

Mechanical Characterisation of N-Isopropylacrylamide (NIPA) Gels for Use in Smart Actuators

Carlo Santulli

Università di Roma-La Sapienza
Department of Electrical Engineering, Via Eudossiana 18, 00184 Roma, Italy

ABSTRACT: Polymer hydrogels can be used to produce smart actuators, constructed from lightly cross-linked polymer inhomogeneous networks that contain solvent. Gel actuators are able to change their stiffness with gel hydration, and as an effect of other parameters, such as pH, temperature, chemical composition, etc. In this work, N-isopropylacrylamide (NIPA) gels are mechanically characterised to possibly serve as actuating cylinders and fibres in braids with vibration-damping purposes. Mechanical properties are obtained at different hydration levels and for different cross-linking density, using N,N'-Methylenebisacrylamide (BIS) as crosslinker, and the effect of these two parameters is studied statistically. The results indicate that both the addition of crosslinker and gel hydration yield a quite predictable effect, not far from linearity, on the mechanical properties of NIPA gel, which is promising for their use in actuators upon a wide range of crosslinker content and water/gel ratio. In general, it is proposed that a 7:1 ratio water/gel, or slightly inferior, with the maximum possible amount of crosslinker that allows retaining the swelling/deswelling properties, would be optimal for the operation of the actuator.

KEYWORDS: N-isopropylacrylamide (NIPA) gels, N,N'-Methylenebisacrylamide (BIS) crosslinker, hydration level, crosslinking density, compression testing, flexural testing.

1. INTRODUCTION

Gel systems, capable of changing shape and/or volume as a result of chemical or electrical stimuli, can be used to obtain variable stiffness actuation. The designs can be tailored to give a range of responses, large displacements-low forces at one end, or small displacements-large forces at the other [1]. A recent review summarises stimuli-responsive gels in terms of their memory shape and/or rapid reversibility: in this regard, water/solvent stimuli are on one side the easiest one to achieve, whilst on the other side their reversibility needs to be ensured by a separate physical action (e.g., electrical current) [2]. Gel actuation is well diffused in nature, for example in the mechanics of fish swimming motion: here, neural force provides the required reversibility [3]. A number of devices have been produced, which demonstrated the feasibility of polymer gel based actuation, including robot grippers [4], artificial muscles [5] and most recently self-walking devices with wormlike motility [6]. Actuation times lower than a second and a force of up to 100 N/cm² have been obtained using polyacrylonitrile (PAN) fibres [7-8].

Corresponding author: Carlo Santulli, E-mail : carlo.santulli@uniroma1.it

Actuators based on polymer gel systems are limited in their response speed by diffusion processes, so that, to obtain a quick response, the gel has to be fashioned into small units, e.g., spheres, cylinders, or thin fibres [9]. The kinetics of swelling and deswelling in these gels are governed by diffusion-limited transport in water of the polymeric components of the network. Some studies on the swelling kinetics of NIPA gels do exist, though they are not correlated with their mechanical properties [10]: in other cases, trying to improve the mechanical properties and especially the temperature response, inorganic phases e.g., silica, are introduced [11]. The rate of swelling is inversely proportional to the square of the smallest dimension of the gel [12]. In this regard, the practical design and control of the actuator still presents some problems, in particular in relation with the non-linearity of the mechanical behaviour of gels, which could have a significant effect on the extent of force produced by the actuator [13].

Previous work had showed the possibility of a tension-compression operation of batteries of gel-braid actuators (one of such actuators is depicted in Figure 1) for coupling of low forces with high strains: a prototype was realised using acrylic gel powder, including a woven container between the gel and the braid [1]. This allowed tension-compression operation in a range of water dilutions (water/gel ratio in mass) between approximately 4.5 and 6.5, as shown in Figure 2. Selection of a purposely-produced gel and in-braid polymerisation for removal of the woven container is deemed capable of increasing the actuator performance. This would in principle avoid the need for another reversibility procedure (e.g., electrolyte pH change, operation at transition temperature). It is suggested that the actuator would ultimately yield a maximum force in the region of 2-3 N, when adopting batteries of gel+braid units.

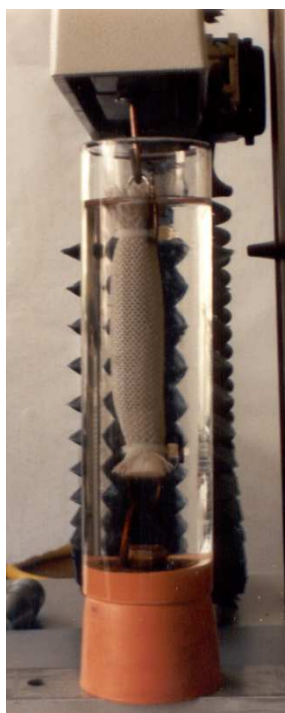


Figure 1. Prototype of gel-braid actuator (with gel acrylic powder)

However, it needs still to be ensured that these gels are not only able to offer a fast and high degree of swelling, but especially yield good mechanical properties for limited hydration level variations, which should guarantee the durability of the gel actuator, in spite of its low rigidity. In principle, acrylamide based gels present sufficiently high mechanical properties to allow for a long life as actuators: this happens, however, at the

expenses of their constructive simplicity, which may involve extensive structural modification e.g., to enable the formation of double network structure [14]. For this reason, an evaluation mechanical suitability for actuation on the barely cross-linked gel is needed, which is the aim of this work, involving static mechanical characterisation of the gel with varying crosslinking density and at different levels of hydration. This would possibly lead to some indications on the selection of appropriate crosslinker and water content for NIPA gel, or else the effect of these two parameters on the gel mechanical performance. The only modifications of these gels which are deemed necessary for their use in the above described actuators would concern crosslinker content and hydration levels.

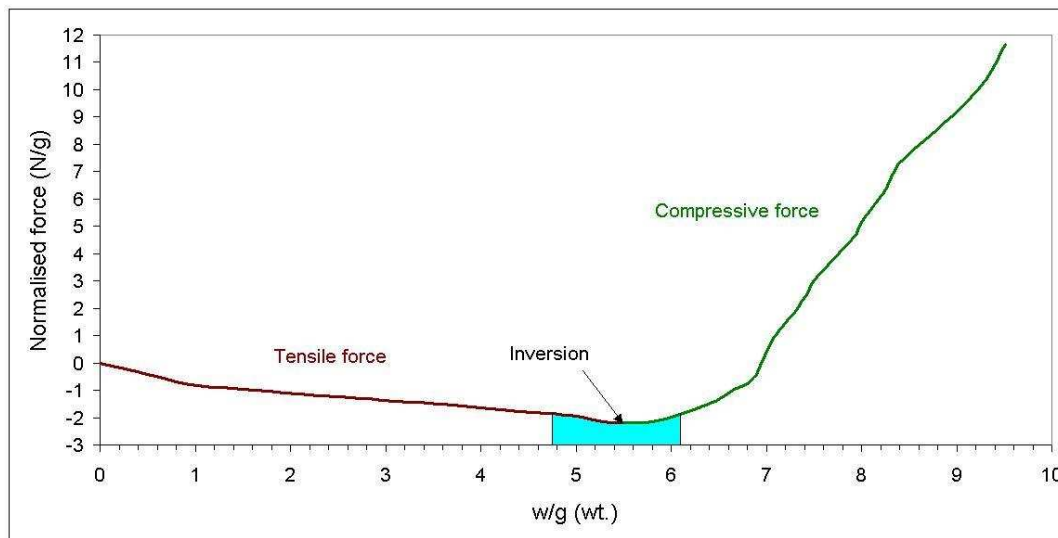


Figure 2. Tension-compression operation (coloured area) from a battery of six 5 mm. diameter gel-braid actuators (12:1 gel 3% crosslinker)

This is because polyNIPA gels, prepared by adding a bifunctional cross-linker such as N,N'-methylenebisacrylamide (BIS), did not always appear to yield sufficient mechanical strength, when modified in order to increase their shrinkage velocity [15]. Methods used for this purpose include e.g., modification of the structure with a macroporous network [11] or introducing carboxylic side groups [16]: here, the increase of shrinkage rate is largely obtained at the expense of the mechanical strength of the structure. Also, the possible oscillation of NIPA gels in a limited range of hydration levels, as suggested in Figure 2, would lead to its possible working as a self-oscillating gel [17] with easy reversibility, possibly not even involving the application of an electrical field or a change in pH. The principle of this self-oscillation has been described in [1] for NIPA gels, but its real operation would need first the assessment of the mechanical properties in the gel. In this work, mechanical properties (bending and compression) of NIPA gels are studied at different hydration levels and for different cross-linking density, using N,N'-Methylenebisacrylamide (BIS) as crosslinker, and the effect of these two parameters is studied statistically. The possible operation of the braid-gel actuator described in [1] is finally briefly discussed.

2. METHODS AND MATERIALS

2.1 MATERIALS

A NIPA (N-isopropylacrylamide) based gel has been synthesised, according to the polymerisation process summarised in Figure 3a, using BIS (*N,N'*-Methylenebisacrylamide) crosslinker contents of up to 3%, which is known to improve the response rate of NIPA gels with a controllable crosslinking kinetics [18-19]. Chain termination occurs by cyclization of the inhomogeneous network at the amounts of BIS crosslinker used in this work, as reported in [20].

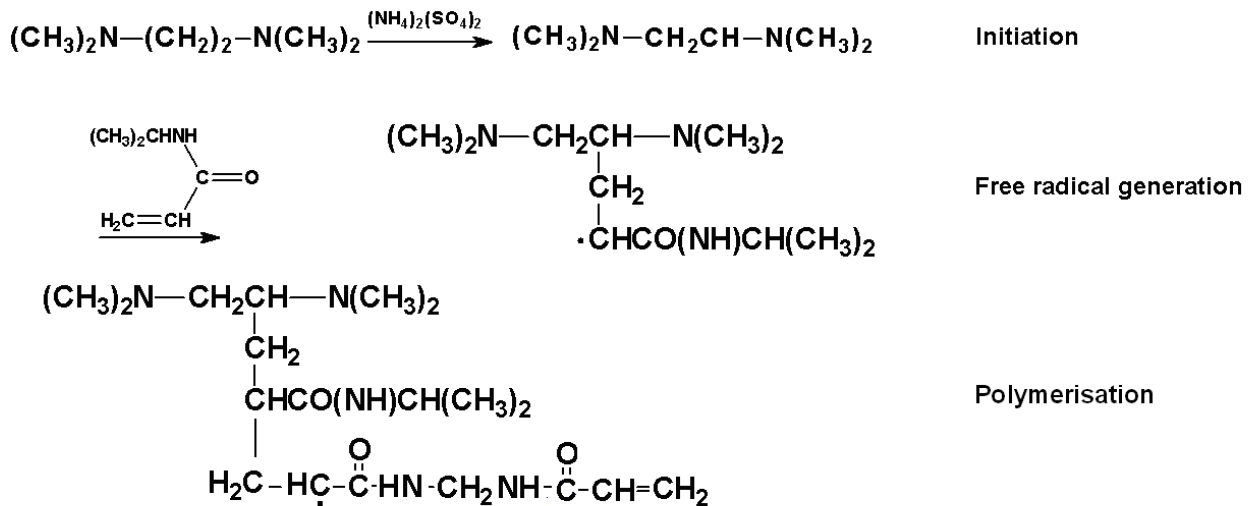


Figure 3. NIPA synthesis process

2.2 SAMPLES PREPARATION

The typical procedure involved dissolving the NIPA monomer (5 g, 44 mmol), BIS cross-linker (77 mg, 0.5 mmol) and free radical accelerator, *N,N,N,N*-tetramethylethylenediamine (58 mg, 0.5 mmol) in distilled water (35 ml). Glass capillaries were immersed in the solution followed by the addition of the initiator, ammonium persulphate (25 mg, 0.11 mmol). The reaction was left to stand at ~2°C for 12 hours. The resulting gel samples were washed and left to stand in "carbon dioxide-free" water for 24 hours, followed by further washings with water and hexane to remove residual monomer, cross-linker, accelerator and initiator. The aim was to shape the gel in cylinders and fibres, so to ease mechanical properties characterisation and allow an easier reversibility of the actuator operation for a high number of cycles. This gel showed the typical volume transition in the range of 32-34°C, which allowed rapid collapse of the gel, also of interest to produce fast reversible actuators [21].

To find the most suitable range of utilisation for gels in actuator, gel stiffness measurement was required at different levels of water dilution. With this aim, NIPA gels cylinders were manufactured (5.00 ± 0.75 mm. diameter, as measured just before testing under an optical microscope) with different water/gel ratios (7:1, 10:1, 12:1). With 12:1 water/gel ratio, also 1 mm diameter fibres were produced to allow for a comparison with the performance of cylinders having the same dilution. Water/gel ratios exceeding 12:1 appeared to compromise the mechanical resistance of the gel, which was no longer able to retain its geometry in the fully swollen configuration for a 5 mm diameter cylinder.

2.3 MECHANICAL TESTING

Mechanical tests were carried out on an Instron 5564 testing machine fitted with a 10 N load cell. For compression tests, cylindrical specimens of the different gels were sectioned to a height of (7.0 ± 0.7) mm. and tested in displacement control mode with crosshead speed of 5 mm/min, being compressed under a cylindrical pickled steel plate of 25 mm diameter and 10 mm thickness. Unconstrained compression tests were carried out on the fully swollen gel, and not by immersion in a solvent, to perform testing in conditions as close as possible to the real operational conditions of the actuator. Tests were then repeated at various intervals during gel natural drying at 23°C, up to 24 hours time, a time deemed more than sufficient to include the swelling interval of real application of the actuator.

The *linear modulus* of the gel was measured by intercepting the slope of the stress-strain curve in the first 10% strain or in the quasi-linear region, whichever was shorter, as proposed in [22]. The strain rate influence has also been evaluated by preliminarily testing samples of the same gels (7:1 and 12:1 both with 1% crosslinker) at different crosshead speeds (1, 5, 10 and 50 mm/min). These crosshead speeds, albeit too fast in general terms, were selected in a range suitable for the actuator operation. The crosshead speed of 5 mm/min yielded the lowest differences in the values of linear modulus between the samples, not exceeding $\pm 4\%$, and was therefore finally adopted throughout the compression tests.

Three-point bending tests have also been carried out on 5 mm diameter and 40 mm long gel cylinders, with a bending rig with 6.35 mm diameter cylinders separated with a 20 mm span, using a 1 mm/min crosshead speed. The value of shear modulus was obtained again via the method exposed in [22]. The gel was assumed as fully compressible (Poisson's ratio equal to zero), so that linear modulus was obtained by doubling the measured value of the shear modulus.

Compression tests were also carried out on gels during deswelling in isopropanol alcohol at room temperature: water-swollen gels were tested at the moment they had reached a definite shrinking, expressed as a relation with the original weight of dry gel.

2.4 STATISTICAL ANALYSIS OF COMPRESSION TEST RESULTS

The significance of the differences between average values in compression test values were determined according to Tukey's test, basing on a suggestion from [23]. The two considered factors were volume of crosslinker introduced and hydration level of the gel. In practice, three sets of results were compared: dataset G1 was obtained from samples of 10:1 gel with 1% crosslinker, dataset G2 from samples of 10:1 gel with 3% crosslinker and dataset G3 from samples of 12:1 gel with 3% crosslinker. Differences between G1 and G2 would indicate the effect of the change in crosslinker content and differences between G2 and G3 would indicate the effect of the change in hydration levels on the gel properties: differences between G1 and G3 would offer some indication on the combined effect of the two factors on the gel properties.

The comparison was performed on four mechanical parameters obtained from unconstrained compression tests. These were: *true rupture stress* $\sigma_u = [F(h_o - \Delta h)] / (A_o h_o)$; *true rupture strain* $\epsilon_u = \ln[h_o / (h_o - \Delta h)]$; *linear modulus*, as defined in Section 2.3; *deformation modulus* i.e., the ratio between σ_u and ϵ_u , where F is the maximum force applied in N, h_o the initial height of the specimen in mm, A_o the initial section of the specimen in mm², and Δh the height reduction of the specimen during the compression in

mm. The three sets were formed by 30 measurements each: every specimen was tested just once, and the four mechanical parameters obtained.

These data have been statistically analysed using a Tukey's test, hence a student's t-test corrected for error rate, obtaining an experimental value Q , equal to $(Y_A - Y_B)/SE$, where Y_A and Y_B are the two means being compared, and SE is the standard data error. This Q value can then be compared to a $q_{critical}$ value from the *studentized range* distribution [24]. If the Q value is larger than the $Q_{critical}$ value obtained from the distribution, the two means are said to be *significantly different*. All the calculations were performed using WINKS software by Texasoft, setting a probability coefficient for student's t-test at $p > 0.05$.

3. RESULTS

Compression tests carried out on the completely swollen gel allowed the measurement of the effect of water/gel ratio, crosslinker content and geometry on gel stiffness. The average values and standard deviation of linear modulus obtained for all the gels under investigation are reported in Figure 4. As expected, lower water/gel ratio and higher amount of crosslinker resulted in gels with slightly higher stiffness. However, due to the non complete homogeneity of gel cylinders, and to the solvent-free testing procedure adopted, a large scattering in values of compressive modulus was also observed. This suggests that, as highlighted in Figure 5, at 10% strain the gel could have variation in modulus of about an order of magnitude. This scattering is reduced, but still very significant at 20% strain, and it should be noted that this level of strain is reached only by a limited number of samples in unconstrained compression. As regards the statistical analysis of differences, the increase in crosslinker content from 1 to 3% leads to gels with higher strength and moduli, as shown by the higher difference between G1 and G2, whilst the effect of modifying the level of hydration from 10:1 to 12:1 is less evident, as shown by the lower difference between G2 and G3 (Figure 6). However, the large scattering in data obtained partially reduces the significance of the above results (Table 1), showing that the only meaningful difference in behaviour (Q greater than $Q_{critical}$) is relative to deformation modulus, which is consistently higher for highly crosslinked gel. In addition, it was important to measure the maximum possible deflection of the actuator: this was defined as the maximum deflection with no squeezing of the surface of the gel cylinder, which is still visually flat. This was in the order of approximately 11% on 7:1 gels, and just above 20% for 10:1 gels, with modest effect of the crosslinker content. The 12:1 gels showed the largest deflection prior to failure, in the region of 40%. The effect of the water/gel ratio was confirmed in the flexural tests results, reported in Figure 7. A decrease of water/gel ratio from 12:1 to 7:1 i.e., equal to approximately 42%, results in an average increase of flexural modulus exceeding 60%.

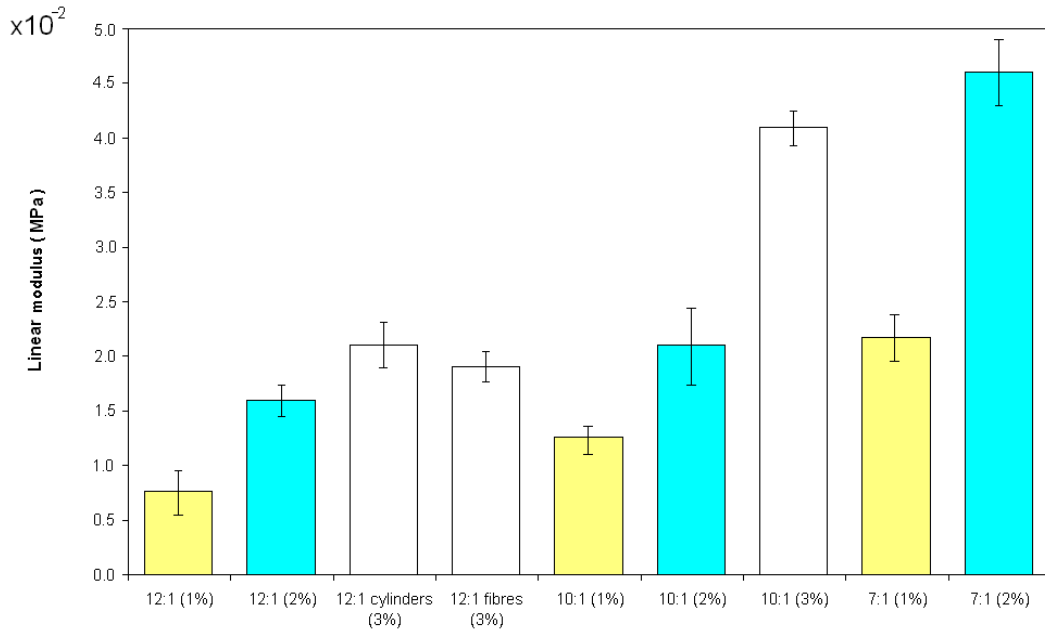


Figure 4. Unconstrained compression modulus for gels with different dilutions (water/gel ratio) and crosslinker content

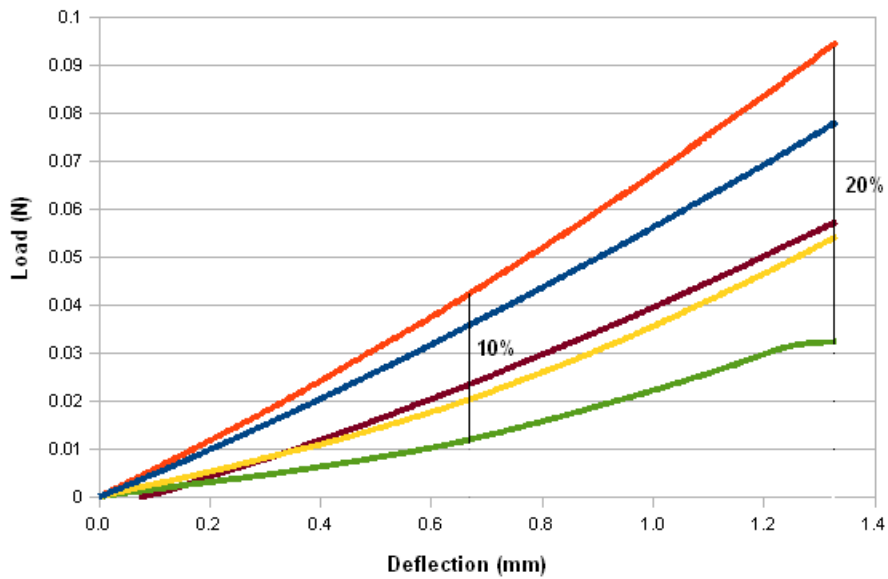


Figure 5. Scattering in compression linear modulus, measured by the slope of the load-deflection line, between different samples of 10:1 gel (1% crosslinker)

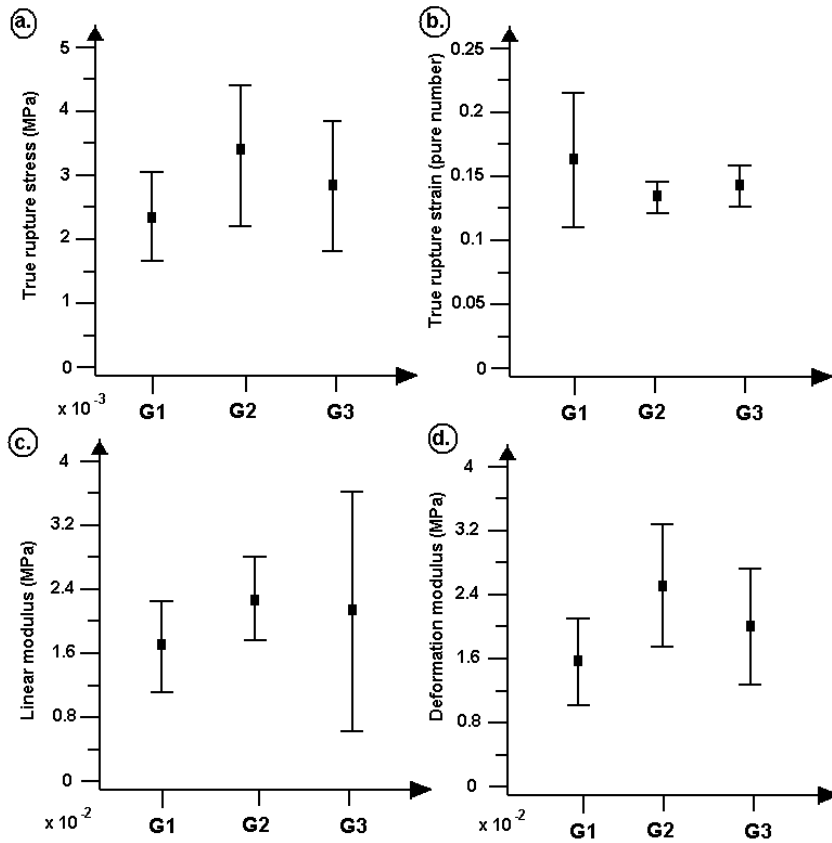


Figure 6. Mechanical parameters for statistical analysis G1: 10:1 gel (1% crosslinker) G2: 10:1 (3%) G3: 12:1 (3%)

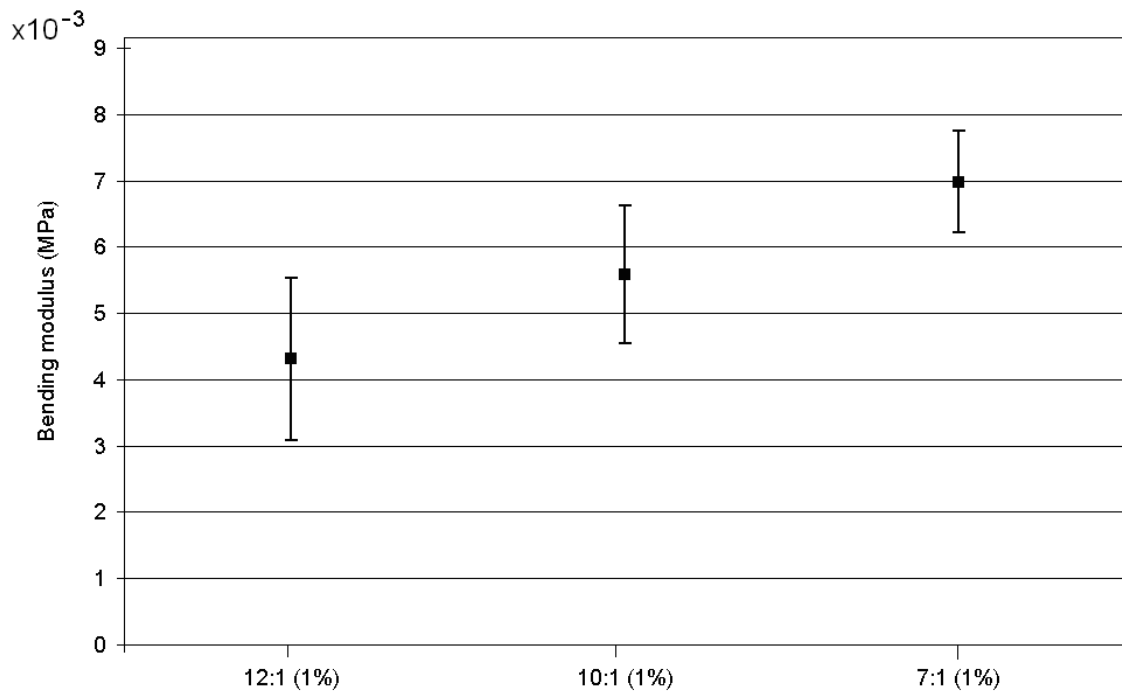


Figure 7. Bending linear modulus of gels with different dilution (average value and standard deviation over 30 tests)

Values of linear modulus for different levels of water content during deswelling of a number of gels configurations are reported in Figure 8. Here, linear modulus appears to be constant for a water/gel ratio (w/g) approximately exceeding 3, indicating that the gel is sufficiently soft above this level of hydration. Continuing the gel natural drying process, linear modulus is gradually increasing, until reaching a value in the order of tenths of MPa for completely dry gel. During deswelling, the gel is increasingly cloudy and inhomogeneous and gel cylinders tend to be inflected, because water is not uniformly desorbed. This is not surprising, because only a part of the water tends to be structurally linked inside the gel, whilst most of it is quite easily lost during gel drying. It has been found in effect that these gels consists of non uniform distributions of water-rich areas and polymer-rich areas, and that most of the mechanical properties variation could be ascribed to their visually inhomogeneous structure, which is shown in Figure 9 [25]. Typically, the variable intensity of scattered light on cross-linked hydrogels allows visualizing their inhomogeneous structure i.e, a mix of regions with relatively high polymer concentration with more diluted or swollen regions [26].

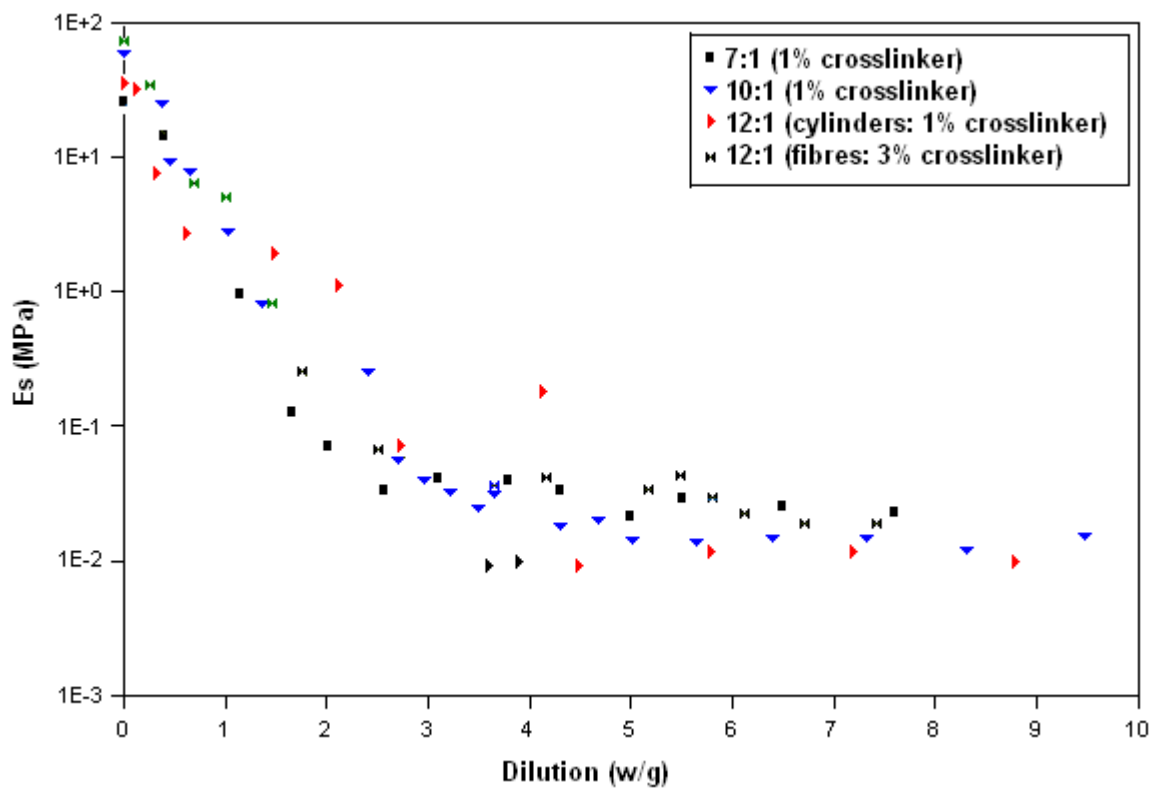


Figure 8. Compression linear modulus during deswelling for gels with different dilutions (water/gel ratio) and crosslinker content



Figure 9. Micrograph of a partially deswollen 7:1 gel (1% crosslinker) at approximately 5:1 dilution

From the above results, the continuous tension-compression operation of a 100 mm long actuator with 5 mm diameter at a dilution between 5 and 7 appear possible and surely reversible for shrinking of the gel cylinder not exceeding 15%, using the gel with intermediate dilution i.e., 10:1. It could be discussed in the design of the specific actuator whether it would be more sensible to obtain a stiffer gel using a lower water/gel ratio or rather a higher deflection of the actuator using a higher water/gel ratio. As a whole, a compromise between these two exigencies would be possibly needed. Moreover, it is also suggested that more emphasis could be placed on obtaining a more crosslinked and stiffer gel, in that the statistical analysis indicates that the effect of hydration level on the mechanical properties of the gel is not very significant, at least on limited hydration ranges (e.g., passing from 10:1 to 12:1). This could enable, in the two ideal conditions of fully stretching and complete braid filling [1], to obtain a total force approaching 0.1 N in a few seconds interval. In addition, the operation of large batteries of actuators would allow tailoring the force on the design requirements. Of course, future work in this regard will concentrate on further characterisation of the gel configuration selected for actuation, including e.g., fatigue testing and toughness measurements.

4. CONCLUSIONS

These tests confirm the effect of cross-linking on NIPA gel mechanical properties and suggest that operation of an actuator is possible in mechanical terms in a wide range of water dilutions, although operation in a limited range, possibly between a water/gel ratio of 5 to 7, would preferable in terms of reversibility. In particular, there is scope for reversible tension-compression operation of NIPA gel/braid actuators in a controlled range of dilutions: however, it is still difficult to control the mechanical properties of the gel in the real operational conditions for the actuator, especially as regards controlling the effect of gel hydration. It is suggested that it could be useful to dispose of a database of mechanical data, aimed at the goal of actuator design, on a wide range of hydrogels, to allow for comparison and optimisation of performance in terms of swelling-deswelling cycles.

References

- [1] Santulli C., Patel S.I., Jeronimidis G., Davis F.J., and Mitchell G.R., 2005, Development of smart variable stiffness actuators using polymer hydrogels, *Smart Materials & Structures* 14 (2): 434-440.
- [2] Meng H., Hu J., 2010, A brief review of stimulus-active polymers responsive to thermal, light, magnetic, electric, and water/solvent stimuli, *Journal of Intelligent Material Systems and Structures* 21 (9): 859-885.
- [3] Guo S.X., Fukuda T., and Asaka K., 2003, A new type of fish-like underwater microrobot, *IEEE-ASME Transactions on Mechatronics* 8 (1): 136-141.
- [4] Shahinpoor M., Bar-Cohen Y., Simpson J.O. and Smith J., 1998, Ionic polymer-metal composites (IPMCs) as biomimetic sensors, actuators and artificial muscles - a review, *Smart Materials and Structures* 7 (6): R15.
- [5] Maeda S., Hara Y., Sakai T., Yoshida R., and Hashimoto S., 2007, Self-walking gel, *Advanced Materials* 19 (21): 3480-3484.
- [6] Brock D., Lee W., Segalman D., and Witkowski W., 1994, A dynamic model of a linear actuator based on polymer hydrogel, *Journal of Intelligent Materials, Systems and Structures* 5 (6): 764-771.
- [7] Marra S.P., Ramesh K.T., and Douglas A.S., 2002, The actuation of a biomimetic poly(vinyl alcohol) –poly(acrylic acid) gel, *Phil. Trans. R. Soc. London* 360 (1791): 175-198.
- [8] Schreyer H.B., Gebhart N., Kim K.J., and Shahinpoor M., 2000, Electrical activation of artificial muscles containing polyacrylonitrile gel fibers, *Biomacromolecules* 1 (4): 642-647.
- [9] Kim S.J., Spinks G.M., Prosser S., Whitten P.G., Wallace G.G., and Kim S.I., 2006, Surprising shrinkage of expanding gels under an external load, *Nature Materials* 5 (1): 48-52.
- [10] Xue W., Hamley I.W., and Huglin M.B.; 2002, Rapid swelling and deswelling of thermoreversible hydrophobically modified poly(*N*-isopropylacrylamide) hydrogels prepared by freezing polymerisation, *Polymer* 43 (19): 5181-5186.
- [11] Strachotová B., Strachota A., Uchman M., Šlouf M., Brus J., Pleštil J., and Matějka L, 2007, Super porous organic–inorganic poly(*N*-isopropylacrylamide)-based hydrogel with a very fast temperature response, *Polymer* 48 (6): 1471-1482.
- [12] Tanaka T., Fillmore D.J., 1979, Kinetics of swelling of gels, *Journal of Chemical Physics* 70 (3): 1214-1218.
- [13] Corr D.T., Herzog W., 2005, Force recovery after activated shortening in whole skeletal muscle: transient and steady-state aspects of force depression, *Journal of Applied Physiology* 99 (7): 252–260.
- [14] Dai T, Qing X, Zhou H, Shen C, Wang J, and Lu Y, 2010, Mechanically strong conducting hydrogels with special double-network structure, *Synthetic Metals* 160 (7-8): 791-796.
- [15] Imran B.A., Seki T., Ito K., and Takeoka Y, 2010, Poly(*N*-isopropylacrylamide) gel prepared using a hydrophilic polyrotaxane-based movable cross-linker,

Macromolecules 43 (4): 1975-1980.

- [16] Ebara M., Aoyagi T., Sakai K., and Okano T., 2000, Introducing reactive carboxyl side chains retains phase transition temperature sensitivity in N-Isopropylacrylamide copolymer gels, *Macromolecules* 33 (22): 8312–8316.
- [17] Yoshida R., 2010, Design of self-oscillating gels and application to biomimetic actuators, *Sensors* 10 (3): 1810-1822.
- [18] Huang J., Huang Z.M., Bao Y.Z., and Weng Z.X., 2006, Thermosensitive poly(N-isopropylacrylamide-co-acrylonitrile) hydrogels with rapid response, *Chinese Journal of Chemical Engineering* 14 (1): 87-92.
- [19] Tobita H., Hamielec A.E., 1990, Crosslinking kinetics in polyacrylamide networks, *Polymer* 31 (8): 1546-1552.
- [20] Okay O., Naghash H.J., and Capek I., 1995, Free-radical crosslinking copolymerization: effect of cyclization on diffusion-controlled termination at low conversion, *Polymer* 36 (12): 2413-2419.
- [21] Ohmine I., Tanaka T., 1982, Salt effects on the phase transition of ionic gels, *Journal of Chemical Physics* 77 (11): 5725-5729.
- [22] Mrani I., Fras G., and Benet J.C., 1995, Microstructure et propriétés hygro-mécaniques du gel d'agar, *Journal Physique III France* 5 (7): 985-998.
- [23] Bayarri S., Izquierdo L., Durán L., and Costell E., 2006, Effect of addition of sucrose and aspartame on the compression resistance of hydrocolloids gels, *International Journal of Food Science and Technology* 41 (8): 980–986.
- [24] Lachenbruch P.A., David H.A., 1968, Non-central distribution of range and studentized range in normal samples, *Annals of Mathematical Statistics* 39 (3): 1092.
- [25] Appel R., Xu W., Zerda T.W., and Hu Z.B., 1998, Direct observation of polymer network structure in macroporous N-isopropylacrylamide gel by Raman microscopy, *Macromolecules* 31 (15): 5071-5074.
- [26] Gurtovenko A.A., Gotlib Y.Y., 2001, Dynamics of inhomogeneous cross-linked polymers consisting of domains of different sizes, *Journal of Chemical Physics* 115 (14): 6785-6793.