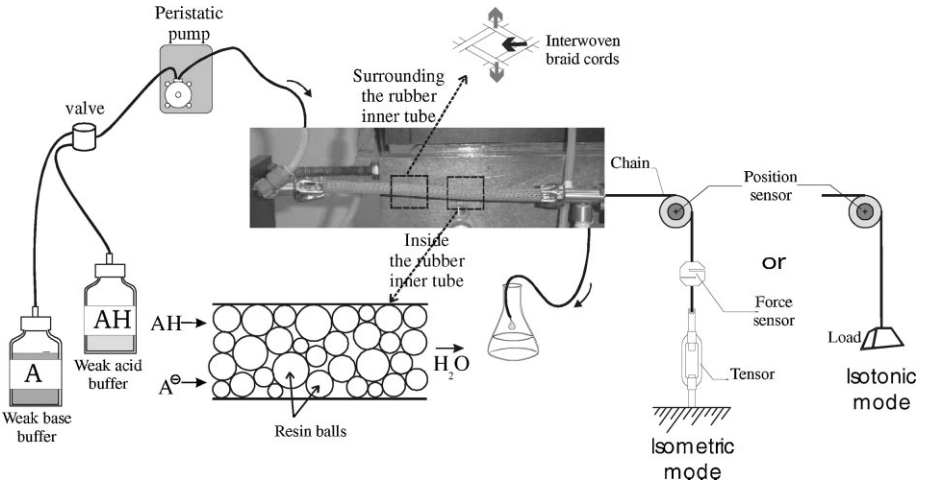

Figure 1.
Experimental set-up for determining the static and dynamic performances of a polymeric McKibben artificial muscle fed alternatively by a weak base buffer and a weak acid buffer.

determine its maximum force since it is known, in analogy with skeletal muscle, that McKibben muscle produces its maximum force at a zero contraction ratio. Figure 2 gives the static characteristics, according to this isometric mode, of the pH-muscle defined in Figure 1: curves 1a and 1b, respectively, correspond to the swelling/de-swelling pH-muscle triggered by the couple 0.1 M strong NaOH base-strong HCl acid, similar to our already published results, while curves 2a and 2b, respectively, correspond to the swelling/de-swelling of pH-muscle triggered by the couple weak base buffer-weak acid buffer.

It clearly appears that the use of the buffer solution leads to the same maximum force. However, the response time during the swelling phase measured at 95% of this value, is changed from about 40 min to about 70 min. The weak base and weak acid buffers were tested under similar concentrations, equal to 0.125 mol/L which correspond to the concentration of HCO_3^- ions in the extra-cell physiological liquid, and thus to a feasible integration of the device inside the human body. The effect of this concentration on pH-muscle response time can, however, be questioned. Figure 3 gives the result obtained for the previously considered pH-muscle prototype fed by identical weak acid-weak base buffer concentrations varying from 0.1 to 0.5 mol/L. Increasing buffer concentration implies, as in the case of strong acid-strong base, higher ionic strengths and, as a consequence, quicker response times. It is interesting to note that the use of a 0.5 M basic buffer leads to a quicker response than with a 0.1 M NaOH solution, without us being fully able to explain it. However, a drawback to this ionic strength increase is a limited swelling and, consequently, maximum force is lower, as illustrated in Figure 3.a for the 0.5 M basic buffer solution. For this reason, we have limited our search for the ''best'' concentration to buffer solutions generating the same maximum force of about 80 N, in the case of our pH-muscle prototype. In each experiment, pH was electronically determined. In Figure 3.b response time change during isometric concentration is given, and Figure 3.c shows response time change during isometric relaxation for solutions with 0.1 M, 0.125 M and 0.25 M concentrations. In each case, comparison is made with strong base-strong acid solutions. It clearly appears that a 0.25 M concentration of our buffer solutions leads to a response time in concentration close to, and even lower than, the best one generated with a strong base, although in the same conditions this response time is about twice that generated with strong acid in case of isometric relaxation. This latter point could be explained by the size difference between the HCl molecule – responsible for the

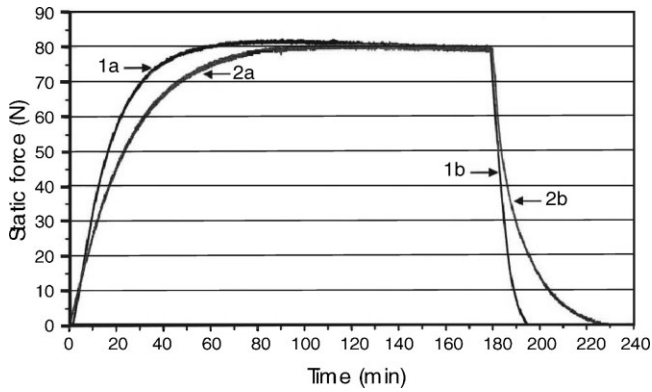

Figure 2.
Comparison of the static characteristics of the pH-muscle between a 0.1N strong base NaOH-strong acid HCl (1a and 1b) and a weak base buffer $NaHCO_3$ – weak acid buffer $CH_3COOH + CH_3COONa$ (2a and 2b).

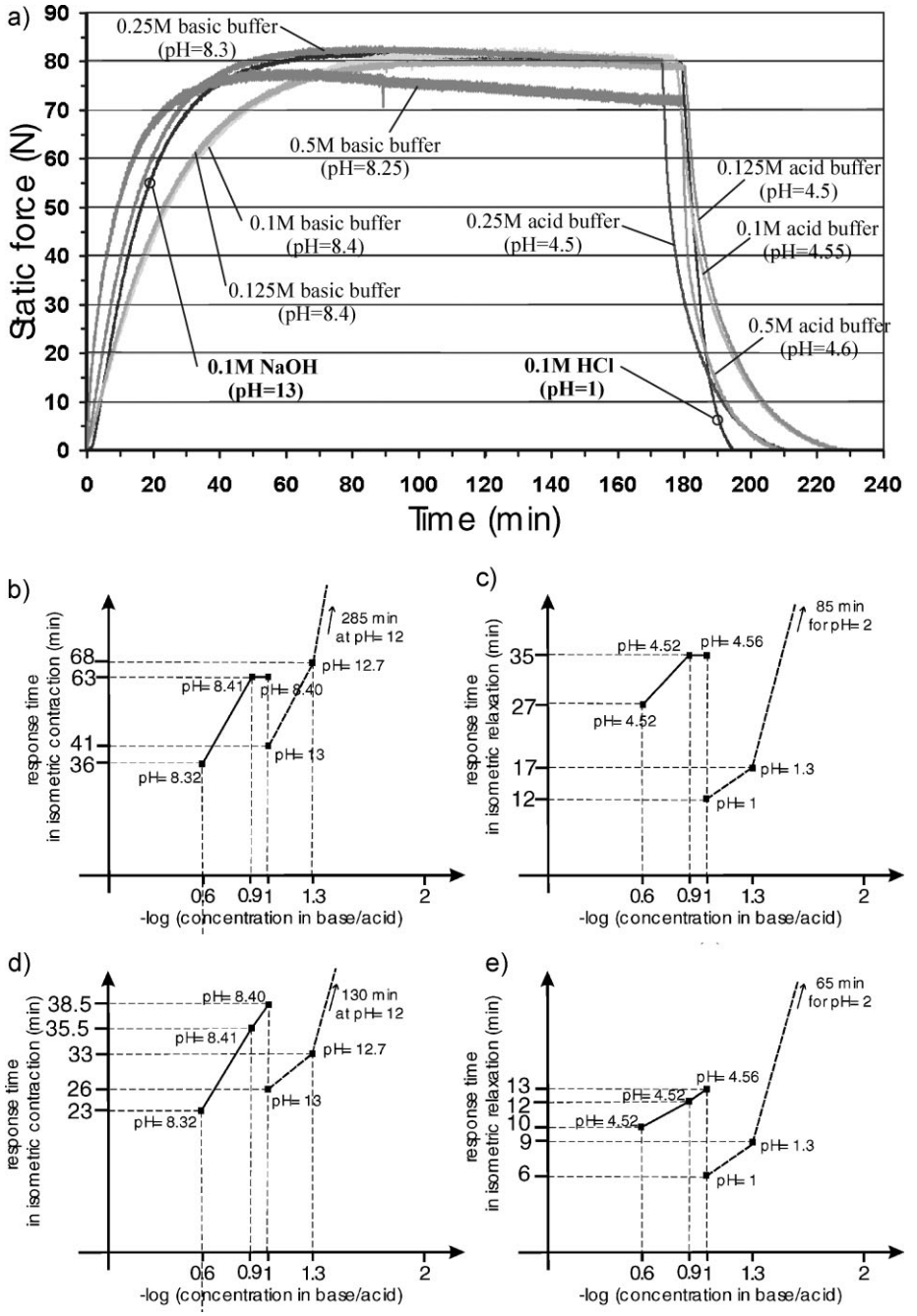

Figure 3.

Influence of buffer concentration on artificial muscle response time, (a) isometric contraction and relaxation for 0.1 M to 0.5 M buffer solutions, (b), (c) corresponding change of the 95% response time in contraction (b) and relaxation (c) as a function of base/acid concentration (solid line) and in comparison with artificial muscle control by means of 0.1 M NaOH/HCl solutions (broken lines), (d), (e) ditto for 80% response time.

de-swelling (Eq. 3) in the strong acid case – which is lower than the CH_3COOH molecule – responsible for de-swelling in the weak acid case (Eq. 4) – and, as a result, moves slowly in the buffer solution. This result is in any event very promising for a future use of weak base and weak acid buffer to trigger pH-muscle: our ion-exchange resin muscle is now able to produce 95% of a maximum isometric force of about 80 N in about 36 min, and to relax reversibly in about 27 min in a limited range of [8.3-4.5] compared to the efficient strong base-strong acid [12-1] pH-range. Moreover, the 80% instead of 95% response time was considered, using the same experimental data as in Figures. 3.d and 3.e.

This choice was motivated by resin-swelling properties: they swell or de-swell rapidly at the beginning of the ion-exchange process, and subsequently at a slower rate when only a limited part of the resin has not exchanged ions. It clearly appears that 80% response times correspond to about half of 95% response time, which is still a very positive complementary result. This leaves us with having to prove experimentally that weak base-weak acid buffer use does not limit the dynamic behaviour of our pH-muscle.

Dynamic Characteristics in Isotonic Conditions

In accordance with McKibben artificial muscle theory, the maximum force produced by the artificial muscle is independent of its initial length. Let us call ε the muscle contraction ratio defined as $\varepsilon = (l_0 - l)/l_0$ where l_0, as already specified, is the initial muscle length and l its current length. Theoretically, maximum contraction ratio is independent both of l_0 and of muscle control pressure.[18] In practice, this is not true due to the bound effect which causes a loose force in the proximity of the muscle tips where the contracted muscle diameter is lower than in its centre. This phenomenon is particularly obvious for very short-length muscles. It is still not true, however, because of static and kinetic friction forces inside the braid muscle which provoke a high maximum contraction ratio at low control pressure. In the case of pneumatic McKibben artificial muscles, whatever the choice of braided sheath material, the maximum contraction can vary from about 25–30% at 5 bar to about 15–20% at 1 bar. Concerning our pH-muscle, the pressure inside the rubber inner tube is a consequence of the swelling phenomenon. By analogy with a pneumatic muscle, and in the knowledge of geometrical initial braid angle α_0, initial length l_0 and initial internal radius r_0 - (see our paper[9] for a rigorous definition of these parameters), it is possible to determine an ''equivalent'' pressure P_{equ} from estimated maximum isometric force value $F_{0,}$ given in Figure 2 above. We established the general formula relating, for a given pressure P, McKibben static force F to contraction ratio ε:[18]

$$F(\varepsilon, P) = (\pi r_0^2)\, P\,[a(1-\varepsilon)^2 - b] \quad \text{with}$$
$$a = 3/\tan^2(\alpha_0) \quad \text{and} \qquad (5)$$
$$b = 1/\sin^2(\alpha_0)$$

For $\varepsilon = 0$ we obtain the maximum force expression:

$$F_0 = (\pi r_0^2) P (a - b) \qquad (6)$$

and thus, in the case of our pH-muscle, the expression of the ''equivalent'' pressure:

$$P_{equ} = F_0/[(\pi r_0^2)(a - b)] \qquad (7)$$

From the estimated values $r_0 \approx 0.35$cm, $\alpha_0 \approx 25$deg and $F_0 \approx 80$N, we obtain: $P_{equ} \approx 2.5$bar. Note that for the same geometrical parameters and the same choice of reactive chemical agents, product quantity inside the muscle is a factor influencing maximum force value and, consequently, equivalent pressure. For example, in reported isotonic experiments, a more compact fulfilment of the muscle in comparison with Figures 2 and 3 experimental results leads to a maximum force of about 120 N, and an equivalent pressure of about 4 bar. In accordance with our studies on McKibben pneumatic artificial muscle,

these swelling pressures are well adapted to our McKibben structure. However, in comparison with an artificial pneumatic muscle whose dynamic response in isotonic conditions can be determined in response to a pressure step-response, there is no evidence that the pressure inside our pH-muscle will keep near-constant during the swelling process generated by the base flow circulation. Knowledge of the swelling pressure change inside the pH-muscle is, in fact, secondary as it concerns the fluid flow aimed at producing the control pressure of a pneumatic artificial muscle. However, this comparison between pneumatic McKibben muscle and its pH version highlights a dynamic working principle: the pH-muscle dynamic contraction occurs along its length since the swelling process allows the muscle sheath to open and thus generate a contraction force. In other words, as long as the pH-muscle can produce an ''equivalent'' pressure force generator in accordance with pneumatic McKibben artificial muscle theory. In our previous work[10] we demonstrated a maximum contraction ratio of about 15% with a 0.25 kg load. In order to test the dynamic ability of our new control process, and more particularly its maximum contraction ratio, we designed a longer muscle of $l_0 \approx 170$mmwith the same r_0 and α_0 parameters. Figure 4 gives the corresponding time responses of this muscle for constant loads varying from 0.25 kg to 10 kg, and Figure 5 the corresponding powers.

In comparison to our previous results showing the isotonic contraction of a similar pH-muscle triggered by 0.1 M NaOH/HCl solutions (Figure 7 in,[11]) these curves exhibit similar dynamic performances:

- The maximum contraction ratio of 11% with a 1 kg load is in good agreement with the mechanical properties of McKibben artificial muscle, for which it is known that a maximum contraction load-free ratio of 25–30% can be expected. The maximum contraction of 13% obtained with a light load of 0.25 kg could, however, be improved by increasing the quantity of resins inside the muscle inner tube. We did indeed emphasize in our previous study[10] the significant role of resin quantity in the production of maximum isometric force and in maximum contraction ratio, as a consequence of the resulting swelling pressure. We have as yet not defined a standardization of the muscle ''filling'', and thus we still have to determine the optimum quantity of resins which should be inserted inside the rubber inner tube without distorting the shape of the braided sheath, or inhibiting fluid circulation.
- The experimentally tested ability of the artificial muscle to lift loads from 0.25 kg to 10 kg extends our previous dynamic

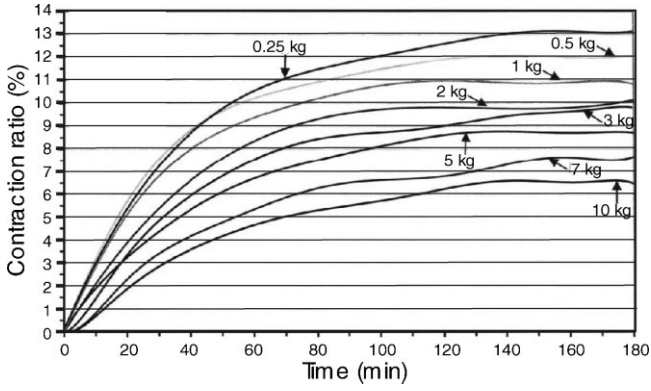

Figure 4.
Dynamic characteristics of pH-muscle obtained in isotonic conditions with given loads.

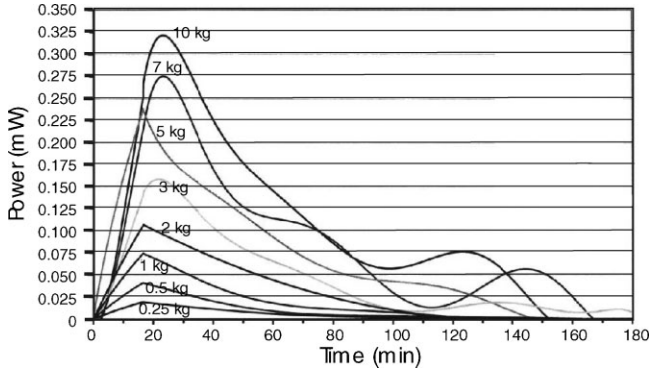

Figure 5.
Corresponding powers.

results,[10] which were limited to a load range of [0.5 kg–3 kg]. This clearly demonstrates the ''strength'' of this small muscle and its resistance to breaking, which is directly due to the braided structure.

The time corresponding to maximum power varies from between about 15 min and 22 min, and is in good agreement with the corresponding mean time of 17 min obtained for similar experiments with 1 M NaOH/HCl solutions.

Conclusion

This study is concerned with highlighting the possibility of controlling a pH-muscle derived from a McKibben-type braided structure in a restricted pH range. Weak acid-weak base buffers appeared as a practical way of generating Na^+/OH^- ions concentrations necessary inside the muscle for the swelling/de-swelling phenomenon of a commercial ion-exchange resin with limited basic/acid pH-values relatively close to neutral pH. The standard use of $NaHCO_3$ as a weak base buffer and of $CH_3COOH + CH_3COONa$ as a weak acid buffer led to emphasizing the possibility of triggering pH-muscle with static and dynamic performances close to the ones generated by means of 0.1 M NaOH/HCl solutions, and using 0.25 M solutions. This result can be synthesized as shown in Figure 6, gathering hysteresis cycles corresponding to change with isometric force pH at zero contraction ratio, produced after 90 min. This time reference was chosen to include the trapezoidal-shaped cycle generated with strong base and strong acid near the rectangular shape cycle corresponding to the use of weak base and weak acid cycle; when base and acid molar concentrations are low, maximum muscle force is effectively reached after a very long time (the corresponding values are in accordance with graphs given in our previous paper[10] – see in particular Figure 3). The comparison illustrates the significant restriction of the pH-muscle hysteresis cycle, due to the buffer solutions employed.

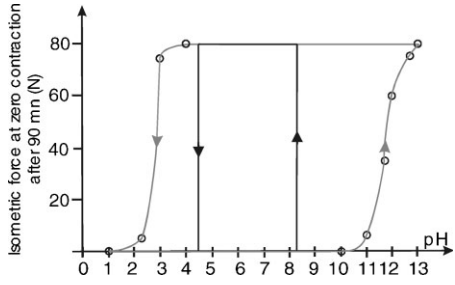

Figure 6.
Reduction of the Static force(pH) hysteresis cycle of our artificial muscle controlled by means of a 0.25 M $NaHCO_3/CH_3COOH + CH_3COONa$ buffer solution in comparison with a 1M NaOH/HCl solution (curve with circles).

This technical possibility of reducing the hysteresis cycle Force (pH) by means of buffer solutions, highlights the fact that the true control variable of our pH-muscle is not pH itself, but ion concentration. In our view this is a general result, and we consider that triggering reactive polymer swelling/de-swelling by means of buffer solutions could be applied to other types of pH-muscles. This pH-range restriction is particularly interesting for a human-friendly use of these artificial muscles. Although the pH-range reduction demonstrated in our study is still higher than the typical extracellular pH of a healthy person, varying between 6.8 and 7.2, it can be considered as a first step towards a more complex process associating our pH-limited range artificial muscle with a primary chemical device able to generate the moderate pH-range needed for artificial muscle working, and to do so using bio-compatible materials. The use of bio-compatible yeasts, for example, triggered by glucose could be a possibility for such a primary device, as was recently discussed in the ANR-OSMOTEUR project[19] whose authors of the paper are project partners. Beyond the integration issue of a complete muscle based bio-compatible device, the present-day relative slowness of contraction and relaxation responses remains questionable. In its present state, the proposed pH-muscle is more a kinetic energy accumulator, whose release necessitates a series-spring like device, than a truly artificial skeletal muscle. Two ways will be considered with the aim to reduce the swelling/de-swelling time inside the artificial muscle enveloppe and, as a consequence, the artificial muscle response time. Firstly, it must be emphasized that currently-reported results have been obtained using commercial resins (Amberlite IC, Rohm & Haas Company). In a further work, we will attempt to synthesize new types of resins with the hope of reducing response time as, for example, developed in[20] where drug release experiments with a novel pH-sensitive ion exchange resin composed of Methy/acrylic acid/styrene cross-linked with divinylbenzene, are reported. As emphasized ''[The drug] is rapidly released in 15 mn'' (page 633), which in accordance with associated curves corresponds to an 80% time response of about the same period. It can be hoped that the incorporation of judicious ionic functional groups onto the cross-linked ion exchange resin could produce even quicker pH-sensitive resin. Secondly, because the ion-exchange principle is also applicable to hydrogels, we also will consider this approach. In a previous paper[10] we have reported preliminary experimental results of a similar artificial muscle filled with a specific hydrogel synthesized from acrylic acid and acrylamid. A time response of about 8 min has been obtained in isometric conditions with 0.1 mol/L strong acid-strong base solutions. However, this performance has a weaker reliability than exhibited performances with the considered commercial ion-exchange resin, due to the powder character of the reactive agent and therefore the risk of drastically reducing or even stopping the percolation process. A solution could then consist in synthesizing a new type of hydrogel derived from our actual acrylic acid-acrylamid structure with a greater degree of cross-linking. The establishment of more chemical bonds between polymer molecule chains would make possible the re-shaping of the hydrogel into micro-balls as done with the used highly cross-linked commercial ion-exchange resins. And so, one way or the other, to tend, due to McKibben technology, towards an artificial muscle whose macroscopic behaviour is statically and dynamically close to skeletal muscle, and in addition triggered by a bio-compatible control variable.

[1] T. Mirfakrai, J. D. W. Madden, R. H. Baugham, Polymer Artificial Muscles'', *Materials Today*, **2007**, *10*(N°4), 30–38.

[2] A. Katchalsky, ''Rapid Swelling and Deswelling of Reversible Gels of Polymeric Acids by Ionization'', *Experienta*, **1949**, *V/8*, 319–320.

[3] W. Kühn, B. Hargitay, A. Katchalsky, H. Eisenberg, ''Dilatation and Contraction by Changing the State of Ionization of High-Polymer Acid Networks'', *Nature*, **1950**, *165*, 514–516.

[4] D. Brock, W. Lee, D. Segalman, W. Witkowski, ''A Dynamic Model of a Linear Actuator Based on Polymer Hydrogel'', *Journal of Intelligent Materials and Structures*, **1994**, *5*(N° 6), 764–771.
[5] D. G. Caldwell, N. Tsagarakis, G. A. Medrano-Cerda, ''Bio-Mimetic Actuators: Polymeric Pseudo Muscular Actuators and Pneumatic Muscle Actuators for Biological Emulation'', *Mechatronics*, **2000**, *10*, 499–530.
[6] K. J. Kim, J. Caligiuri, K. Choe, ''Contraction/elongation Behavior of Cation-modified Polyacrylonitrile Fibers'', *Proc. SPIE*, **2003**, *5051*, 207–217.
[7] K. Choe, K. J. Kim, ''Polyacrylonitrile Linear Actuators: Chemomechanical and Electro-Chemomechanical Properties'', *Sensors and Actuators A*, **2006**, *126*, 165–172.
[8] Yahya A. Ismail, Su Ryon Shin, Kwang Min Shin, Seong Gil Yoon, Kiwon Shon, Sun I. Kim, Seon Jeong Kim, ''Electrochemical Actuation in Chitosan/polyaniline Microfibers for Artificial muscles Fabricated Using an in Situ Polymerisation'', *Sensors and Actuators B*, **2008**, *129*, 834–840.
[9] R. Samatham, I.-S. Park, K. J. Kim, J.-D. Nam, N. Whisman, J. Adams, ''Electrospun Nanosacle Polyacrylonitrile Artificial Muscle'', *Smart Materials and Structures*, **2006**, *15*, N152-N156.
[10] B. Tondu, R. Emirkhanian, S. Mathé, A. Ricard, ''A pH-activated Artificial Muscle Using the McKibben-type Braided structure'', *Sensors and Actuators A*, **2009**, *150*, 124–130.
[11] M. Bassil, J. Davenas, M. El. Tahchi, ''Electrochemical Properties and Actuation Mechanisms of Polyacrylamide Hydrogel for Artificial Muscle Application'', *Sensors & Actuators B*, **2008**, *134*, 496–501.
[12] Jan M. D. Heijl, Filip E. Du Prez ''Fast, Multi-responsive Microgels Based on Photo-crosslinkable Poly(2-dimethylamino)ethyl methacrylate'', *Polymer*, **2004**, *45*, 6771–6778.
[13] Ali Emileh, Ebrahim Vasheghani-Farahani, Mohammad Imani, ''Swelling behavior, Mechanical Properties and Network Parameters of pH- and Temperature-sensitive Hydrogels of Poly((2-dimethyl amino) ethyl methacrylate-*co*-butyl methacrylate)'', *European Polymer Journal*, **2007**, *43*, 1986–1995.
[14] Youwen Lin, Qing Chen, Hongbing Luo, ''Preparation and Characterization of *N*-(2-carboxybenzyl)-chitosan as a Potential pH-sensitive Hydrogel for Drug Delivery'', *Carbohydrate Research*, **2007**, *342*, 87–95.
[15] Seon Jeong Kim, Han II. Kim, Sang Jun Park, Sun I. Kim, ''Shape Change Characteristics of Polymer Hydrogel Based on Polyacrylic acid/poly(vinyl sulfonic acid in Electric fields'', *Sensors and Actuators A*, **2004**, *115*, 146–150.
[16] Anasuya Sahoo, K. R. T. Ramasubramani, Manjeet Jassal, Aswini K. Agrawal, ''Effect of Copolymer Architecture on the Response of pH sensitive Fibers on Acrylonitrile and Acrylic Acid'', *European Polymer Journal*, **2007**, *43*, 1065–1076.
[17] G. R. Mahdavinia, A. Pourjavadi, H. Hosseinzadeh, M. J. Zohuriaan, ''Modified Chitosan 4. Super Absorbent Hydrogels from Poly(acrylic acid-coacrylamide) Grafted Chitosan with Salt- and pH-responsiveness Properties'', *European Polymer Journal*, **2004**, *40*(N°70), 1399–1407.
[18] B. Tondu, P. Lopez, ''Modeling and Control of McKibben Artificial Muscle Robot Actuators, *IEEE Control Systems Magazine*, **2000**, *20*(N°2), 15–38.
[19] Ph. Cinquin, (leader), Final report of the French ANR-OSMOTEUR project, July **2009**.
[20] Hongfei Liu, Shu Zhang, Shufang Nie, Xin Zhao, Xiyang Sun, Xingang Yang, Weisan Pan, ''Preparation and Characterization of a Novel pH-Sensitive Ion Exchange Resin'', *Chem. Pharm. Bull.*, **2005**, *53*(N°6), 631–633.

