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Polymer Gel Actuators: Fundamentals

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1.1 Introduction and Historical Overview

One view of materials development is to search for what materials correspond to empty spaces on a hypothetical multi-dimensional map of the properties of available materials. Following a biomimetic philosophy, for instance, it can be seen that tough ceramics and moldable short fiber composites with high moduli are possible but absent from the list of available synthetic materials. Likewise artificial muscle is missing, where the properties are defined as a developed stress of over 300 kPa, a linear contraction of 25 % and a response time of below one second. Currently dielectric elastomers come closest but have disadvantages [1, 2].

The actin–myosin muscle system provides the performance target for electroactive polymer actuators [3, 4]. The process is driven chemically by the energy change from hydrolysis of the polyphosphate bond as ATP (adenosine triphosphate) binds to myosin and is converted to ADP (adenosine diphosphate) and phosphate. A simple chemical analogy suggests that muscle-like gels should be feasible but it is now clear that the task is much harder than it seems.

Early work on gel actuation by Katchalsky–Katzir demonstrated that engines could be built using the chemical energy in diluting a lithium bromide solution to drive contraction and expansion of a collagen belt [5]. In essence, the collagen expands to take up the salt solution or contract to exclude the water. This change is both a molecular conformation change and a volume change. Other chemically driven gels, for instance polyacrylic acid fibers [6] which respond to a pH change, also rely on a solubility change giving rise to a volume change.

Work by Osada and others explored electrically-driven actuators where pH changes at each electrode drive local volume changes [7]. While electrical power should be a more convenient way of driving artificial muscles, it has proved to be difficult to couple the electrical energy input to provide a mechanical output. As a result the achievable efficiencies for energy conversion are very low.

These systems driven by volume changes are rate-limited by the need for water or solvent to diffuse in and out of the gel. The force developed is also limited by the free energy associated with the change in solvent content. In this regard, the apparent analogy between muscle action and gel contraction breaks down. Muscle contraction is essentially a shape change driven by a conformation change. As such there seems to be no significant volume change and so no diffusion limitation. The energy source is dephosphorylation of ATP, which is also large compared to many solvation interactions. The fact that early work of Katchalsky used collagen, which so resembles muscle, may have been misleading. Subsequent work that has focused on similar artificial muscles has developed systems that are intrinsically too slow and too feeble to provide the force and speed associated with natural muscle.

In this chapter the properties and applications of current gel actuators are summarized and the developments needed to produce a true artificial muscle are discussed.

1.2 Properties of Gels

To be useful as actuators, gels must be stiff enough to exert the desired force and must be strong enough to carry the desired load. If the change in shape is caused by swelling, the fluid must flow into the gel in a short time. The transport of fluid will also be important to whether the actuator can be used without drying out. In addition, because gels cannot be readily machined or molded, it must be possible to form the gel into a suitable shape for an actuator by polymerization *in situ*.

If gels are to be used as actuators, they must be mechanically robust. Most current applications of gels are in food, pharmaceuticals and cosmetics where mechanical properties are not a major concern. Muscle as an actuator develops a force of about 300 kPa and a strain of 25 %. If these are regarded as target numbers, a gel actuator should be strong enough to easily withstand the force developed, and so the fracture strength should be at least 1 MPa. In addition, it should be stiff enough that, in lifting a weight for instance, an active contraction is not simply cancelled by passive extension under the load. If it is said that the passive extension should be less than one-tenth of the contraction, the elastic modulus would be greater than 12 MPa. While a low force gel actuator may be useful for some applications, such as a microfluidics valve, the mechanical requirements on a muscle-like actuator are quite demanding.

1.2.1 Biological Gels

In biology there are many examples of structural gels in the marine environment, including seaweeds and the bodies of many invertebrates, such as sea anemones. In the human body, cartilage, cornea, the dermis and arterial wall are all fiber-reinforced gels. Although soft and not very strong, these materials are very tough and so survive the impacts of life in motion better than many hard materials in machines.

Many biological tissues show a ‘J-shaped’ tensile stress–strain curve [8] that combines a low initial modulus with high strength. The reinforcing fibers initially rotate as the soft gel is stretched and then the fibers take up the load as they become parallel to the stress axis. Other variations occur depending on whether the fibers are bonded into a network. Unbonded fibers can flow with the gel under slow loading but give rigidity under fast loading [9].

Articular cartilage is a proteoglycan gel reinforced with about 20 % of collagen fibers. It has a strength of about 1.5 MPa and an extension to break of about 100 %. The structure is layered and the properties vary greatly with depth below the surface, with strength up to up to 30 MPa in layers with higher fiber contents [8, 10–13]. Costal (rib) cartilage has a strength of 5–7 MPa [14]. The large extension to break and large work of fracture (1 kJ/m^2) [15] allow cartilage to function effectively under impact even though the average strength is not high.

An unfamiliar aspect of the mechanical properties of gels is that they will tend to lose water under compression and take up water under tension. As a result, the mechanical properties will be different depending on the test speed. Thus the fast modulus of cartilage is 2.5 MPa while the equilibrium modulus, measured as water is displaced from the structure, is about 0.7 MPa [8, 12]. The transition between these two values will depend on sample size, as the water has to flow out of the gel. Likewise, testing under water will result in properties that differ from those measured in air.

Cornea is another tissue that is reinforced with collagen fibers. As with cartilage, there is an immediate need for a synthetic substitute to replace damaged corneal tissue. Cornea contains about 20 % of collagen fibers in a gel matrix. The fiber diameter is of the order of 20 nm, so that light is not scattered and the material is transparent [16]. The tensile strength is about 4 MPa and the elastic modulus is about 6 MPa at 20 % strain on the J-shaped stress–strain curve [17].

The properties of these soft tissues and marine gels suggests that a combination of a higher polymer content and fiber reinforcement should let us form materials which retain the responsive properties of gels whilst having sufficient mechanical strength to be used in engineering systems. As a target system, we could envision seeking a synthetic gel with a tensile strength of 5 MPa and an extension to break of 100 % but we do also need to develop a better understanding of the mechanical properties of gels.

1.2.2 Mechanical Properties of Simple, Single-Phase Gels

Because gels are weak and so do not currently have many synthetic applications, there is not a large coordinated literature on their mechanical properties. For many materials we can consider elastic modulus and tensile strength as sufficient to characterize the mechanical properties. The first of these reflects the rigidity or degree of bending under stress, the second the ability to withstand static stress without breaking or deforming irreversibly. For hard materials that have to withstand impacts, we are also concerned with the toughness, often measured as the energy absorbed in propagating a crack through the material. These concepts are substantially derived from the consideration of metals and ceramics where their stress–strain relationship is essentially linear up to about 1 % strain and then yield or fracture occurs. They serve well in most engineering situations where objects are designed to be rigid.

Many tissues operate in a different regime, where there are large reversible strains and substantial impacts can be tolerated without damage. In this case the energy needed to produce damage may be more important than the strength. The stress–strain curve may be very nonlinear and the shape of the curve out to large strains becomes important. The same is true of rubbery materials, but these are also not very familiar in structural engineering. Thus, engineering with gels will put us into a regime that is unfamiliar to many mechanical engineers.

1.2.3 Elastic Moduli

One view of a gel is as a modified rubber. The properties of amorphous polymers change dramatically above the glass transition point where the chains become mobile. Since polymer chains are mobile in solution and we think of a simple gel as a cross-linked solution, we can regard a single phase gel as a dilute rubber. Dense polyacrylamide, for instance, is a glassy polymer. We do not want to compare the gel properties with this state but with the same polymer as a cross-linked rubber above its glass transition.

Gels are soft materials, so we would expect elastic moduli to be below 10 MPa and we would expect the modulus to decrease as the volume fraction of solvent increases. As an example, a gelatin gel swollen to five times its dry weight, has a modulus of about 0.8 MPa and a fracture stress of about 70 kPa with an extension to break of 10 %. At a swelling of 40 times, the modulus is only 40 kPa and the strength 6 kPa with the extension to break 11 %. This soft, weak, brittle behavior is characteristic of most simple gels.

The initial elastic modulus of a nonionic gel can be derived from rubber elasticity theory as:

$$G = A \frac{\rho}{M_c} RT (v_2^0)^{2/3} (v_2)^{1/3} \quad (1.1)$$

where A is close to one, ρ is density, M_c is the average molecular weight between cross-links, v_2 is the volume fraction of polymer in the swollen gel and v_2^0 is the volume fraction in the gel as synthesized. Thus swelling after synthesis decreases the modulus relative to the G_0 , the modulus as synthesized [18, 19]:

$$\frac{G}{G_0} = \left(\frac{v_2}{v_2^0} \right)^{1/3} = V_r^{-1/3} \quad (1.2)$$

Many natural gels are highly charged polyelectrolytes. It might be expected that there would be a strong difference in modulus between otherwise comparable ionic and nonionic gels. For weakly charged groups (acrylic acid), charge seems to have little effect on elastic properties [20]. Other studies show that charged groups increase the modulus and decrease the dependence of modulus on swelling [21].

1.2.4 Strength

Synthetic gels, based on cross-linked soluble polymers, are mostly too weak to be used in any structural application. Many natural gel structures, such as are found in marine organisms, seem to be quite strong. As discussed next, possibly this difference arises from the microstructure of natural gels, which most synthetic gels lack.

In determining the strength of gels, there are important factors which can often be ignored in dense materials. Gels often fracture at much higher strains than conventional engineering materials, properties can be very time dependent and liquid may be taken up or lost during the test. Likewise, the properties of immersed gel samples differ from samples tested in air, as water is normally taken up in tension and exuded in compression. The degree of confinement and timescale of testing is also going to be important for the same reasons. At high compressive strains sample geometry will also be crucial, since friction at the platens will result in shear stresses which effectively put the sample into hydrostatic compression where failure cannot occur. Thus properties at high strain in compression must not be regarded as directly comparable to a true strength.

Most hard amorphous polymers under tension show brittle fracture. The strength, σ , is determined under the Griffith equation (Equation (1.3)) by the fracture surface energy, γ , which in turn mostly depends on the energy absorbed by the plastic deformation and void formation (crazing) that occurs immediately at the tip of the crack. E is the elastic modulus and c is the crack length:

$$\sigma = \left(\frac{2\gamma E}{\pi c} \right)^{1/2} \quad (1.3)$$

Since elastomers are essentially liquid polymers, the elastic modulus is low and crazing is not believed to occur. Most of the fracture energy probably goes into pulling individual chains out across the fracture and so the energy increases with the chain length between cross-links [22]. Fracture of rubbers does not follow the Griffith theory because of the higher extensions at fracture, but the role of fracture energy in limiting crack extension still applies. Most unreinforced elastomers lack significant energy absorbing mechanisms and so readily tear at any cut or notch.

Based on the comparison between gels and elastomers, we would expect the strength of unstructured gels to be lower than that of rubbers with a similar cross-link density by factors reflecting the dilution of the gel by water or solvent and reflecting the degree of pre-extension of the chain due to swelling by the solvent. We thus expect gels to be weak and to get weaker as they swell more.

There are exceptions to the generally low strength of elastomers where some energy-absorbing deformation can occur. One example is natural rubber, where the crystallization occurs under tension, resulting in increased stiffness at high stress and a large energy to fracture as chains slip through the ordered crystals. Large fracture energies are also obtained when diene rubber chains slip over the surface of reinforcing carbon black particles or through the hard regions of two-phase polyurethane elastomers. It may be possible to build similar energy-absorbing mechanisms into gels. Theoretical discussion of gel fracture has focused on gelatin gels, which are important in food. Both fracture mechanics and fracture energy approaches have been considered but understanding is still imperfect [23–25].

Synthetic gels based on acrylates are unstructured and so would also be expected to be weak. Natural gels, such as agarose [26] and the calcium alginates, do seem to form ordered regions of double helix or multiple helices [27–29]. As a result, the mechanical properties are very dependent on the extent of structure developed during gelation [30]. The disruption of these structures during fracture could be expected to be a source of energy

absorption and so increase strength and toughness. 2 % Agarose gels have a strength of about 0.14 MPa and a strain to failure of 40 %. In contrast, the strength of similar gelatin gels is about 1 kPa [31]. It is possible that similar ordered structures, to those in agarose, exist in gels of hydrogen-bonding polymers, such as hydroxyethylmethacrylate and vinylpyrrolidone, which do seem to be stronger than less polar synthetic gels.

One area where there has been a vigorous search for improved mechanical properties is in gels for contact lenses but there is no clear picture of what determines strength [32, 33]. Contact lenses have water contents of 30–50 % and strengths of 2–4 MPa [34]. Tests on vinylpyrrolidone gels with low water contents (30–40 %) gave strengths up to 2 MPa, which is in the range of cartilage and so could be considered adequate for construction of equipment [35]. On the other hand, contact lens gels made from mixed acrylic and vinylpyrrolidone monomers with 40–70 % water content have strengths from 100–600 kPa [36]. There is no simple relationship between polymer structure or water content and gel strength but gels based on vinylpyrrolidone do tend to be stronger. Work on cross-linked acrylic acid gels for microfluidics showed similar strengths, with a dramatic decrease as the gel was swollen at high pH [37]. A cross-linked copolymer gel of hydrophilic and hydrophobic segments was reported to have a strength of 200–500 kPa [38].

1.2.5 Multi-Phase Gels

Many gels are two-phase composite systems. Polyacrylamide gels are often quite turbid, suggesting phase separation into polymer-rich and polymer-poor regions. The cross-linked structure prevents large-scale separation, so unambiguous evidence for two phases is hard to obtain. Crystallizable synthetic polymers form solvent-containing gels, which apparently contain crystallites connected by segments of solubilized polymer chain. Similar combinations of regions of nanoscale order linked by disordered solution probably characterize many biological gels, such as gelatin, agarose and calcium alginate. In principle the phase behavior of a lightly cross-linked gel would be expected to be the same as that for a high molecular weight sample of the same polymer in the same solvent. Heavier cross-linking would restrict the entropy of the chain and might induce phase separation.

The search for an artificial cartilage material has long driven the search for strong gels. Various multi-phase systems have been found that are much better than simple gels but, until recent unexpected results on ‘double network’ gels, none have been strong enough to look really promising.

It has been known for some time that the properties of poly(vinyl alcohol) and mixed polyacrylic acid/poly(vinyl alcohol) gels can be enhanced by a series of freeze–thaw cycles that drive more extensive aggregation of the polymer [39]. Exactly what happens is unclear but growth of ice crystals will probably concentrate the polymer to the crystal boundaries and drive formation of insoluble hydrogen-bonded complexes of the polymers [40]. Addition of DMSO as a co-solvent enhances the gel strength, possibly by limiting ice crystal size. Early work on two-phase freeze–thaw modified neutral gels of poly(vinyl alcohol) mixed with cationic and anionic polymers found a strength of 1 MPa at 85 % water [41]. More recently, such poly(vinyl alcohol) gels with water contents of around 80 % were found to fail in compression at a few MPa [42]. This freeze–thaw process produces a two-phase composite structure which has recently been studied in more detail [43, 44]. Composite gels with poly(vinyl alcohol) and other water-soluble polymers have also been studied [45].

There have been many recent studies of composite gels made by irradiation of mixed solutions of polymers and increases in strength have been reported when compared to single polymer gels [46]. It would be expected that the properties of these disordered systems would primarily follow the water content.

A number of studies have considered reinforcement of gels with inorganic fibers or plates both added before gelation and grown *in situ* in the gel and a significant increase in modulus is certainly seen [47–49]. With exfoliated clays as reinforcement, moduli increased from 4 to 20 kPa as the clay was added and the tensile strength increased from 0.1 MPa to 0.3 MPa [50–52].

One very attractive approach, based on the analogy to collagen-reinforced biological gels, is to reinforce gels with fibrils of rigid-rod polymers [53]. This particular system does show a significant increase in modulus but from very low values and no strength data was given. Thus the full potential of composites of this type has yet to be fully explored. A simple variant of this approach is to reinforce a gel with a textile, such as non-woven polypropylene [54, 55].

1.2.6 Double Network Gels

Gong *et al.* [56] have formed gels with compressive strengths up to 17 MPa at 90 % water content by forming an interpenetrating network of ionic and nonionic gels in a two-step process (Figure 1.1). This compares with a strength of 0.2 MPa in compression for the equivalent single-component gel. These gels are produced by forming a moderately tightly cross-linked network, then swelling this gel in a solution of a second monomer with a low ratio of cross-linking agent and carrying out a second polymerization. As a result of the high degree of swelling in the monomer solution, the first gel network is highly extended in the final product while the second network is relaxed. The weight fraction of the second network in the final gel is 10–20 times that of the first network.

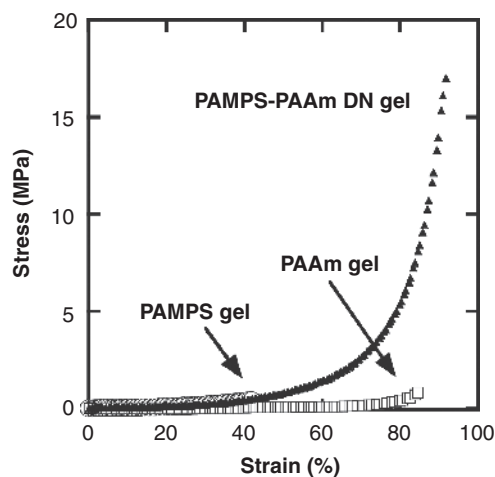


Figure 1.1 Stress–strain curves from DN gels show much higher strength than conventional gels (Reprinted with permission from Gong, J. P., Katsuyama, Y., Kurokawa, T. and Osada, Y. *Double network hydrogels with extremely high mechanical strength*, *Advanced Materials*, **15**, 1155–58, Copyright (2003) Wiley-VCH Verlag GmbH).

Other gels with a more lightly cross-linked first network show yield and necking in tension with extensions to break over $10 \times (1000 \% + \text{strain})$ and a strength of 0.3 MPa [57]. Using a tear test, a fracture energy of 300 J/m^2 was measured, compared to $0.1\text{--}1 \text{ J/m}^2$ for conventional gels [58]. Yield is characteristic of metals and semicrystalline polymers where molecular slipping sets in at high stresses. It is not normally seen in rubbers or gels where the permanent cross-linked network prevents slippage.

While strength was greatly increased by the addition of the second component, the initial modulus was affected little when compared to a conventional gel at the same concentration. If these double gels are made with a linear polymer in place of the second network, the fracture strength and fracture energy rise steeply at a molecular weight over 10^6 , where the second polymer becomes highly entangled and these entanglements can act as physical cross-links [59]. Cyclic loading tests do show hysteresis, with a loss of modulus after successive cycles to high strain. This implies that breakage or other irreversible loss of some highly strained cross-links is occurring [60].

Other workers have found similar enhanced strengths in poly(ethylene oxide)–polyacrylic acid double network gels [61, 62]. These gels have tensile strengths which range up to 12 MPa depending on composition and swelling. Molecular dynamics simulations have been carried out for these PEO–PAA gels and show that the elastic modulus rises suddenly at strains of about 100 % where the first network becomes fully stretched [63]. This combination of high stress with a large strain to break increases the fracture toughness.

Other interpenetrating networks, formed without the extension of the first network, have not shown similar improvements in strength. For instance HEMA–gelatin gels reach strengths of 65 kPa, just slightly above gelatin alone [64] and polyacrylamide/poly-N-isopropylacrylamide IPN gels reach strengths of just 10 kPa [65]. Templating gels on a colloidal crystal and then removing the colloid has also been reported to give good toughness, although the modulus and strength remain low [66]. Reinforcing polyacrylamide gels with a rigid-chain polyelectrolyte does lead to a large increase in modulus [53].

Shull has recently emphasized that there is a need to develop better understanding of fracture toughness in these double network gels and in biological gels [67]. The preceding discussion also shows that microstructure control can lead to greatly enhanced strength and toughness in gels. Improvements obtained by double networks, by freeze–thaw and by fiber reinforcement suggest that there are many possible routes to better properties. A J-shaped stress–strain curve, that is an increase in elastic modulus at high strain, seems to be one signature of better toughness and strength. In this view, cartilage is a similar cross-linked network of collagen microfibers with a second network of coiled proteoglycan chains that can absorb fracture energy. Thus it seems that modulus and strength of networks can be separately controlled in order to design suitable mechanical performance into any functional matrix [68]. A useful objective for future work would be to develop some design rules.

1.2.7 Transport Properties

Many potential applications of active gels, as muscles, for drug release or as sensors, depend on their ability to respond to external influences by changing volume or shape or by taking up or releasing small molecules. If this responsiveness is not important, their mechanical properties can be duplicated by a range of dense elastomers and there is no

reason to employ a gel. Small molecule transport properties are thus crucial. Since drug release has been well discussed earlier [69], the focus here is on the faster diffusion times appropriate for sensing and actuation.

It would be expected that diffusion coefficients of small solutes in gels should be intermediate between those in solution and in an elastomer. The diffusion coefficients of solutes in dilute gels have been measured and do not differ dramatically from those in solution [70]. Diffusion processes in gels can also be conveniently studied by conductivity [42]. For low levels of soluble small molecule additives in an elastomer, the diffusion coefficient can be estimated from the properties of the polymer and the size of the molecule [71]. At the other extreme, of a highly swollen hydrogel, the diffusion of water and of soluble compounds in the water have been shown to be reduced roughly in proportion to the water content of the gel.

A significant difference will result when the diffusion process causes swelling or deswelling of the gel. The resulting nonuniform volume changes through the gel will result in highly non-Fickian behavior and may also cause significant internal stresses or fracture. Tanaka and co-workers [72] studied many of these interactions. As gel concentration changes in a single-phase gel, diffusion and solubility of a solute will change, such that the resulting changes in permeability can be quite complex. Two-phase gels will be even more complicated and so should be a source of many complex changes in release or uptake of solutes.

In building a gel based machine, it will probably be equally desirable that the gel can swell and deswell over a range without dramatic changes in the properties of the surface region. This requirement imposes a coupling of effective sample size, diffusion rate and response time on any gel device. The self-diffusion coefficient of water is $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and diffusion times can be roughly estimated as $x^2/2D$, where x is the effective half-thickness of the gel. This gives a response time for a gel one millimeter thick of about one minute, which would probably be the longest acceptable response time for many devices.

It is clear that any responsive structure that is larger could have a finely divided sponge-like structure that allows for fluids to flow in and out through channels rather than simply diffusing. If a hypothetical microstructural scale of 100 microns thickness is adopted, a diffusion coefficient of about $3 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ can be accepted in a working device.

1.2.8 Drying

Engineering materials are generally dry and there is a reluctance to use materials that may lose liquid and dry out. However, we do work with systems that need to retain liquids, such as foods, cosmetics, paints and inks. Our experience with houseplants suggests that it would be quite possible to develop long-lived systems that depend on occasional replenishment of a water reservoir if there were desirable and unique properties. This survey of recent work on gels focuses on whether it is possible to reach a combination of mechanical properties, stability and activity that would allow more use of gel devices and structures.

Drying time is also clearly an issue in gel devices. The evaporation rate of water is very dependent on temperature, humidity and air flow but measurements on drying of snails give a rate of about 100 microns/h as typical for still air with an active snail

being able to reduce this by about 20-fold by maintaining a surface coating [73]. If some similar mechanism was available to gel devices with a size of about one centimeter, they would experience 10 % water loss in a week and so would need only occasional rehydration.

1.3 Chemical and Physical Formation of Gels

While linear polymers can be purchased in bulk and processed in the melt or solution to the desired form, cross-linked gels must be chemically formed *in situ*. Gel actuators will have to be built as systems containing multiple layers or material, structured pores and electrodes. Processing methods that lend themselves to building these systems must be available. Many gels, are chemically cross-linked like vulcanized rubbers and this limits our ability to process shape them. Just as thermoplastic elastomers have allowed an expansion of the range of applications of rubbery materials in complex shapes, so meltable gels, like agarose, can be more readily shaped than chemically cross-linked gels.

Most of the work on synthetic gels uses gels formed by free radical polymerization of the families of hydrophilic acrylate, methacrylate and acrylamide monomers plus vinylpyrrolidone. While these methods give a very versatile family of hydrogels, it is worth noting that the polymers are atactic or otherwise irregular and this limits formation of any microstructure that might give rise to toughness. Also, free radical polymerization is oxygen sensitive and this can make it difficult to get good control of the polymerization in small or air-exposed devices. For these reasons, it may be valuable to explore other approaches to forming synthetic hydrogels.

The kinetics of free radical linear polymerizations has been thoroughly studied [74] and the relationships between molecular weight distribution and polymerization conditions are well known. Gels are made by incorporating a small fraction of bi-functional or multi-functional monomers that becomes part of more than one kinetic chain so that a network forms. The statistics of network formation are also well known.

Two factors act against being able to make reproducible samples of muscles. These reactions are very sensitive to small amounts of impurities as well as oxygen, and these can be difficult to control in small samples. In addition, the structure of a network is much more difficult to characterize in detail than is a linear polymer. As a result, it is hard to know what is the real structure of a gel sample and usually they are not characterized to any significant extent.

Many gel samples are formed by UV irradiation. Quite reproducible samples can be formed by irradiation of de-oxygenated samples held between glass plates under conditions where the UV is only slightly attenuated as it passes through the sample (Figure 1.2). On the other hand, samples made in air under strong UV will tend to have structures that change properties through the thickness and many residual unpolymerized chain ends in the network.

The reaction kinetics will depend on the water content of the monomer solution during polymerization. This, in turn, will affect the network structure and so the swellability of the final gel network. Many studies of gel actuators use gels with low cross-link densities that show very large equilibrium swelling. To get good mechanical properties, it is preferable to work with gels that are more like contact lenses and only swell to become about 50 % water at equilibrium.

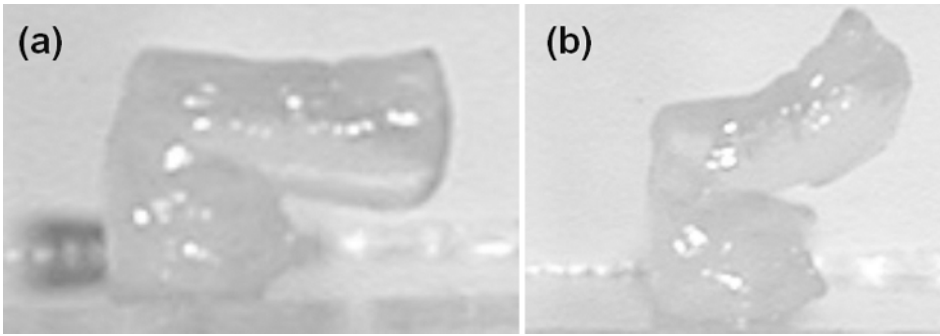


Figure 1.2 Gel microcantilever in water before (a) and after (b) UV irradiation (Reprinted with permission from Watanabe, T., Akiyama, M., Totani, K. et al. *Photoresponsive hydrogel microstructure fabricated by two-photon initiated polymerization*, *Advanced Functional Materials*, **12**, 9, 611–4, Copyright (2002) Wiley-VCH Verlag GmbH).

To avoid the oxygen-sensitivity problem, Yoshioka and Calvert studied epoxy hydrogels for small artificial muscles and sensors (Figure 1.3) [75, 76]. Water-soluble polymers and hydrogels have also been made by ring-opening metathesis polymerization [77–80]. It would also be expected that it is possible to form stable hydrogels based on polyamides and other polymers formed by condensation chemistry that might form tough microstructures.

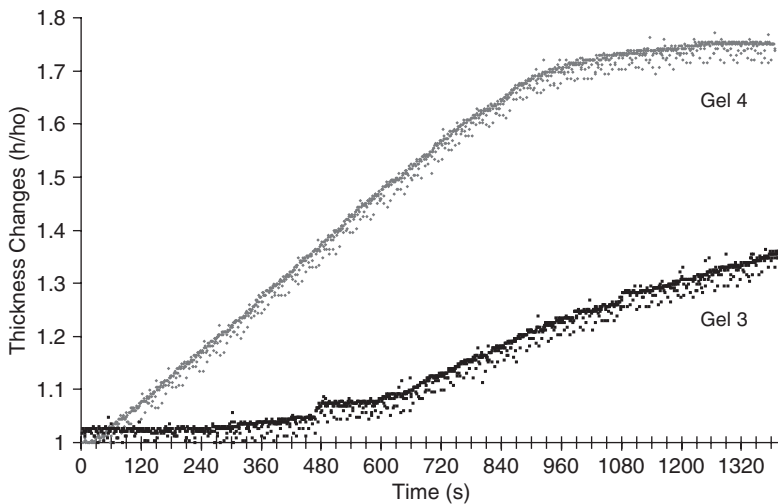


Figure 1.3 Swelling–collapse behavior of two epoxy gels in 0.01 M NaCl at pH 4.3; gel dots are printed on the platinum plate, which contacted the anode side. Average dot diameter (d_0) was approximately $460\ \mu\text{m}$ and the initial thickness (h_0) was $130\ \mu\text{m}$. Applied voltage was 6.0 V and current was 3.6 mA (Reprinted from dissertation work of Y. Yoshioka, Courtesy of University of Arizona).

It has long been known that many pairs of polymers self-assemble to form gels through inter-chain bonding. Gelled capsules can be formed by dripping a solution of cationic polymer into a solution of anionic polymer [81, 82] or by dripping alginate into calcium [83]. This process results in a thick-walled capsule with a nonuniform structure. There is no way of simply mixing the two components so that a uniform block of material is formed. Ionic self-assembly by sequential dipping into anionic and cationic polymers [84] or by repeated contact printing [85] does produce uniform thin films of ionic gels in a more controlled fashion. While these systems have been shown to have many potential applications, there has been little work on the structure and properties of the gels themselves. One structural study is from Lewis *et al.* [86] where a fine capillary was used to make micron-scale 3D structures by extruding a stream of solution into water at a pH that induced gelation (Figure 1.4). Such writing systems could be used to make a wide range of gel microdevices.

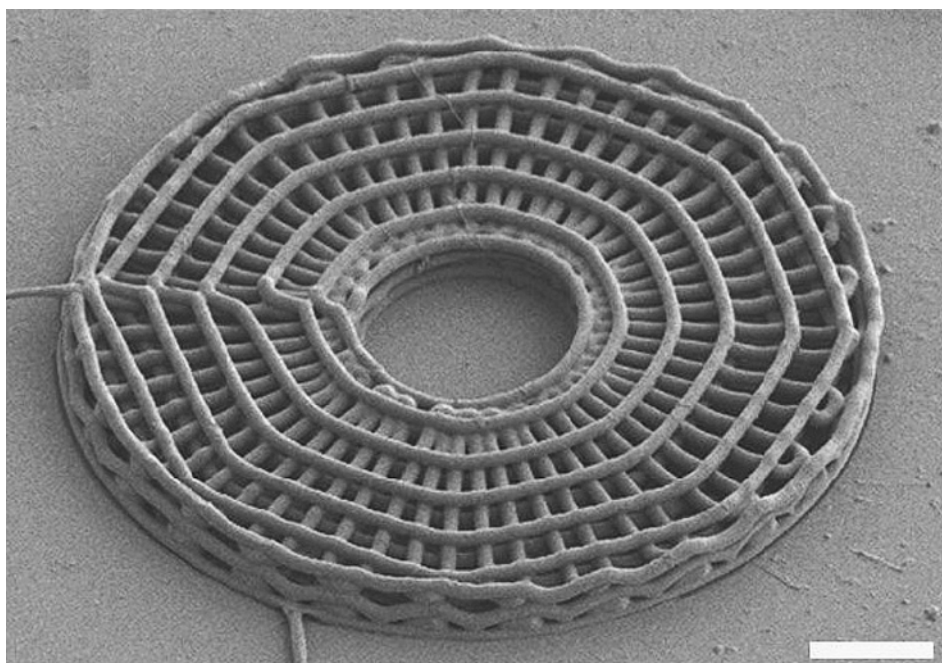


Figure 1.4 Printed polyelectrolyte complex filaments, written with a micron-sized nozzle. Scale bar = 10 μm (Reprinted with permission from Gratson, G. M., Xu, M and Lewis, J. A. *Microperiodic structures: Direct writing of three-dimensional webs*, *Nature*, **428**, 386, Copyright (2004) Nature Publishing Group).

Natural proteins form structures by a combination of ionic interactions, binding to multivalent cations and hydrogen bonding. It is possible to design synthetic proteins to form similar structures [87–89] and demonstrate that they gel. Thus there would seem to be considerable opportunities for better characterization of gelation of synthetic ionic

polymers and for the study of more structured synthetic gel systems formed by other polymerization chemistries. This should lead to a better understanding of the whole structure–mechanical properties map for gels.

1.4 Actuation Methods

The merit of a muscle-like actuator depends on a fast response time, a high contractile force and a large actuation strain. The state of swelling of a gel is dependent on temperature, solvation and pH. These factors may in turn be influenced by the application of chemical changes, light, heat, electrical and magnetic fields. The most desirable way to control a gel actuator is via an electric field but electrically driven actuators have so far produced little force. The simplest form of control, for understanding the response, is to change the temperature.

1.4.1 Thermally Driven Gel Actuators

Polymer chain coils in solution will undergo conformational changes as the temperature changes [90]. In many cases, the coil contracts as the temperature is raised until the solution separates into polymer-rich and dilute phases at the lower critical solution temperature (LCST). A homopolymer gel with a low density of cross-links is thermodynamically similar to a solution of very high molecular weight polymer. Thus, the gel will contract under conditions where the linear polymer coils contract. Tanaka studied this process in gels using the concepts of phase transitions and distinguishing between gels which show a continuous change from the expanded to the contracted state and those which go through a phase separation [91].

Poly-N-isopropylacrylamide (NIPAM) solution in water precipitates above 40 °C, so NIPAM gels have provided the most fruitful example of a thermally driven phase change. A swollen cross-linked NIPAM gel deswells at the same temperature, 40 °C. Homopolymer gels show a discontinuous phase transition while copolymer gels with ionizable groups such as acrylic acid can show a continuous transition or critical point behavior. Having resolved the thermodynamics of the system, the kinetics of the phase change become important.

The kinetics of gel swelling can be treated as a two-step process. Solvent diffuses into the gel causing some regions to swell and then there is an instantaneous shape change to minimize the elastic energy between the swollen and unswollen regions. For swelling involving small changes in volume in the continuous region of the phase diagram, the kinetics and dependence on the gel shape correspond to those expected for diffusion of solvent. Thus the response time of a long acrylamide gel cylinder 1.3 mm in diameter was about one hour, in agreement with a theory based on the coupling of the diffusion coefficient of water in the gel and the shear modulus of the gel [92]. In the two-phase region, or where there is a large volume change, the changes in diffusion coefficient and gel properties with the local state of swelling will lead to complex kinetics which depend on the details of the initial and final gel states.

A number of workers have addressed the diffusion time by making the gels porous, so that simple diffusion only occurs over a small distance. The effective diffusion rate can be

linked to the degree of porosity [93]. For instance, polymerizing the gels under reduced pressure produces a macroporous gel that responds to temperature changes in a few minutes, about 10 times faster than normal gels [94]. After freeze drying this porous gel had an apparent pore size of 20 microns although the actual structure prior to drying was not studied. Viewed as an actuator, these porous systems have the disadvantage that the forces developed will also be reduced as the porosity increases. Polymerizing gels in the presence of poly(ethylene oxide) also yields porous, fast-responding gels [95], as does polymerization of gels on micron-scale liquid templates [96].

A related, second approach to increasing response time is to prepare a two-phase gel so that a nonresponsive matrix can allow fluid flow into and out from the gel. This has been shown for solutions of linear NIPAM as a block or graft copolymer with poly(ethylene oxide) [97]. The collapsed, precipitated state of the graft copolymer is more open than pure NIPAM and so allows more rapid water penetration and redissolution when the temperature is decreased. This type of approach addresses the problem that a rapidly shrinking gel tends to form a dense skin that inhibits water loss from the interior, both slowing the volume change and possibly leading to fracture of the gel under the resulting shrinkage stresses. The effect of such skin formation on deswelling kinetics has been studied by Hirose and Shibayama, who showed that pure NIPAM gels form a dense layer and shrink much more slowly than weakly charged copolymers of NIPAM and acrylic acid that retain more mobility for water in the collapsed state [98].

NIPAM has been most widely discussed but other aqueous gels are also thermally responsive, including poly N-vinylcaprolactam (PVCL) and hydroxypropylcellulose (HPC) [99]. In the unswollen (high temperature) state, PVCL is much stiffer than in the swollen state and resembles a glassy polymer, whereas in HPC the modulus decreases as it shrinks.

These thermally driven gels have been widely studied with a view to use as actuators or in drug delivery. While the volume change is large, the response is slow, primarily because water must diffuse into and out from the gel. In addition, rapid heating may be quite easy to achieve but it can be difficult to cool the gel rapidly in any practical fashion. The stress developed on shrinkage can be estimated from a knowledge of the relationship between elastic modulus and degree of swelling, as discussed below.

1.4.2 Chemically Driven Gel Actuators

While electrical actuation would be the most practical method to control and drive gel actuators, gels primarily respond to the chemistry of their environment and so chemical actuation has proved to be the most efficient method to drive gel actuators.

Muscle is a chemically driven actuator where the energy of the ATP to ADP conversion is used to drive a cyclic shape change in myosin that causes it to 'walk' along actin filaments. From the viewpoint of building an artificial muscle, it is important to note the points that:

- i. the energy to drive this process in the short term is stored locally in the cells as glucose and oxygen;
- ii. muscle develops force only while it is burning energy and will passively extend once the cells cease to produce ATP. It does not move between two states as gels do.

Thus the analogies between real muscle and chemically contracting gels are not as close as they might seem [3, 4, 100].

In most cases the source of chemical energy for gel actuators is either a change in pH or a change in solvent. Many gels are based on cross-linked polyacrylic acid. The linear polymer is very soluble in water at pH values above about five where it is in the ionized form as a sodium or other salt. At low pH, below four, the acid form predominates and is only slightly soluble in water. Repulsion effects between adjacent ions on the polymer chain cause the pH range over which the polymer goes from the acid to salt form to be much wider than for a simple acid such as acetic acid [90]. The chain is also much more extended due to Coulombic repulsions in the salt form. The chain extension is sensitive to the ionic strength of the aqueous solution, since other ions in solution will screen the repulsions and allow the chain to coil. In terms of the phase transition treatment of Tanaka discussed above [72, 101], both commonly used gel muscles, polyacrylic acid and polymethacrylic acid, are soluble in water at all pH values and so the acid to ionized change is a continuous phase transition in water. In mixed solvents the change can be discontinuous.

The response of polyacrylic acid and polymethacrylic acid gels to changes in pH and solvent have been widely studied [102]. Other acid gels [103] and chitosan gels [104] have also been studied. However, the number of systems explored only represents a tiny sample of the potential range of chemically actuating gels. These two monomers can be easily copolymerized with a wide range of other monomers to form gels with different solubility characteristics. It can be expected that: addition of a more hydrophobic monomer will induce phase separation at low pH; addition of a strongly ionized monomer, such as a sulfonated monomer, will limit shrinkage at low pH; and addition of a neutral water soluble monomer, such as hydroxyethylmethacrylate, will limit the maximum swelling at high pH. These remarks apply to random copolymers. Graft or block copolymers could be made with a wide range of responses to pH, ionic strength or solvent.

An amine-functional monomer such as aminoethylmethacrylate can be expected to respond as a mirror-image to the acidic gels, swelling at low pH and expanding at high pH. Yoshioka and Calvert have studied the response of epoxy–amino gels [75, 105]. Amine gels could also be formed with a wide range of comonomers. One interesting but little-studied case is amphoteric gels containing both amino and acid groups which may be swollen in acid, in base or in salt solutions [106–108].

Other chemistries may also be used to reversibly change the properties of hydrogels. Thus, gels with reversible disulfide cross-links have been studied [109–111]. Reversible metal-ligand cross-links with a self-repairing function have also been described [112]. Suitable modification of these systems could also be used to form chemically driven actuators.

In most studies, pH is adjusted by exchange with a mineral acid such as hydrochloric acid and sodium hydroxide. Ammonium and potassium counter-ions would be expected to act very similarly but lithium or divalent ions, such as calcium, will not result in such large solubility changes. Lightly cross-linked gels with more than about 20 monomer units between cross-links will be expected to act as a polymer of infinite molecular weight as it responds to the medium by expanding and contracting. Higher cross-link densities will decrease the tendency of the gel to swell, both by limiting the extent to which the chains can coil and uncoil but also by limiting the solubility of the chains.

Gels with more acidic side groups, such as sulfonated gels, will be less responsive because very low pH would be needed to deionize the gel. Phosphated gels would be expected to show several ionization steps but have not been much studied. In addition to

acid gels, gels with amine side groups respond to pH. They show a mirror of the behavior of acids, contracting in strong base but ionizing and expanding in acid [75].

Gels will also expand and contract as a result of being moved between water and a water-miscible organic solvent such as acetone. The expansion and contraction of the gel reflects the solubilization and precipitation of the equivalent linear polymer in the solvents.

The best performance of chemically driven gels is by polyacrylonitrile fibers which are partially converted by heat and alkali to cross-linked polyacrylic acid fibers. Previous work has shown that these can be made into muscle-like actuators that respond to pH changes with good force and strain characteristics [6, 113]. The good characteristics of this material arise because the spun fibers are oriented and so the swollen gels are stronger than unoriented gels. Orientation must also affect the actuation properties but this does not seem to have been studied. Also, the fibers have a small diameter and so respond rapidly to pH changes.

Recent work has found that commercial poly(acrylonitrile) (PAN) yarns treated in this way could give actuator strains of about 80 % and stresses of 100 kPa to 1 MPa with a response time of about 10 seconds [114]. The same fibers can be driven electrically at 5 V, using an electrode embedded in or adjacent to the fiber, to produce similar stress but the response time is much longer, about 10 minutes [113, 114]. Electrospinning has been used to make fibers of less than one micron diameter that could then be twisted into yarns [115]. Actuator strains of 38 % were obtained in cycling from pH 1 to pH 12 with a response time of about five seconds. The authors claim an actuator stress of about 10 kPa but the data presented suggest this value is actually closer to 1 MPa. Other similar stiff synthetic gels have also developed higher forces in response to chemical activation [116].

Actuation that relies on pH changes has the advantage that hydrogen ions diffuse rapidly. In biology, changes in calcium ion concentration often drive changes in molecular conformation. Forisomes, plant proteins responsible for opening and closing of leaf pores, produce a force of 11 kPa in response to calcium and pH [117]. An actuator based on changes in copper ion concentration has been described [118]. As the copper was oxidized to Cu^{2+} and reduced back to copper metal, the gel contracted and swelled. The oxidation and reduction could be driven chemically or electrochemically.

1.4.3 Gels Driven by Oscillating Reactions

Several groups have recently studied self-oscillating gels that swell and contract cyclically in response to an oscillating chemical reaction in the medium. Yoshida and co-workers have demonstrated patterns of contraction in NIPAM gels that cycle through the lower critical solution temperature (LCST) as the gel cycles between two oxidation states [119]. Yashin and Balasz have modeled the moving patterns of expansion and contraction set up in these gels [120]. Jones and co-workers have used oscillating pH reactions in the liquid surrounding an acidic block copolymer to drive a gel motor [121, 122]. However, their calculations of power density for these gels do give very low values. This approach does suggest that it might be possible to use an electrical signal to set off such a chemically driven oscillation. This would be a good mimic of natural muscle, where an electrical impulse triggers chemically driven contraction of the muscle.

1.4.4 Light Actuated Gels

With the availability of powerful LEDs and solid state lasers, light would seem to be an excellent way of communicating with gels in order to drive actuators or read out from sensors. Light can be used to heat an absorbing gel and cause a shape or volume change. Light could also be used to change pH in order to produce a volume change in a gel. Gels can also be made with light-sensitive groups that undergo a chemical conversion that results in a shape change. So far none of these systems has shown a strong enough response to be attractive as an actuator.

Light can also be used as a heat source to swell and deswell thermally-sensitive gels. Suzuki and co-workers showed that a NIPAM gel containing copper chlorophyllin, a soluble dye derived from chlorophyll, can be induced to swell and contract as the light is turned on and off [123]. A copolymer of NIPAM with sodium polyacrylate showed similar behavior but with a large hysteresis, such that the gel could be switched to the unswollen state at high intensity but would remain in either the swollen or unswollen state over an intermediate intensity range [124]. Similar bi-stable behavior was shown with pH or temperature. In principle, this type of bi-stable switching would be of interest for many applications. The bi-stability was analyzed in terms of a Landau model for phase transitions and might also be viewed as relating to skin effects. In lieu of a dissolved dye, a similar response to heating from a near-IR laser was obtained in NIPAM gels containing dispersed gold nanorods [125]. Beebe and co-workers have produced gels containing gold nanoparticles that respond by swelling on absorption of selected wavelengths of light and so act as valves to open or close channels in a microfluidics system [126]. Similar gold-hydrogel composites also show a change to becoming electrically conducting as the collapse [127].

The photoisomerization of azobenzene between the *cis* and *trans* forms is well known and gels containing attached azobenzene units have been shown to respond to UV illumination by stiffening [128]. Leucocyanides are photoresponsive dyes that convert between ionized and unionized forms on irradiation with light and cause osmotic swelling and contraction of a gel [129]. Marder and co-workers developed a hydrogel that responds to UV irradiation with a keto to enol tautomerization that results in mechanical deflection of a cantilever [130]. Nitrocinnamate chemistry has been used to create a hydrogel which can be reversibly photocross-linked and photocleaved [131].

A copper cross-linked polyacrylic acid gel, containing titanium dioxide particles, has been shown to swell under UV light and contract again in the dark [132]. A similar system with silver-coated titanium dioxide has also been described [133]. The volume change is large but the response time is hundreds of minutes.

1.4.5 Electrically Driven Gel Actuators

A recent review [134] of electroactive gels focused particularly on polyelectrolyte gels based on cross-linked polymers of acrylic acid. Such acidic hydrogels can show a large volume change in water as the pH changes from acidic to basic and the gel becomes ionized.

A pair of electrodes in a suitable salt solution will produce hydrogen at the cathode and oxygen at the anode. This results in decreasing the pH at the cathode and increasing pH at the anode. A pH-sensitive acid gel will thus shrink if it is attached to the cathode in a

solution at neutral pH. Depending on whether one or both electrodes are embedded in the gel or are in the surrounding solution, a gel may shrink, expand or bend [135, 136]. Several groups have demonstrated actuation by these gels, while immersed in solution, with embedded or external electrodes. Osada and co-workers made gel ‘loopers’ that would crawl along a bar between electrodes [137, 138].

Shiga and co-workers carried out an extensive series of studies on poly(vinyl alcohol)–polyacrylic acid gel actuators driven electrically (Figure 1.5) [136, 139–143]. These gels are prepared by a freeze–thaw method that produces a strong and highly porous structure. A ‘fish’ was made that would swim along a channel between external electrodes (Figure 1.6) [39]. Although the forces are small, such gels can be used to transport ‘cargo’ as they expand and contract in a tube [144].

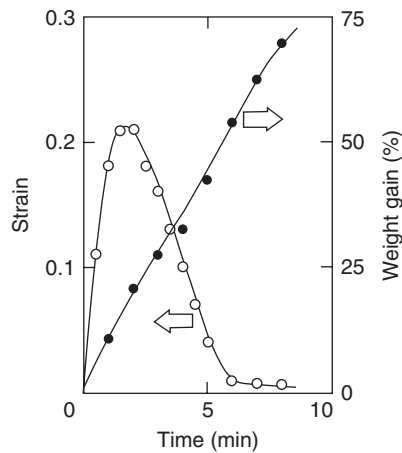


Figure 1.5 Strain in bending and weight gain of poly(vinyl alcohol)–poly(sodium acrylate) composite hydrogel under an electric field of 10 Vcm^{-1} (Reprinted with permission from Shiga, T., Hirose, Y., Okada, A. and Kurauchi, T. Bending of poly(vinyl alcohol)-poly(sodium acrylate) composite hydrogel in electric fields *Journal of Applied Polymer Science*, **44**, 249–53, Copyright (1992) Wiley-VCH Verlag GmbH).

Natural muscle undergoes a linear contraction. A single-component gel placed symmetrically between electrodes will bend as one side expands and one contracts. A combination of layers of two different gels that expands and contracts in a linear fashion when the cathode is embedded in one layer and the anode in the other has been demonstrated [145]. This can be achieved by having gels of opposite ionic charge or by having a high modulus contractile gel layered onto a soft neutral gel. In this second case, as the stiff gel contracts the water is pushed into the neutral, soft gel and this expand in thickness.

Almost all gel actuators work in solution or with embedded electrodes but gels have been demonstrated which respond to large electrical fields in air [146]. The gels showed a crawling motion driven by electrostatic response of the gels to the applied field.

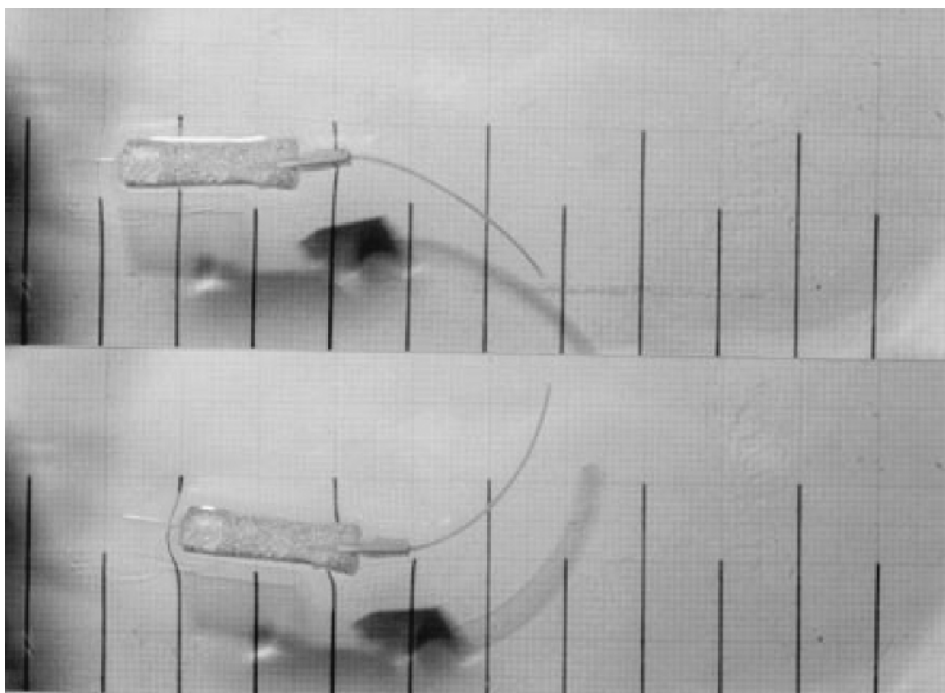


Figure 1.6 An ‘eel’ gel of PAMPS moving in an oscillating electric field (Reprinted with permission from Osida, Y., Okuzaki, H. and Hori, H. A polymer gel with electrically driven motility, *Nature*, **355**, 6357, 242–4, Copyright (1992) Nature Publishing Group).

1.4.6 Electro- and Magneto-Rheological Composites

Recently there has been much interest in composites of magnetic particles in a soft matrix which respond to a magnetic field by a change of shape and properties [147]. These materials are the elastomeric equivalents of magneto-rheological fluids and electro-rheological fluids.

The prototypical system is a dispersion of 25 % of micron-sized iron particles in gel of silicone rubber and silicone oil but polyurethanes and other rubbers have been investigated. When cured in a magnetic field the particles form chains [148]. After curing, the stiffness of the material increases in a magnetic field. At a strain of 5 %, an increase in stress of about 50 % is seen in a field of 123 kA/m (1500 Oe). In a study of magnetostriction, a field of 800 kA/m (1 Tesla) produced a strain of 0.3 % in a sample preloaded in compression to 100 kPa, a strain comparable to magnetostrictive alloys (Terfenol-D) [149]. These materials also show an electric field response if they can be formed to be nonconductive [150]. A shear stress of a few kPa can be produced at a field of 1 MV/m.

A study on barium ferrite particles in carrageenan hydrogels showed a modulus decrease of about 75 % (from 20 MPa) on magnetization at 800 KA/m [151]. Strains of about 0.2 % could be produced in these gels. This effect is clearly not the same as that seen in the iron-filled elastomers since it is larger, in the opposite direction and irreversible.

1.4.7 LC Elastomers

Liquid crystalline (LC) elastomers show a contraction on heating from the nematic to isotropic phase and so can be pictured as actuators [152, 153]. Similar behavior can also be seen in liquid crystalline gels [154], which opens the possibility for combining electrical switchability, the shape change associated with liquid crystalline elastomers with the volume change associated with gels [155, 156]. Similar changes have been demonstrated in hydrogels [157]. These systems can deliver rapid large shape changes, stresses of 130 kPa have been reported for thermal actuation [158], which is enough to be useful as actuators.

1.5 Performance of Gels as Actuators

The performance of muscle has been measured well on scallop [159]. Muscle is characterized by a response time of less than one second. The maximum actuator stress is about 300 kPa at a mid-point of contraction, corresponding to about 12 % shortening. The maximum strain is 25 %. The energy density of muscle is about 50 kJ.m⁻³. The power output is 200 W/kg peak or 50 W/kg for sustained cyclical contraction. Reaching or exceeding these characteristics is now the goal for an artificial muscle system.

Unlike many mechanical systems, muscle uses power as long as stress is needed to hold a static position. As a result, the normal mechanical concept of efficiency is hard to apply. For instance, the position of the arm may be held by balanced force between a muscle pair trying to extend and contract the elbow. No motion occurs, but considerable energy is expended in this isometric exercise. As a result, discussions of efficiency can be misleading, since the conditions of measurement need to be well defined.

The actin–myosin system is essentially the only type of actuator in animals but there are a few other examples of muscle-like tissues. The jelly bodies of jellyfish, sea anemones and other sea animals contain proteoglycan hydrogel, elastic fibers, collagen and muscle fibers in various arrangements [160–162]. The sub-micron reinforcing fibers are loosely connected to the matrix and so provide strength at high extensions and slow the viscoelastic response of the tissue [8]. In sea cucumbers, starfish and other echinoderms, the mechanical properties of the gel can be quickly changed from soft to hard. This was thought to occur by release of calcium ions to harden the polyanionic matrix but actually seems to be due to the release of proteins that temporarily bond to and cross-link the collagen fibrillar network [163]. This response is essentially a change in elastic modulus, as opposed to an active contraction such as is characteristic of muscle.

In legumes, specialized cells open and close to control fluid flow in the vascular system of the plant. These ‘forisomes’, which are 30 microns in diameter, contract in response to calcium ions in about 50 milliseconds and develop a force of 11 kPa [117]. The available energy density has been estimated at 0.5 MJ.m⁻³, which is close to what would be needed for an artificial muscle [164], and preliminary tests have been made of forisomes in a microfluidic system [165]. It may be that this system will provide a better model for artificial muscle than the much more complex actin–myosin system.

The target performance characteristics for a biomimetic muscle would be a response time of about one second, an actuator strain of about 25 % and a developed stress of about

300 kPa. In the absence of any current good answers, any approximation to these values would be of interest. At present, the only systems that approach this are the converted PAN fibers acting as chemical actuators.

The actuation stress for a gel of known elastic modulus can readily be estimated. Consider, for example, a gel that initially contains about 50 % water. This is a much lower water content than most experimental hydrogels but is similar to a contact lens formulation and would have an elastic modulus in the region of 1 MPa [36]. Assume the gel will act as an actuator in compression, by pushing a weight upwards. A change in thickness of 25 % would correspond to a volume change of $2\times$, assuming width, length and thickness change equally. To develop a substantial force at this new thickness, the volume change would have to be greater, for instance to $3.4\times$, which corresponds to an unconstrained thickness change of 50 %. Using the equation for modulus and swelling above, the elastic modulus will have dropped to about 660 kPa at this swelling. When this swollen gel deforms elastically back to a thickness of 25 % greater than the original value, the stress generated will be 165 kPa. In contrast, more lightly cross-linked gels, with water contents of 90 % or more, have moduli of a few kPa and can exert little force in this format [166]. This then shows that an elastic gel, acting as an actuator in tension or compression, can only generate a substantial force if the elastic modulus is quite high and the water content relatively low.

The swelling pressure exerted by these dilute gels can be much higher than the modulus [20, 166]. This can be up to hundreds of kPa at low degrees of swelling but drops rapidly as the polymer swells toward equilibrium. Ionic gels show higher swelling pressures under conditions where they are charged [21]. To use this to drive an actuator, the gel would need to be confined, for instance in a rigid cylinder with porous walls and a moveable piston. It should also be possible to exploit the swelling pressure in a suitable composite structure or oriented structure where swelling is free along one axis but is very constrained in the other two directions. Some of the marine animal structures, with reinforcing fibers wound spirally at an angle to one axis, may fulfill this requirement by only allowing expansion along one axis.

These preceding arguments apply however the change in gel swelling is brought about, whether through thermal, chemical or electrical energy input. Thermal activation provides a convenient method for driving the actuator, which can clearly be engineered by a number of different routes. Cooling will be very slow for actuation occurring at 40 °C but a higher temperature could allow both rapid heating and cooling. Nonetheless, the associated systems for removing heat could add substantially to the weight and volume. It is also not clear that the phase changes necessary for thermal actuation can occur in gels at the high solids loadings needed to produce a significant stress.

Hinkley *et al.* report an estimated maximum work achievable by the thermally driven PVCL gels of $1 \text{ MJ}\cdot\text{m}^{-3}$ of dry gel, considerably higher than that for poly(vinyl alcohol) gels and comparable with muscle [99]. However, the response is very slow. This maximum work reflects the higher mechanical strength of these gels. In many other gels, the mechanical work done by thermal actuation is small because the gels have a low elastic modulus and low strength. A measure of the efficiency of these gels as actuators or transducers is the mechanical energy density and the power density, the rate at which energy can be delivered. Gels driven by solvent-induced contraction have achieved 135 J/kg but only 2 W/kg, which compares with 70 J/kg and 100–200 W/kg for muscle that is in turn similar to the energy storage density of a lithium battery (Figure 1.7) [167].

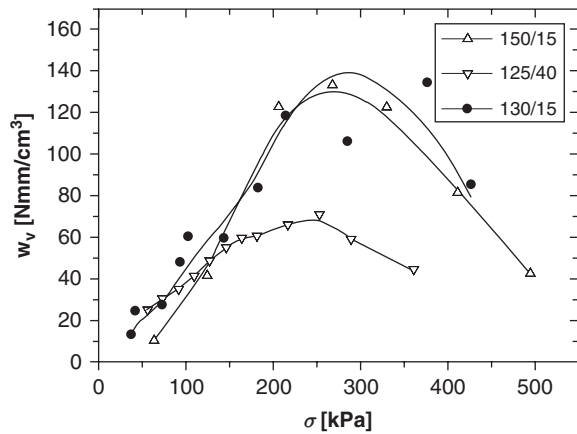


Figure 1.7 Working energy of poly(vinyl alcohol)/poly(acrylic acid) hydrogels, cross-linked under different conditions of temperature/time, versus applied stress (Reprinted with permission from Arndt, K., Richter, A., Ludwig, S. et al. *Poly(vinyl alcohol)/poly(acrylic acid) hydrogels: FT-IR spectroscopic characterization of crosslinking reaction and work at transition point*, Acta Polymerica, **50**, 383–90, Copyright (1999) Wiley-VCH Verlag GmbH).

Chemical actuation, as discussed above, can give a response with acceptable force, strain and speed parameters but has the drawback that delivering the fluid reagents requires inconvenient amounts of associated pumping and piping. In this context the human body can be viewed as a large amount of muscle with a roughly equal amount of piping to provide the driving energy and a supporting skeleton.

Electrical actuation may be much more convenient in principle but brings a further set of engineering problems. The current flow necessary to ensure expansion or contraction of a gel can be estimated on the basis of the number of ions that must be inserted or removed to convert from the acid to the ionized state, of a carboxylate gel for instance. One gram of acrylic acid gel at 50 % by weight of water, contains 7 mM of acid groups, which corresponds to 670 Coulombs or 11 amperes for one minute. Any practical system will thus demand substantial currents, which in turn places requirements on the conductivity of the surrounding liquid. If the associated electrode reactions also produce gas, there will be 75 cm³ of gas produced per gramme of gel switched.

The previous estimate assumes that all the ions generated at the anode react with the surrounding gel. This is probably true if the electrodes are far apart, so that the acid generated at the anode and the base generated at the cathode do not diffuse but essentially remain in separate compartments. However, this wide separation will add to the volume and weight of the system and reduce the current flow at any given potential difference.

A further design problem is that the electrodes themselves must be flexible enough to expand and contract without significantly restraining the volume changes of the gel. This can be achieved with flexible wire electrodes or some other type of soft electrode system.

Thus, in the two-gel multi-layer system made by Liu and Calvert [145], the performance is still constrained by current flow and the ability of the gels to contract and expand over

the wire electrodes. Likewise, the performance of electrically driven PAN fibers is quite inferior to that of similar fibers chemically driven [113] and it is hard to retain stability of the electrodes as the fibers cycle.

The electrical response of many soft actuators has been demonstrated as a bending beam. Typically, a strip of gel will bend in alternating directions as the potential difference across the gel is cycled. These thin sheets typically show a fast response and large deflection. However, the actual strain in the surfaces of the gel can be quite small. It is less obvious how to assess these bending actuators as a muscle-mimic but one measure is the blocking force, the force delivered at the end of the actuator, as a fraction of the weight of the actuator. Ionic Polymer–Metal Composites (IPMCs), for example, can deliver a blocking force of about $50\times$ the weight of the sample [168]. Muscle in linear contraction would deliver about $300\times$ its own weight. The elastic modulus of most experimental gel actuators is so low that the blocking force also will be very low.

Earlier work showed that the response of gels in an electric field depends on the composition of the gel itself, whether the gel is touching the electrode and on the composition of the solution [135]. More recently a number of finite element models have been developed to calculate the response of a gel to an electric field (Figure 1.8) [169–171]. These have the advantage of being able to take into account all the competing effects and provide a prediction for the response of a gel actuator under any conditions.

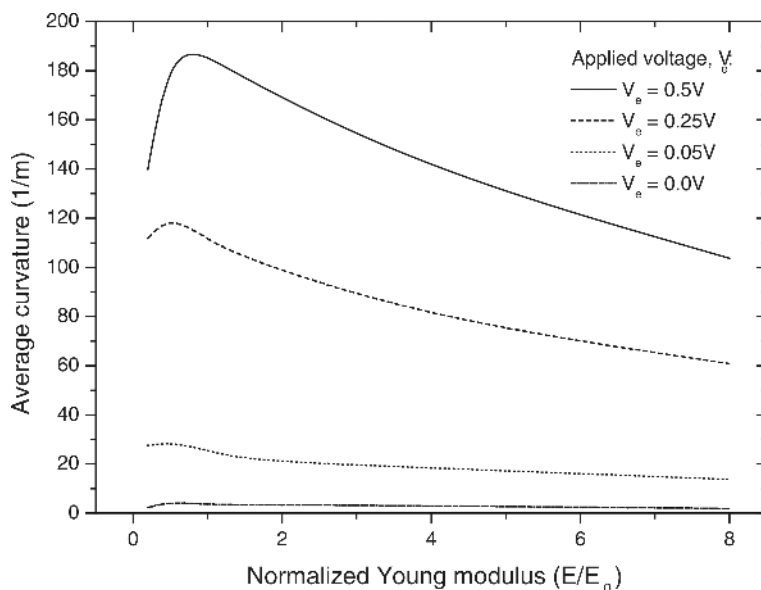


Figure 1.8 Bending curvature of hydrogels in an applied field, effect of gel modulus [200] (Reprinted with permission from Li, H., Ng, T. Y., Yew, Y. K. and Lam, K. Y. Meshless Modeling of pH-Sensitive Hydrogels Subjected to Coupled pH and Electric Field Stimuli: Young Modulus Effects and Case Studies, *Macromol. Chem. Phys.*, **208**, 1137–46, Copyright (2007) Wiley-VCH Verlag GmbH).

It should be remembered that the chemical changes can both cause volume and stiffness changes, such that the results of combining pH changes and applied force can be unexpected [172]. This coupling between swelling thermodynamics and mechanical stress leads to a number of other peculiar phenomena, such as negative Poisson's ratios [173–175], and may result in strange responses to complex loads, such as bending.

Thus the challenge for gel actuators is to devise a practical solution to the whole system. Three possible approaches are:

- Develop a chemical actuator with a compact and reliable supply of the needed chemical energy, not necessarily depending on acid and base.
- Develop a thermal actuator based on expansion against a piston of a gel within a porous but rigid enclosure, similar to an automobile radiator thermostat.
- Develop a two-compartment fine scale electrically driven gel muscle as an extension of the electrically-driven PAN fibers.

1.6 Applications of Electroactive Gels

Recent papers have explored producing faster responses by inducing porosity into the gels. While the application as artificial muscles is not practical, low stress applications, such as sensors and valves, are possible [176]. Lenses and light modulators have been demonstrated recently [177, 178].

1.6.1 Gel Valves and Pumps

Active gels have been developed as valves for microfluidic systems, where swelling of the gel in response to light, pH, thermal or electrical stimulation can be used to close a fluid channel or act as a pump [37, 126, 176, 179–181]. Electrically driven gels essentially respond to local changes in pH or ionic strength caused by electrolysis of the water [179, 182]. Bassetti *et al.* show that, at high electrical fields, there is a fast response due to ion migration within the gel and then a slower response due to pH changes in the solution as hydrogen ions are released from the anode. These effects were also seen by Shiga and co-workers [136]. In a flowing system, the hydrogen ions are swept away and so only the fast response to ion migration in the gel remains. Advantages of this type of application are that large forces are not needed and the response time could be several minutes.

1.6.2 Light Modulators

A series of papers have described light modulators based on the temperature driven shrinkage of colored N-isopropylacrylamide in a second gel matrix [178, 183, 184]. As the colored particles expand at lower temperature, they extract water from the surrounding matrix and occupy most of the volume, thus cutting off light transmission (Figure 1.9). Clearly, an electrically driven system based on temperature or pH change could be constructed.

Thermally responsive systems have also been developed for use as optical modulators. Particles of pigmented NIPAM gels are embedded in a dilute host gel that is selected to

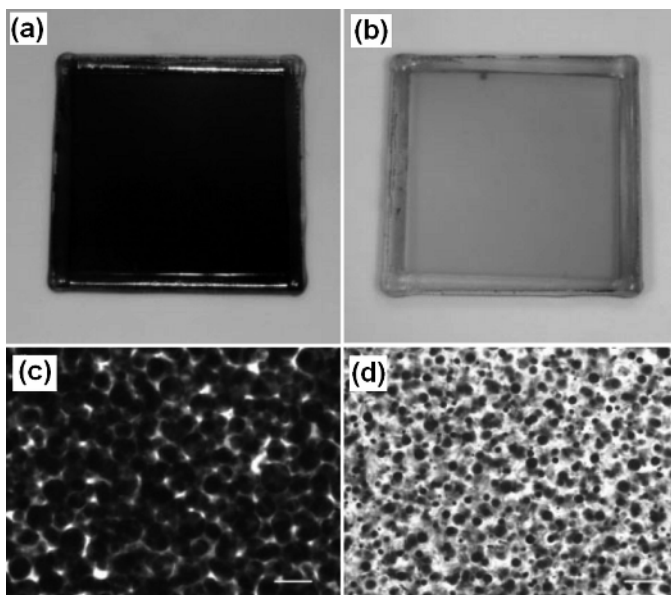


Figure 1.9 A gel-in-gel thermally driven light modulator at 20 °C (a, c) and 60 °C (b, d) (Reprinted by permission from Tsutsui, H., Mikami, M. and Akashi, R. All-polymer-gel light modulator consisting of a 'gel-in-gel' system, *Adv. Mater.*, **16**, 1925–9, Copyright (2004) Wiley-VCH Verlag GmbH).

allow ready exchange of water with the particles without opposing osmotic forces. The external gel must also be formed by cross-linking a polymer precursor in order to avoid forming an interpenetrating network with the gel particles. An external temperature increase results in a decrease in the absorbance of a thin sheet of the gel composite within one second as the particles shrink and the pigment becomes more localized [178, 183, 184].

1.6.3 Gel Drug Delivery

Controlled drug release has been a subject of intense academic interest for many years. The bulk of commercial controlled release systems depend on pH sensitive release in the stomach or intestine. The matrix polymer may also dissolve or swell slowly to allow sustained release. Similar controlled-release systems may also be used to release flavors in food and rinks or to release fragrances during laundry or cleaning processes. Most such systems are essentially solid polymers because hydrogels would normally release the active small molecule too rapidly for most applications. This has changed in recent years as methods are developed to deliver much larger and sensitive protein and peptide drugs. These drugs also tend to be active at very low concentrations, so there is less need to produce high loadings of the drug in the matrix.

Among the niche applications now being considered for hydrogels are the protection of protein drugs in the digestive system, adhesion of drug delivery patches to the mucus membranes and the protection of nanoparticulate drugs from the immune system [185].

The fact that the swelling and contraction of these systems can be driven electrically, as discussed above, means that there are potential applications for adhesive patches [186] or implanted gels with electrically-triggered release. The thermo-responsive gels have been suggested for drug eluting stents, and here too an electrical mechanism might be used to trigger the temperature change and release [187].

1.6.4 Gel Sensors

Many biochemical sensors depend on enzymes immobilized at an electrode surface, such that an analyte reacts to produce a compound that is readily oxidized or reduced at the electrode. Hydrogels bound to the electrode surface can be used to immobilize the enzyme without deactivating it [188]. In this case the gel is acting as a passive matrix but there are also systems where the responsiveness of the gel drives the sensing process.

Gel-coated silicon microcantilevers can be used to detect swelling in response to changes in pH or other species [69, 189, 190]. Changes in swelling can also be sensed by attaching the gel to a pressure sensor. Sensors can also be based on fluorescence changes in sensitive molecules in the gel [191], on volume changes of gel particles changing the diffraction angle from a colloidal crystal [192, 193], by color changes in a gel hologram [194, 195] and other responses [196].

Sensors have been made which depend directly on the electroactivity of the gel. Glucose sensors have been made based on the binding of glucose by phenylboronic acid attached to a gel, where the change in ionic conductivity of the gel is measured as the binding reaction changes the swelling of the gel [197, 198].

Although the biocompatibility of gels is not an electroactive property, it should be noted that they may be important for implantable sensors. Many sensors have been developed that work well on implantation but almost all surfaces become coated with proteins and lose sensitivity over days after implantation [199]. Many gels are known to resist protein binding and may be able to protect implanted sensors and electrodes.

A colloidal crystal contains an ordered array of sub-micron particles that will diffract light at an angle that depends on the spacing of the particles, following Bragg's law. If the array is in a gel matrix, any volume change by the matrix will change the particle spacing and the diffraction angle, and so can be used as the basis of an optical sensor. This effect has been studied by many groups since the original work by Holtz and Asher [193, 192, 189].

1.7 Conclusions

In just over 40 years since Katchalsky's demonstration of a collagen engine, useful gel actuators remain elusive. A number of recent developments offer hope that this problem will be resolved before too long. Good chemically driven actuators can be made although they are not very practical for machinery. There have been significant advances in the understanding of gel responses to electrical fields and in the design of gels with superior mechanical properties. The challenge now is to design an electrochemical system that provides a suitable reversible chemical change to drive a gel and a mechanical design that

subdivides the gel enough to give a rapid response. Problems such as this have been solved in the battery field many times, but with much greater inputs of researchers' effort than have been applied to gels.

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