

REVIEW

Mechanical properties of hydrogels and their experimental determination

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By their nature, hydrogels are highly swollen solids which are water-swollen, cross-linked, hydrophilic polymers. The properties of a specific hydrogel are extremely important in selecting which materials are suitable for a given application. However, these same properties are highly dependent on the environmental conditions. With this combination of factors, it is imperative that hydrogel properties are determined and that they are measured under conditions which are as close to the *in situ* conditions as possible. In this work we will explore methods for analysing mechanical properties and their dependence on polymer structure, specific methods for testing hydrogel properties, and parameters that affect hydrogel properties.

The mechanical behaviour of hydrogels is best understood using the theories of rubber elasticity and viscoelasticity. These theories are based on time-independent and time-dependent recovery of the chain orientation and structure, respectively. By using theories to describe the mechanical behaviour, it is possible to analyse the polymer structure and determine the effective molecular weight between cross-links as well as elucidate information about the number of elastically active chains and cyclization versus cross-linking tendencies. It is also possible, and sometimes necessary, to use theories to extrapolate mechanical properties to conditions in which the material may be used. In many instances it is not possible to test the hydrogel under the exact conditions in which the device is used. For these applications it is of particular importance to use theories to extrapolate properties to these conditions.

In addition to theories for network behaviour, we focus on outlining specific experimental procedures for testing hydrogels. Unlike the majority of other polymers which are tested, swollen hydrogels are extremely weak materials which can exhibit poor mechanical strength. This weakness and the

requirement that the sample does not deswell during testing requires unique measurement procedures.

Finally, we will focus on the dependence of hydrogel mechanical properties on various properties. These properties correspond to those that would typically be examined in a material selection process: the monomers used, the polymerization conditions, the cross-link density, the degree of swelling, and the type of medium in which the material is swollen. The advantages and disadvantages of varying each of these parameters with respect to the ultimate hydrogel mechanical properties will be explored.

This work explores the fundamental origins of mechanical properties in polymers, methods of testing hydrogel samples under a variety of conditions, and methods for altering the hydrogel properties. A large amount of work has previously been performed to model and characterize this behaviour.

GENERAL THEORY OF MECHANICAL BEHAVIOUR

Rubber elasticity

Rubbers are materials that respond to stresses with nearly instantaneous and fully reversible deformation^{1–6}. Whereas glasses can be reversibly stretched only up to ~1%, rubbers typically exhibit reversible behaviour up to ~1000% elongation. Normal rubbers are lightly cross-linked networks with a rather large free volume that allows them to respond to external stresses with a rapid rearrangement of the polymer segments. In their swollen state, most hydrogels satisfy these criteria for a rubber. When a hydrogel is in the region of rubberlike behaviour, the mechanical behaviour of the gel is dependent mainly on the architecture of the polymer network. At low enough temperatures, these gels can lose their rubber elastic properties and exhibit viscoelastic behaviour. Viscoelastic behaviour will be discussed in the following section. General characteristics of rubber

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elastic behaviour include high extensibility generated by low mechanical stress, complete recovery after removal of the deformation, and high extensibility and recovery that are driven by entropic rather than enthalpic changes.

To derive relationships between the network characteristics and the mechanical stress-strain behaviour, classical thermodynamics, statistical thermodynamics, and phenomenological approaches have been used to develop an equation of state for rubber elasticity. From classical thermodynamics, the equation of state for rubber elasticity may be expressed as¹⁻⁴

$$f = \left(\frac{\partial U}{\partial L} \right)_{T,V} + T \left(\frac{\partial f}{\partial T} \right)_{L,V}, \quad (1)$$

where f is the retractive force of the elastomer in response to a tensile force, U is the internal energy, L is the length, V is the volume, and T is the temperature. For ideal rubber elastic behaviour, the first term in Equation 1 is zero (bonds are not stretched with changes in L). This behaviour is not true for most other materials (e.g. metals) where changes in length cause internal energy driven retractive forces. For elastomeric materials, an increase in length brings about a decrease in entropy because of changes in the end-to-end distances of the network chains. The retractive force and entropy are related through the following Maxwell equation

$$-\left(\frac{\partial S}{\partial L} \right)_{T,V} = \left(\frac{\partial f}{\partial T} \right)_{L,V}. \quad (2)$$

Figure 1 graphically depicts these quantities for the thermodynamic equation of state for rubber elasticity. Stress-strain analysis of the energetic and entropic contributions to the retractive force (Equation 1) indicates that entropy accounts for more than 90% of the stress. Thus, the entropic model for rubbery elasticity is a reasonable approximation.

From statistical thermodynamics, the retractive force of an ideal elastomer may be expressed as

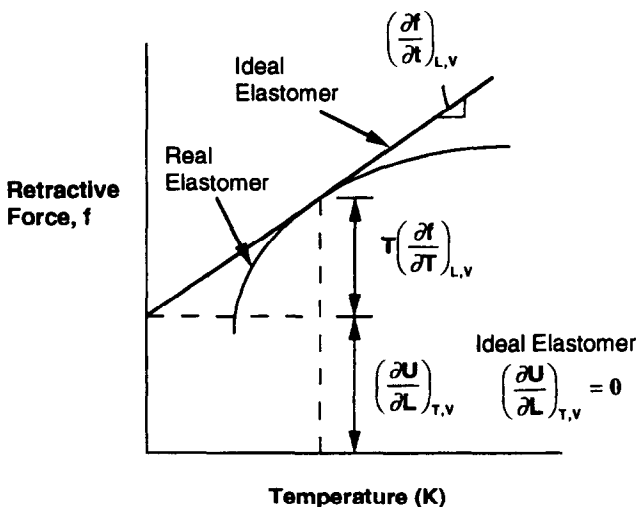


Figure 1 The retractive force versus temperature illustrating the thermodynamic analysis of the equation of state for rubber elasticity.

$$f = -T \left(\frac{\partial S}{\partial L} \right)_{T,V} = -kT \left(\frac{\partial \ln \Omega(r,T)}{\partial r} \right)_{T,V}. \quad (3)$$

Here, k is the Boltzmann constant, r is a certain end-to-end distance, and $\Omega(r,T)$ is the probability that the polymer chain with an end-to-end distance r at temperature T will adopt a certain conformation. Equation 3 assumes that the internal energy contribution to the retractive force is constant or zero. Only entropy contributions to the retractive force are considered. Evaluation of Equation 3 for a single chain leads to

$$f = \frac{3KT}{r_f^2} \quad (4)$$

where r_f^2 is the end-to-end distance in the bulk state for linear chains.

If the analysis is expanded to n network chains, then

$$\Delta A_{el} = \frac{3nkT}{r_f^2} \int_{(r_f^2)^{1/2}}^{(r^2)^{1/2}} r dr. \quad (5)$$

Here, ΔA_{el} is the change in Helmholtz free energy caused by elastic deformation. After integration and assuming no volume change upon deformation, the statistical thermodynamic equation of state for rubber elasticity is obtained below¹⁻⁴

$$\tau = \left(\frac{\partial A}{\partial \lambda} \right)_{T,V} = \frac{\rho RT}{M_c} \frac{r_0^2}{r_f^2} \left(\lambda - \frac{1}{\lambda^2} \right). \quad (6)$$

Here, τ is the shear stress per unit area, ρ is the density of the polymer, M_c is the number average molecular weight between cross-links, and λ is the extension

ratio. The quantity, $\frac{r_0^2}{r_f^2}$, is the front factor and is the ratio of the end-to-end distance in a real network versus the end-to-end distance of isolated chains. In the absence of knowledge concerning these values, the front factor is often approximated as 1.

From Equation 6, the elastic stress of a rubber under uniaxial extension is directly proportional to the number of network chains per unit volume (i.e. ρ/M_c). This equation assumes that the network is ideal in that all chains are elastically active and contribute to the elastic stress. Network imperfections such as cycles, chain entanglements, and chain ends are not taken into account. To correct for chain ends

$$\tau = \frac{\rho RT}{M_c} \frac{r_0^2}{r_f^2} \left(1 - \frac{2M_c}{M_n} \right) \left(\lambda - \frac{1}{\lambda^2} \right) \quad (7)$$

where M_n is the number average molecular weight of the linear polymer chains before cross-linking. This correction becomes negligible when $M_n \gg M_c$.

From constitutive relationships, the shear modulus G is then

$$G = \frac{\rho RT}{M_c} \frac{r_0^2}{r_f^2} \left(1 - \frac{2M_c}{M_n} \right) \quad (8)$$

and the force per unit area is

$$\tau = G \left(\lambda - \frac{1}{\lambda^2} \right). \quad (9)$$

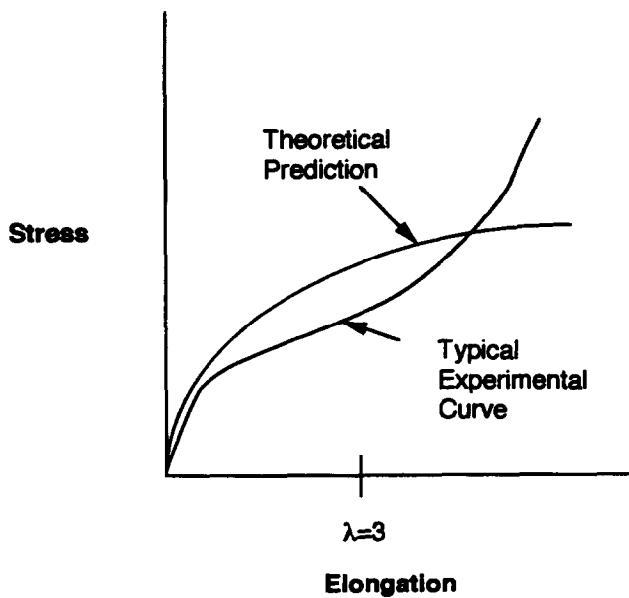


Figure 2 Typical stress–strain behaviour of a lightly cross-linked material and comparison to the statistical thermodynamic predictions.

Note the dependence of the shear modulus on \overline{M}_c . Also, the stress–strain behaviour of rubbery elastic materials is nonlinear. Figure 2 illustrates the typical experimental behaviour, along with the statistical thermodynamic predictions. While the thermodynamic and statistical thermodynamic approaches describe observed rubber–elastic behaviour at low extensions quite well, the equations are less applicable and invalid at higher elongations (i.e. $\lambda > 3$).

Equation 7 can be modified to apply to the mechanical behaviour of a swollen rubber as follows

$$\tau_s = N_o v_r^{1/3} RT \left(\frac{r_o^2}{r_f^2} \right) \left(\lambda_s - \frac{1}{\lambda_s^2} \right) \quad (10)$$

where τ_s and λ_s are the shear stress and elongation measured in the swollen state. Here, v_r is the ratio of the unswollen volume to the swollen volume (i.e. the polymer volume fraction), and N_o is the effective number of cross-links determined from

$$\frac{\rho}{\overline{M}_c} \left(1 - \frac{2\overline{M}_c}{\overline{M}_n} \right) = N_o v_r^{1/3}. \quad (11)$$

Therefore, for a given hydrogel at a fixed temperature, a higher degree of swelling results in a reduction of the stress. Alternatively, if the degree of cross-linking is increased (i.e. \overline{M}_c is decreased), the stress is increased.

In the regime of very high extension ratios, the thermodynamic equations of state are less satisfactory and phenomenological treatments are used. The phenomenological approach does not consider the molecular structure of the gel and is concerned only with the observed macroscopic behaviour of the system. The fundamental issue is to develop an equation for the energy stored in the polymer. The most general form of an equation for the work that is stored in the body of an isotropic material as strain energy, W , is a power series expression^{1–4, 7, 8}

$$W = \sum_{i,j,k=0}^{\infty} C_{ijk} (I_1 - 3)^i (I_2 - 3)^j (I_3 - 1)^k. \quad (12)$$

Here, I_1 , I_2 , and I_3 are the strain invariants given by

$$I_1 = \alpha_1^2 + \alpha_2^2 + \alpha_3^2 \quad (13)$$

$$I_2 = \alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2 \quad (14)$$

$$I_3 = \alpha_1 \alpha_2 \alpha_3. \quad (15)$$

The Mooney–Rivlin equation, which is an expression describing uniaxial extension of an incompressible material, retains two of the terms in the series given in Equation 12. The first is the lowest member of the series, $i = 1, j = 0$, and $k = 0$, and the second term is $i = 0, j = 1$, and $k = 0$. For the case of uniaxial extension and letting $C_1 = C_{100}$ and $C_2 = C_{010}$, one obtains the Mooney–Rivlin equation^{1–4, 7, 8}

$$\tau = \left(\frac{\partial W}{\partial \lambda} \right) = 2 \left(C_1 + \frac{C_2}{\lambda} \right) \left(\lambda - \frac{1}{\lambda^2} \right). \quad (16)$$

The equation of state from statistical thermodynamic analysis given in Equation 7 predicts that the quantity $\tau/\lambda - \frac{1}{\lambda^2}$ should be constant, whereas the Mooney–Rivlin equation predicts a dependence of this term on λ . Thus, the Mooney–Rivlin equation is able to better predict the stress–strain behaviour at higher elongations.

Equation 16 can be modified to describe the behaviour of a swollen hydrogel, and this expression is given below^{1–4, 7, 8}

$$\tau_s = 2C_1 v_r^{1/3} \left(\lambda_s - \frac{1}{\lambda_s^2} \right) + 2C_2 v_r^{5/3} \left(1 - \frac{1}{\lambda_s^3} \right). \quad (17)$$

Viscoelasticity

The viscoelasticity theory considers the relationships between elasticity, flow, and molecular motion in polymeric materials^{1–6}. While the mechanical behaviour of all materials exhibit some degree of elasticity and flow, the size of polymer molecules often lead to a viscoelastic response. The magnitude of the viscoelastic response is strongly dependent on the nature of the imposed mechanical motion. For example, the viscoelastic response is at a maximum when the time scale of the mechanical motion is on the time scale of the molecular motion of the polymer. In general, hydrogels are not simply elastic materials, but behave viscoelastically. Thus, the time dependence of the applied stress or strain is as important as the magnitude in predicting the material's mechanical response.

An applied mechanical stress (or strain) leads to a time dependence on the strain (or stress) as the segments of the polymer chains move. This movement engenders an internal response that results in a time-dependent recovery when the initial condition is removed. If the recovery is complete at long times, the behaviour is termed viscoelastic. If the recovery is incomplete, the behaviour is called viscoelastic–viscoplastic. In general, a polymer may have several viscoelastic processes each associated with a particular molecular motion in the material.

The following discussions describe experiments performed in the shear mode. Analogous definitions can be applied to normal stresses and strain.

Creep behaviour

If a constant shear stress, σ , is applied to a viscoelastic material, the shear strain, γ , is observed to be time dependent as shown in *Figure 3*. The ratio of the time-dependent shear strain to the applied stress is defined as the creep compliance, $J(t)$. If $J(t)$ is measured over long times, $J(t)$ shows little time dependence at very short and very long times. At very short times, the time scale of the mechanically induced stress is much shorter than the time scale for the molecular motions in the polymer. The system remains in an unrelaxed state and the creep compliance is J_u . In contrast, at very long times the time for complete molecular rearrangements is much shorter than the time scale of the experiment.

Thus, the material is completely relaxed, and the creep compliance is J_r . Since, in practice, it is easier to vary the experimental temperature than the frequency, it is common to present data as a series of isochronals, with each curve representing data obtained at a specific frequency. If a number of isochronals are obtained, the linear viscoelastic region can be identified. In the linear region, $J(t)$ is independent of the magnitude of the stress that is imposed (i.e. the magnitude of the stress used to determine $J(t)$ will not affect its value). For nonlinear-viscoelastic behaviour, each value of the applied stress leads to a time-dependent strain which can only be determined by an experiment conducted at that stress.

Stress relaxation

A constant shear strain is applied and the time dependence of the stress required to maintain that

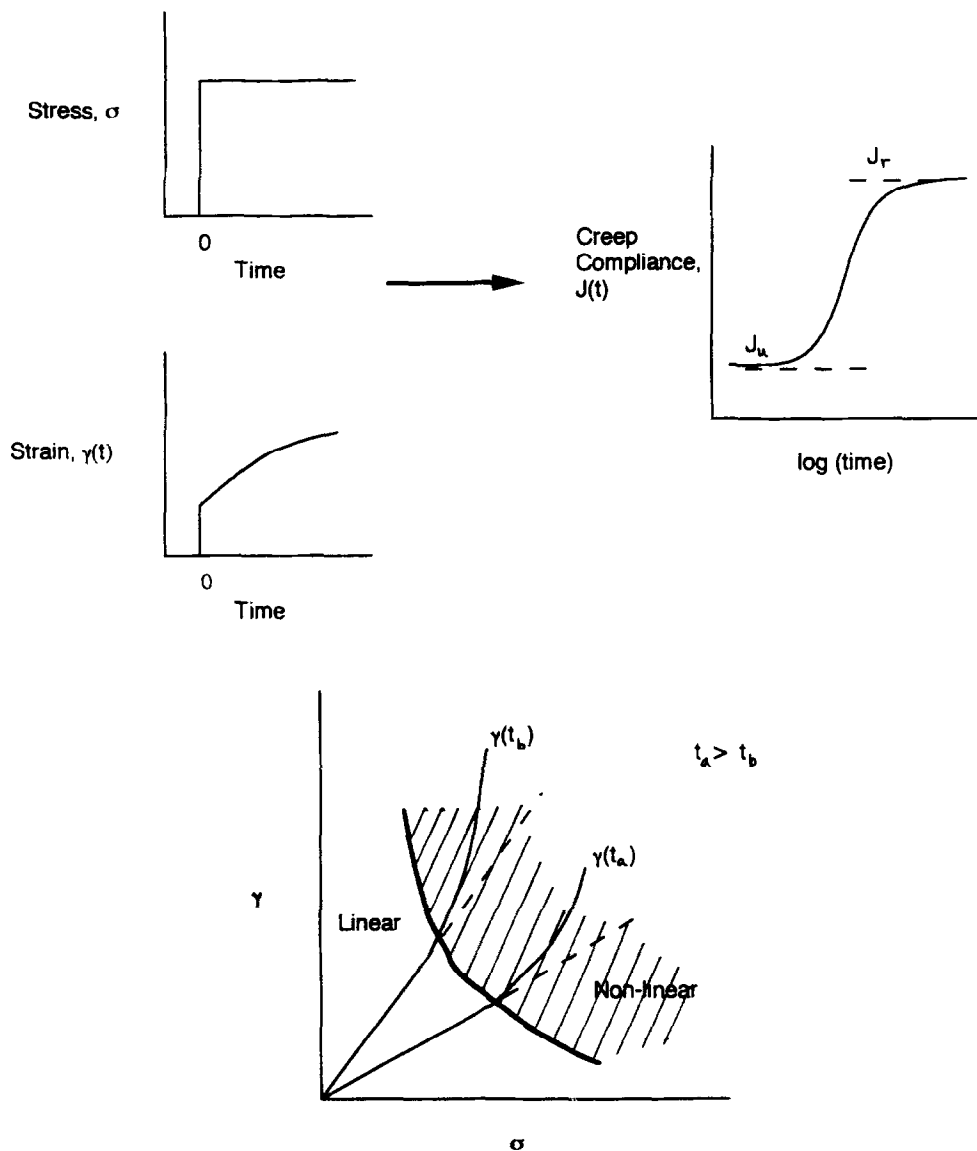


Figure 3 Creep: a constant stress applied at $t = 0$ leads to a time-dependent strain. From these experiments, the dependence of $J(t)$ on log time during one relaxation is determined. J_u and J_r are the unrelaxed and relaxed compliances. From several isochronal strain–stress plots, the regions of linear and nonlinear viscoelastic behaviour are identified. This plot is not obtained from a conventional stress–strain test, but the data are taken from several creep experiments at different stresses.

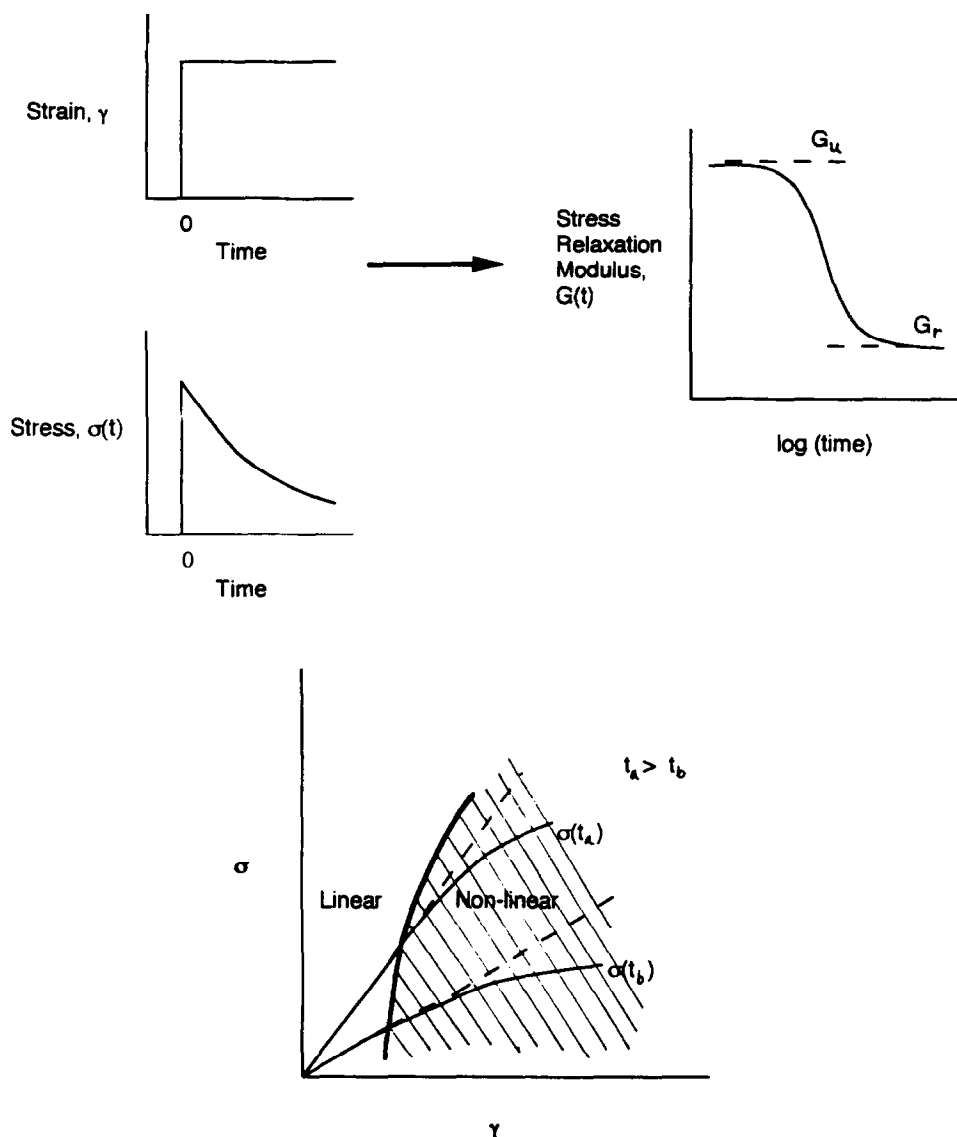


Figure 4 Stress relaxation: a constant strain applied at $t = 0$ leads to a time-dependent stress. From these experiments, the dependence of $G(t)$ on log time during one relaxation is determined. G_u and G_r are the unrelaxed and relaxed stress relaxation moduli. From several isochronal stress-strain plots, the regions of linear and nonlinear viscoelastic behaviour are identified. This plot is not obtained from a conventional stress-strain test, but the data are taken from several stress relaxation experiments at different strains.

strain is measured. The experiment is illustrated in *Figure 4*. Likewise, we can define a stress relaxation modulus, $G(t)$, which is defined as the stress-strain ratio at constant deformation. As in the case of creep, several isochronals can be plotted to determine the range of linear stress relaxation behaviour. Unlike creep, nonlinear behaviour leads to slower stress relaxation. In certain regions, $J(t)$ and $G(t)$ have a nearly reciprocal relationship, especially at short times and, for cross-linked systems, at long times as well.

Dynamic mechanical behaviour

Dynamic mechanical thermal analysis provides quantitative information on the viscoelastic and rheological properties of a material by measuring the mechanical response of a sample as it is deformed under periodic stress (or strain). Generalized input and response curves are depicted in *Figure 5*. A common

notation for sinusoidal tests is the complex dynamic modulus, G^* , defined below

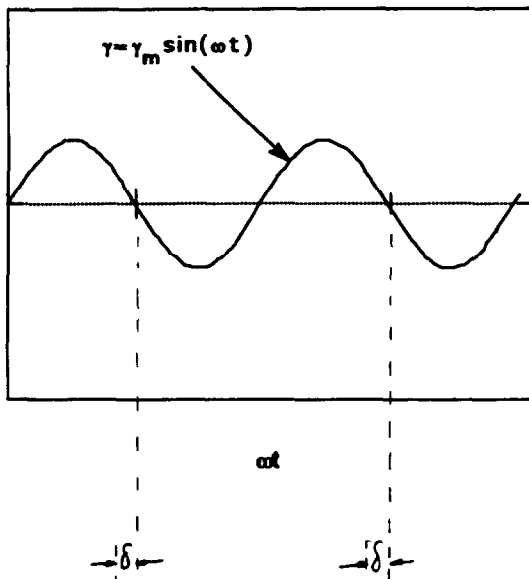
$$G^* = G' + iG'' = \frac{\sigma^*}{\gamma^*} \tag{18}$$

Here, G' is the real (also elastic or storage) modulus and G'' is the imaginary (also viscous or loss) modulus. These definitions apply to testing in the shear mode, where G refers to the shear modulus, σ to the shear stress, and γ to the shear strain. Likewise, similar definitions can be applied for testing in the normal mode for the complex modulus and complex compliance.

In the dynamic mode of testing, if the strain is a complex oscillatory function of time with maximum amplitude γ_m and frequency ω , then

$$\gamma^* = \gamma_m \exp(i\omega t) \tag{19}$$

Input



Response

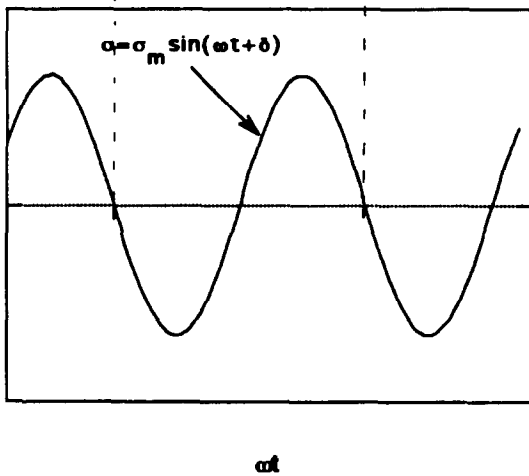


Figure 5 Typical input–response curves during dynamic mechanical testing.

By analogy with the Maxwellian element of viscoelasticity

$$\frac{d\gamma^*}{dt} = \frac{1}{G} \frac{d\sigma^*}{dt} + \frac{\sigma^*}{G\theta} \tag{20}$$

where θ is a characteristic time constant and is equal to η/G . Here, G has no physical meaning related to the dynamics of the polymer, but describes the modulus of the analogue. The same is true of η , which has no physical meaning related to the viscosity dynamics of the polymer, but again describes the viscosity of the analogue. Taking the derivative of the shear strain in Equation 19 and substituting into Equation 20, we can then solve the linear differential equation and the solution is given below¹⁻⁴

$$\frac{\sigma^*}{\gamma^*} = \frac{G\omega^2\theta^2}{1 + \omega^2\theta^2} + i \frac{\omega\theta G}{1 + \omega^2\theta^2} \tag{21}$$

or

$$\sigma^* = \sigma_m \exp(i\omega t + \delta) \tag{22}$$

where the measured response of the shear stress is then shifted by a phase angle δ with a maximum amplitude σ_m . Thus, by comparison of Equations 18 and 21

$$G' = \frac{G\omega^2\theta^2}{1 + \omega^2\theta^2} \tag{23}$$

and

$$G'' = \frac{G\omega\theta}{1 + \omega^2\theta^2} \tag{24}$$

If we define the ratio of the loss to the storage modulus as the damping or dissipation factor, then

$$\frac{G''}{G'} = \frac{1}{\omega\theta} = \tan \delta. \tag{25}$$

The damping factor, $\tan \delta$, measures the ratio of the energy dissipated as heat to the maximum energy stored in the material during one cycle of oscillation. Representative plots of the storage, loss, and damping factor are shown in Figure 6.

At low times or temperatures, the polymer is glassy and the storage modulus, G' , is in an unrelaxed state. As the temperature is increased, the viscoelastic nature of the material is seen and a transition region in G' is observed. At still higher temperatures, another plateau in G' occurs as the polymer is now in a relaxed, rubbery state. In contrast, the loss modulus, G'' , goes through a maximum as the temperature is increased. G'' is a measure of the viscous contribution to the modulus. The viscous contribution is at a maximum near the inflection point of the transition region in G' . Finally, the characteristic shape of the damping factor versus temperature is also shown. This curve provides one of the mechanical definitions for the glass

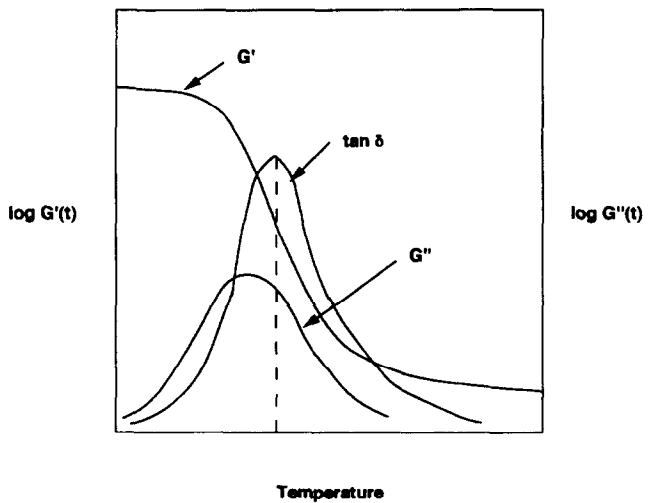


Figure 6 General behaviour of the storage modulus (G'), loss modulus (G''), and damping factor ($\tan \delta$) as a function of temperature.

transition temperature (α -relaxation). The glass transition temperature is taken as the temperature at which the maximum in the damping factor curve is observed. Other transitions associated with side chains or branches are also often observed as peaks. The transition associated at the highest temperature is often termed the α -relaxation, while subsequent temperature transitions are labelled as β -relaxations, etc. in order of descending temperature at which the transition occurs. Depending on the homogeneity of the network, the peak associated with the α -relaxation (T_g) can be quite broad.

MEASUREMENT OF MECHANICAL PROPERTIES OF HYDROGELS

Common methods for measuring mechanical properties of hydrogels include tensile (rubber elastic behaviour) or dynamic mechanical analysis (viscoelastic behaviour). For most uniaxial tensile testing, dumbbell-shaped samples of polymer are placed between two clamps and one end of the material is pulled away from the other at varying loads and rates of extension. Dies are available to cut samples to the appropriate shape. A dumbbell shape is desirable because it prevents samples from breaking at the clamps where the stress concentration would otherwise be high in a uniform strip. In materials without structural defects, a dumbbell-shaped sample should exhibit ultimate fracture at the centre of the sample. Typical sample dimensions and experimental design are discussed elsewhere⁹. Analyses of mechanical testing methods other than uniaxial deformations will not be addressed here.

For hydrogels, samples are cut in their equilibrium swollen state and the sample dimensions must be measured in this swollen state. For tensile testing of hydrogels, samples should be completely immersed in a waterbath (or equivalent bath of the solution in which the hydrogel is at equilibrium, such as a buffered solution or saline, and in which the properties need to be determined) that is thermally regulated during the tensile tests. Most tensile tests are run at constant extension rates with varying loads until the sample reaches ultimate failure. From tensile testing at various loads, one obtains information about several sample properties. In particular, the stress-strain (or elongation) behaviour can easily be determined. In addition, the stress, τ , can be plotted versus $\lambda - 1/\lambda^2$, where λ is the extension ratio. From rubber elasticity theory (Equations 6 and 7), the slope of the data in this plot is equal to G , the shear modulus, which in turn is proportional to the molecular weight between cross-links in the network. Analysis is performed utilizing the Mooney-Rivlin equation (Equation 16), in which $[\tau/(\lambda - \lambda^{-2})]$ is plotted versus λ^{-1} . This curve should yield a straight line with the slope being $2C_2$ and the intercept being $2C_1$, which is equal to G , the shear modulus. Deviations from this behaviour indicate materials which do not conform to the assumptions made in developing the Mooney-Rivlin equation and related rubber elasticity theories. More extensive discussions and analysis of these tests can be found in

the work of Mark and co-workers¹⁰⁻¹⁴ and Peppas and co-workers^{9,15}.

To measure the time-dependent, viscoelastic behaviour of polymers, dynamic mechanical testing is often performed. Samples are usually prepared in thin strips with square edges and uniform cross-sectional area throughout the sample length. Tests are typically performed applying shear stresses (or strains), so dumbbell-shaped samples are no longer an optimal sample shape. The optimal cross-sectional area of the sample is related to the modulus of the material. Researchers have reported sample dimensions of $\sim 6 \times 1 \times 0.3$ cm in testing dynamic mechanical properties of poly(2-hydroxyethyl methacrylate) and poly(2-hydroxyethyl methacrylate-co-methyl methacrylate) hydrogels¹⁶.

A typical dynamic mechanical tester applies a sinusoidal load in shear mode on one side of the sample. A stress transducer measures the applied stress. On the opposite side of the sample, the resulting changes in sample length are measured with a strain transducer. The sample environmental chamber may be kept isothermal or ramped in temperature. The complete viscoelastic behaviour may be determined from several isothermal experiments conducted over a limited frequency range. The master curve is then constructed from time-temperature superposition principles.

When testing samples such as hydrogels, the samples are subject to water loss during the experiment which can significantly influence the mechanical behaviour. In particular, as the temperature is increased, water loss can become more prominent and lead to increases in moduli with temperature which are in reality the result of water loss and subsequent changes in the hydrogel structure. Water loss is minimized by coating the hydrogel sample with petroleum gel (effective up to 45°C) or silicone vacuum grease (effective up to 85°C)¹⁶. Water losses significantly limit the temperature range over which dynamic mechanical tests can be conducted on swollen hydrogels. This limitation can lead to some difficulties in observing transitions in nominally swollen or more highly cross-linked hydrogels since these systems will exhibit their transitions at elevated temperatures. Extended frequency ranges allow determination of these transitions if time-temperature superposition is used.

CONTROL OF MECHANICAL PROPERTIES

Once the mechanical characteristics of a material have been determined, it is often necessary to improve them in some manner to make the material suitable for the desired application. In this section, we will explore three different ways of controlling the mechanical properties: altering the comonomer composition, increasing or decreasing the cross-linking density, and changing the conditions under which the polymer is formed. We will also address the relationship between the hydrogel's mechanical properties and its degree of swelling. It must be remembered that these changes in the polymer will affect not only the mechanical properties but also other behaviour of the material.

Typical adverse effects will be discussed along with the advantageous changes to the mechanical strength.

Effects of comonomer composition

One of the first and simplest changes that can be performed is altering the composition of the comonomers used in preparing the hydrogel. If the hydrogel is not a homopolymer, then increasing the relative amount of physically stronger components will lead to an increase in the mechanical strength of the final product. Such a change may alter the mechanical strength by increasing the stiffness of the backbone polymer by replacing acrylates with methacrylates, or it may alter the hydrophilicity of the polymer by replacing 2-hydroxyethyl methacrylate with methacrylic acid. Additional changes to the comonomer composition can include varying the amount and type of cross-linking agent; however, that will be left for a later discussion on altering the cross-linking density of hydrogels.

A great deal of work has been performed which explores the effects of comonomer composition on the mechanical properties. Studies have been performed on copolymers of HEMA¹⁶⁻¹⁸, *N*-vinyl-2-pyrrolidone (NVP)¹⁸⁻²⁰, sodium acrylate^{21,22}, and other monomers^{23,24}. Results from studies of HEMA copolymers have shown that HEMA and methyl methacrylate (MMA) contribute approximately the same amount of mechanical strength to unswollen copolymers containing these monomers¹⁶. However, the addition of NVP to the HEMA copolymer¹⁸ reduced the Young's modulus, a direct measure of the material's strength, of the swollen polymer by an order of magnitude as the NVP content was increased from 5 to 60%. Similar studies on NVP copolymers with MMA showed that the Young's modulus was decreased by two orders of magnitude when the NVP fraction was increased from 40 to 85%¹⁹. These results are to be expected since NVP is an extremely hydrophilic moiety which significantly increases swelling when compared to HEMA or MMA. As will be mentioned later, increasing the relative content of more hydrophilic monomers will lead to an increased degree of swelling for the resulting hydrogel. This, in turn, will lead to a decrease in the mechanical strength of the polymer.

An example of this behaviour is presented in *Figure 7* where the relative amounts of a cationic monomer (a trimethyl ammonium chloride acrylamide) and an anionic monomer (sodium styrene sulphonate) are varied while maintaining the total amount of ionic monomer at 4.7%²⁴. The data clearly show that when all of the ionic monomer is charged either positively or negatively, a maximum in swelling exists. This factor would cause the hydrogel to be weakest when all of the monomer was either cationic or anionic.

Effects of cross-linking density

As demonstrated in an earlier section on theoretical and phenomenological treatment of mechanical properties, the mechanical strength of a hydrogel is often derived almost entirely from the cross-links in the system. Particularly in the swollen state where

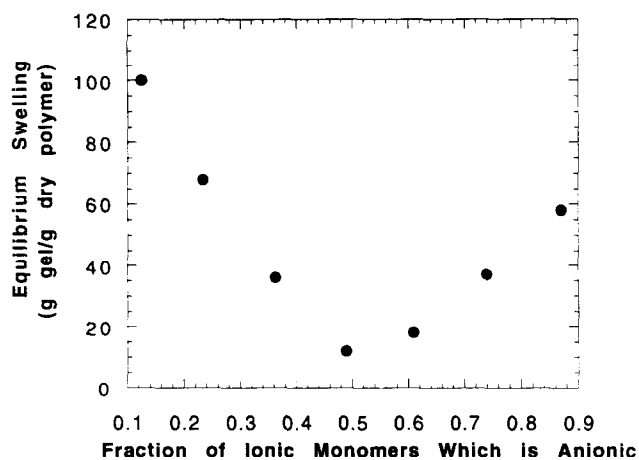


Figure 7 The equilibrium degree of swelling as a function of the fraction of ionic monomer feed (anionic sodium styrene sulphonate) with the cationic monomer (trimethylammonium chloride acrylamide). The total ionic monomer feed is maintained at 4.7 mol% and the remainder of the monomer feed consisted of acrylamide (data from reference 24).

physical entanglements are nearly nonexistent, the strength of the material increases dramatically with increasing cross-linking density.

Previously, it has been clearly demonstrated that the cross-linking density can easily be increased by the addition of a larger amount of cross-linking agent. A wide range of studies on the dependence of mechanical properties on the concentration of cross-linking agent have been performed, both on hydrogels^{18,25-29} and other types of polymers³⁰⁻³³. In examining the properties of nonhydrogels³⁰, it was found that increasing the amount of cross-linking agent dramatically increased the mechanical strength and glass transition temperature of the networks. Interestingly, the most significant increases were observed in the shear modulus in the rubbery state. This fact is especially relevant for hydrogel applications since it implies that the material strength in the highly swollen, and therefore rubbery, state can be increased with increasing amounts of cross-linking agent. Though highly dependent on the amount of cross-linking agent, the shear modulus in the rubbery state was not found to depend on the type of cross-linking agent used when less than 5% cross-linking agent was present³⁰.

For hydrogel polymers, poly(acrylic acid) (PAA) copolymers have been shown to have small-scale heterogeneities²⁵ which were found to increase as the amount of cross-linking agent was increased. This heterogeneity, identified by small-angle neutron scattering, was found to be of the order of 100 Å in PAA cross-linked with methylene bisacrylamide. In addition, polyacrylamide gels cross-linked with bisacrylamide²⁶ were found to have similar heterogeneities. These highly cross-linked heterogeneities exist when more than 5% cross-linking agent is present during the radical polymerization. Though the material strength increases as the amount of cross-linking agent increases in these polymerizations, the heterogeneities do result in a reduction in the number of cross-links which are

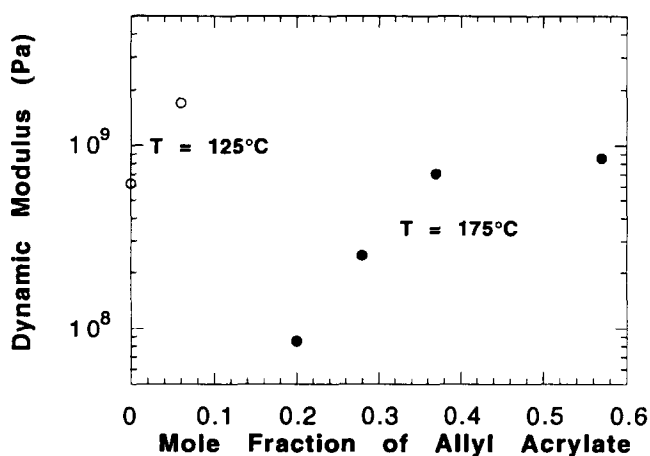


Figure 8 The dependence of the dynamic modulus on the mole fraction of allyl acrylate copolymerized with acrylic acid at 125°C (open circles) and 175°C (filled circles) (data from reference 27).

formed. Within these heterogeneities, the cross-linking agent forms a large number of cycles which do not contribute significantly to the mechanical strength of the polymer.

An illustration of the effects of cross-link density on dynamic modulus is presented in *Figure 8*²⁷. This figure presents data for the dynamic modulus as a function of the mole fraction of cross-linking agent for acrylic acid polymers cross-linked with allyl acrylate. As the amount of allyl acrylate is increased, the dynamic modulus increases dramatically. It was also found in this study that the glass transition temperature increased linearly with the amount of allyl acrylate²⁷.

These studies as well as others have demonstrated that it is possible to significantly enhance material strength with increases in cross-linking agent concentration. However, when the cross-linking density is altered, changes to properties other than the strength are likely to occur. Diffusivities, and hence release and swelling rates, are likely to be reduced and the maximum degree of swelling is also likely to decrease. These changes would likely affect the desired properties of the material and should be re-examined as the cross-link density is changed.

Effects of polymerization conditions

The reaction conditions will dramatically affect the final polymer product that is formed. Considerations with regard to the polymerization reaction are the reaction time, temperature, and amount and type of solvent.

Of particular importance are the type and amount of solvent used during the polymerization. If a large amount of solvent is used during the polymerization, the cross-linking agent will tend to form cycles rather than cross-links. This change will reduce the effective cross-link density, thus lowering the material strength. When the type of solvent or the nature of the solvent (e.g. pH or ionic strength of aqueous solutions) is altered, the copolymer structure may be changed. Since ionic strength and pH affect the reactivity of

monomers differently, it is possible that changes in these conditions would convert the copolymer from random to block or cause significant copolymer compositional changes. In general, monomers will be more reactive in their unionized state or when the solution ionic strength is high and shields ion-ion interactions.

Recent studies on copolymerizations of HEMA and 2-dimethylaminoethyl methacrylate have clearly shown that these relationships between the polymerization conditions and the hydrogel properties exist³⁴. Swelling ratios varied from a minimum of 2.1 to a maximum of 12.6 in polymers that were formed under different pH conditions and with varying amounts of solvent. Increasing the pH over the range of 3–8 slightly favoured lower swelling ratios, while increasing the volume fraction of solvent present during the polymerization (from 0.0 to 0.71) increased the swelling ratio by an average of nearly 400%. Clearly, the structure and nature of the polymer formed in the presence of a large amount of solvent is significantly different from the polymer formed in a bulk polymerization. Interestingly, the copolymer composition is nearly identical for all of these polymers.

Other reaction conditions which can be varied include the reaction time and temperature. In the case of photopolymerizations, the light intensity can be varied as well. With all of these parameters, the functional group conversion can be controlled. Increased double bond conversion lowers the amount of residual soluble fraction and may increase the cross-link density. If hydrogels are to be used without any post-reaction treatments, increasing the double bond conversion can lead to greatly enhanced mechanical strength^{32,35}.

Post-reaction treatments can also be quite effective in changing the network structure and the material strength. One method of altering the polymer structure is to add a compound which complexes with the monomer/polymer³⁶. Another method of altering the structure, common especially to poly(vinyl alcohol) (PVA) hydrogels, is to thermally cycle the polymer^{37–42}. This technique involves the successive freezing and thawing of the PVA polymer. By cycling the polymer in this manner, the Young's modulus of the polymer is significantly increased⁴², while many of the other properties of the gel remain relatively unchanged.

Effects of degree of swelling

As outlined in the earlier section on the theory of mechanical properties in cross-linked networks, the degree of swelling is intimately related to the material strength of a hydrogel. Most of the previously proposed methods for improving the material strength (changing the composition, increasing the cross-linking density, and changing the reaction conditions) are designed to reduce the degree of swelling of the polymer and thus improve its mechanical properties. Typically, as polymers swell in a plasticizing solvent, the glass transition temperature of the mixture decreases and the material is weakened. Under certain conditions, these effects can be quite pronounced,

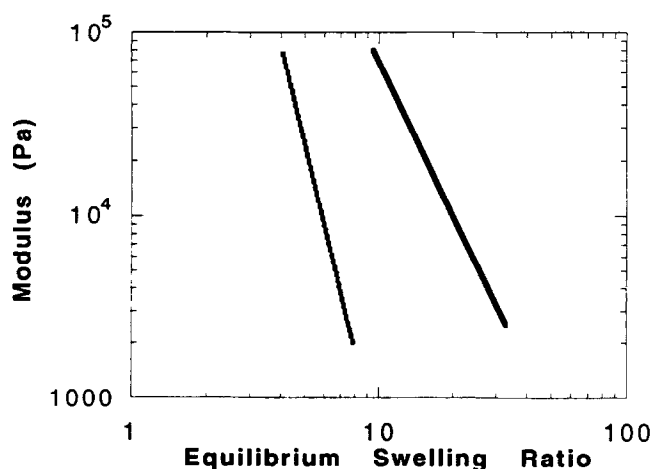


Figure 9 The elastic modulus as a function of the equilibrium degree of swelling for polyacrylamide gels swollen in solutions of ionic strengths of 1.0 (dashed line) and $10^{-4} \text{ mol l}^{-1}$ (solid line) (data from reference 22).

transforming a strong solid glassy polymer, e.g. polyacrylic acid, into a weak gel with the addition of water. Unfortunately, in most hydrogel applications, the swelling conditions are predetermined by the application requirements. If not, then controlling the degree of swelling by controlling external conditions such as pH, ionic strength, temperature, or type of swelling agent can have a pronounced effect on the mechanical properties.

An example of the effects of swelling on the elastic modulus is presented in *Figure 9* for polyacrylamide gels cross-linked with *N,N*-methylene-bisacrylamide²². These results clearly show that as the volume degree of swelling changes from 4 to 8 (in the 1.0 mol l^{-1} ionic strength media), the elastic modulus decreases by nearly two orders of magnitude. The water swelling the copolymer is dramatically plasticizing the polymer and reducing the mechanical strength.

Recent studies in this area have focussed on synthesizing and characterizing hydrogels which are sensitive to pH^{43–46} and/or temperature^{45–49}. Also, theories have been developed for certain hydrogels which predict the degree of swelling based on the temperature and the molecular weight between cross-links⁵⁰. Finally, Dubrovskii *et al.*⁵¹ have characterized the effects of swelling and swelling conditions on the elastic and shear moduli of polyacrylate–starch copolymers.

SUMMARY

The prediction and control of mechanical properties in hydrogels is of great importance in assessing the applicability of hydrogels. In this work we have shown that the mechanical properties are highly dependent on the polymer structure, especially the cross-linking density and the degree of swelling. Methods for measuring the elastic and viscoelastic properties of hydrogels were presented along with mechanisms for controlling the properties. Through variations in the polymer composition, the cross-linking density, and

the polymerization conditions, it is remarkably facile to control the mechanical properties of hydrogels.

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