

Polymer Gel Rheology and Adhesion

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1. Introduction

Polymer gels are found in many applications ranging from foods (Ross-Murphy, 1995; Tunick, 2010) and drug delivery (Andrews & Jones, 2006) to adhesives (Creton, 2003) and consumer products (Solomon & Spicer, 2010). By manipulating the gel's microstructure, a wide variety of physical properties can be achieved ranging from hard rubbery plastics to soft hydrogels. Silicone-based polymer gels in particular have found wide utilization in consumer products ranging from medical implants to cooking utensils. Here we will discuss methods of characterizing polymer gels using rheological techniques to probe their adhesion and mechanical response. Further, we will link the observed adhesion and mechanical behavior to the gel microstructure.

Polymer gels are crosslinked networks of polymers which behave as viscoelastic solids. Because the polymer network is crosslinked, the gel network consists of one very large branched polymer which spans the entire gel. While gels can be soft and deformable, they also hold their shape like a solid. Depending on the physical structure of the polymer network, polymer gels can be classified as strong, weak or pseudo gels (Ross-Murphy, 1995). Chemically crosslinked polymer gels are considered strong gels. The crosslinks are permanent and cannot be reformed if broken. Weak gels contain crosslinks which can be broken and reformed such as colloidal gels and some biopolymer gels (Spicer & Solomon, 2010; Richter, 2007). Entangled polymer systems are sometimes referred to as pseudo gels because, over a range of time scales, physical entanglements between polymer chains mimic chemical crosslinks giving these materials gel-like properties (Kavanagh & Ross-Murphy, 1998). However, the equilibrium response of a pseudo gel to a constant applied stress is to flow like a fluid.

Polymer gel properties can be controlled by manipulating the microstructure of the polymer backbone and the surrounding liquid, if any. The strength of a gel, which is characterized by the equilibrium modulus, is generally proportional to the density of crosslinks with stiffer gels having a higher density of crosslinks (Gottlieb et al., 1981). A gel can be made softer by increasing the spacing between crosslinks either by increasing molecular weight of the polymer chain connecting the crosslinks or diluting the gel with a liquid. Liquid in the gel which is not part of the crosslinked network is referred to as the sol and may consist of a solvent such as water, short chain polymers or long entangled polymers. The crosslinked polymer network is frequently referred to as the gel. Alternately, defects can be added to the network. For a given crosslink density, an ideal end-linked polymer gel where all polymer

chains are connected at both ends to crosslinks and all crosslinks are connected fully to the polymer network will have the highest modulus (c.f. Figure 1a) (Patel et al., 1992). If there is an imbalance between the number of polymer chains and crosslinker, then defects are introduced into the network such as loops and dangling ends (c.f. Figure 1b), which results in a softer gel. Gels which are formed by random processes such as irradiation will form networks with many defects (c.f. Figure 1c). Thus, for a given application, there are many ways to adjust the properties of a polymer gel to optimize performance by controlling gel microstructure and processing conditions.

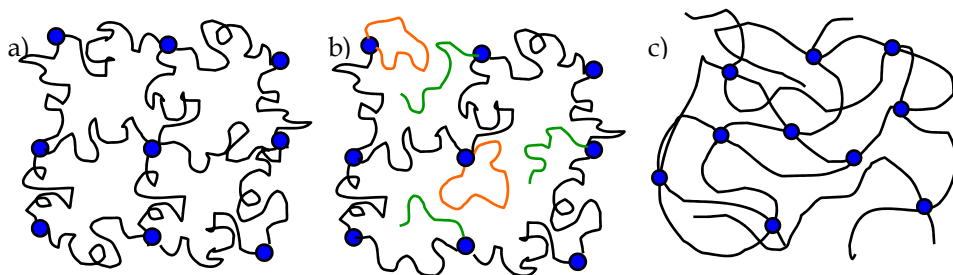


Fig. 1. Diagrams of polymer gel microstructures: a) ideal end-linked polymer gel; b) end-linked gel with dangling ends (in green) and loop defects (in orange); c) randomly crosslinked polymer gel.

The complex structure of a polymer gel dictates that a gel's response to external forces varies widely depending on the time scale of the application of the force. At a basic level, a gel is a collection of polymers. In dilute solution, a polymer chain has a spectrum of relaxation times that defines how quickly the polymer can relax from a deformation (Larson, 1988). Deformations stretch and align segments of the polymer, reducing the number of available conformations and hence reducing the polymer's entropy. Random Brownian motion drives the polymer to increase its conformational entropy and reduce the stored elastic stress. The ends of the polymer can rearrange very quickly but the middle of the polymer is constrained and must wait for the ends to relax before it can relax. The longest relaxation time of a free polymer, which determines the overall rheological behavior, is controlled by the molecular weight of the polymer and the viscosity of the surrounding fluid.

For polymer gels, the effective molecular weight is infinite, as is the longest relaxation time meaning the network will never completely relax from a deformation. But, unlike a purely elastic solid, polymer gels can still internally rearrange and dissipate energy resulting in a viscoelastic character. This is especially true of polymer gels where the length of the polymer chain, either in the solvent or as a part of the gel network, is large enough to allow the polymer to physically entangle with itself (Llorente & Mark, 1979; Patel et al., 1992). Figure 2 illustrates several relaxation mechanisms from an affine deformation. The polymers in the sol will relax the most quickly because their chain ends are unconstrained, followed by dangling polymers which have only one end attached to the network (c.f. Figure 2c). A polymer chain within the gel network will relax more slowly than a free polymer in solution because both ends of the chain are constrained at the crosslinks (c.f. Figure 2d). The final deformation of the gel is determined by its equilibrium modulus.

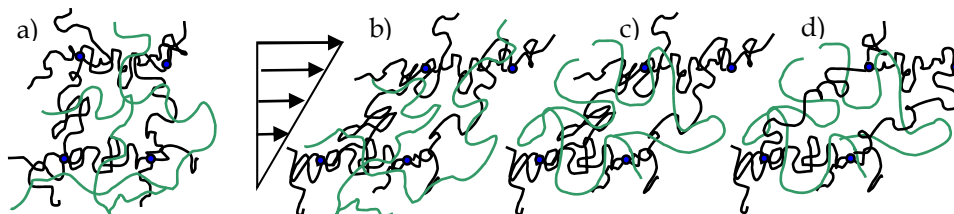


Fig. 2. Stages of relaxation in diluted polymer gel: a) Undeformed gel; b) short times: gel (black) and sol (green) polymers are stretched and aligned; c) intermediate times: sol polymers (in green) relax but gel network (black) is still deformed; d) long times: polymer in gel network relaxes but retains an equilibrium deformation.

The viscoelastic nature of polymer gels plays an important role in their adhesion properties. Adhesive properties of polymeric materials are fundamental to diverse industrial applications. Adhesives have been applied to sophisticated technologies such as nanotechnology, micro-electronics, and biotechnology (Moon et al., 2004). Newtonian liquids make poor adhesives because they flow under sustained forces such as gravity and would not stay in place. It can require a lot of work to peel two surfaces held together by a viscous Newtonian liquid apart due to the high internal friction which dissipates energy as the liquid flows. However, the liquid will leave a residue when the surfaces are separated which is not desirable. At the other extreme, stiff elastic rubbers tend to separate rapidly from a surface because they cannot deform and do not have many internal mechanisms to dissipate energy which leads to poor adhesive performance. Soft polymer gels can have excellent adhesion properties due to both the elastic and viscous properties (Zosel, 1991; Lenhart, 2006; Andrews & Jones, 2006). The gel does not flow or creep under small stresses allowing it to stay where it is applied. As surfaces bonded with a gel are peeled apart, the gel deforms, but because of the internal energy dissipation mechanisms (e.g., physical entanglements, network defects or solvent), only a fraction of the applied energy is stored as elastic energy in the gel network. Thus it requires more work to remove the gel from a surface than for an elastic material of the same equilibrium modulus. When the gel does separate, if the gel modulus is higher than the interfacial strength, it will not leave a residue on the surface.

2. Rheology of polymer gels

Today's modern rheometers allow the precise measurement of a complex material's response to an applied force (stress) or deformation (strain). Historically, rheometers were categorized as stress controlled (applies a force and measures the resulting deformation) or strain controlled (applies a deformation and measures the resulting force) (Macosko, 1994). Advances in instrument hardware and control have resulted in versatile instruments which can perform both types of tests. Strain controlled instruments are more expensive, but they can accurately probe higher oscillation frequencies and do not require frequent inertial calibration (Kavanagh & Ross-Murphy, 1998).

To demonstrate various aspects of gel rheology, a commercial fluorosilicone gel (Dow Corning DC4-8022) is used as an example. This platinum-catalyzed silicone gel is only lightly crosslinked and contains about half by weight of sol diluting the gel network.

Though quite soft, this is still considered a strong gel because the chemical crosslinks are permanent. The viscoelastic nature of these soft gels is readily apparent and contributes to a rich dynamic response. A series of gels varying from extremely soft to hard were examined (Table 1). The equilibrium modulus varied over almost an order of magnitude while keeping the soluble fraction fixed at 45 wt%. Each of these fluorosilicone gels has a glass transition temperature of -65°C indicating that the chemical backbones of the gel polymers are the same. For rheology testing, fluorosilicone gel is placed between parallel plates of a TA Instruments AR-G2 rheometer and cured at 82°C for 24 hours. The gel is then cooled to 25°C prior to further testing.

	G' at 0.01Hz
High	1060 Pa
Medium	471 Pa
Medium-Low	229 Pa
Low	157 Pa

Table 1. Summary of fluorosilicone gel equilibrium modulus.

As a solution of polymer undergoes the crosslinking reaction either through chemical reaction or irradiation, the average molecular weight of the polymer grows. The gel point can be defined phenomenologically as the critical transition point between when the material is classified as a liquid before the gel point and when it is a solid afterwards. At the critical gel point, the liquid viscosity has diverged to infinity so it is no longer a liquid, but the equilibrium elastic modulus is zero so it is not yet a solid. There are several theories for the process of gelation which are described in detail elsewhere (Flory, 1941; Larson, 1999). Figure 3 illustrates the gelation process from a percolation theory perspective assuming a crosslinker with four reactive sites (tetrafunctional crosslinker). Before the gel point, the equilibrium response of the polymer is to flow. As the reaction progresses, the polymer molecular weight and viscosity increase, diverging as the polymer hits the gel point. At the critical gel point, the gel network just spans the entire sample and the molecular weight and relaxation time are both infinite. Both Flory's classical theory and percolation theory predict that the extent of reaction necessary to form a space filling network is $(f-1)^{-1}$ where f is the functionality of the crosslinker. In order to form a gel, the crosslinker must have a functionality of 3 or greater (i.e. the gel microstructure must be branched). Some gels are crosslinked to the point of being almost a solid. Others such as the lightly crosslinked silicone discussed here maintain a pronounced viscoelastic character.

2.1 Creep testing

The easiest way to identify if a polymer is a gel is to place the material under a constant stress and track the deformation with time (Anseth et al., 1996; Kavanaugh & Ross-Murphy, 1998). This type of test is referred to as a creep test. For a solid polymer (e.g., a hard epoxy or pencil eraser), the deformation will immediately reach a steady state value which is related to the material stiffness (c.f. Figure 4). Likewise, a Newtonian liquid will immediately reach a constant rate of deformation which is proportional to the reciprocal of the liquid's

viscosity. A polymer liquid or other viscoelastic liquid will eventually reach a constant deformation rate. The amount of time it takes to reach a constant shear rate is determined by how long it takes for the polymer to reach its equilibrium deformation state and gives a measure of the longest relaxation time of the polymer. When a polymer gel or other viscoelastic solid is subjected to a constant stress τ , it will eventually reach a constant deformation. The equilibrium deformation γ scaled by the applied stress is called the creep compliance $J = \gamma/\tau$ and is indicative of the equilibrium modulus of the gel with stiffer gels deforming less (i.e. low compliance) than softer gels (c.f. Figure 4b). The creep compliance is approximately independent of the applied stress as indicated in Figure 4c showing that the deformation is linearly dependent on the applied stress.

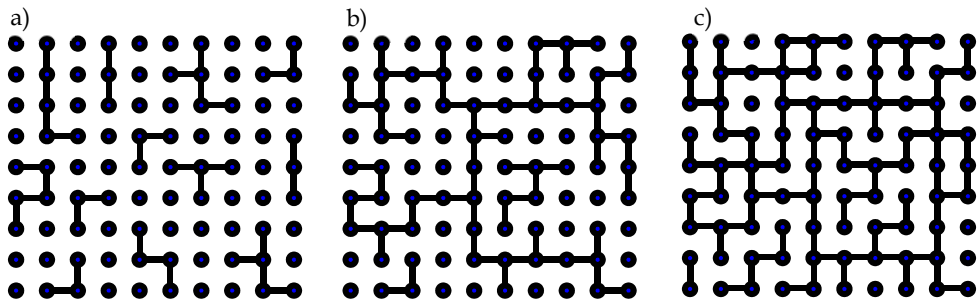


Fig. 3. Illustration of polymer gelation with crosslinker (dots) connecting polymer chains (lines): a) before gel point, isolated polymers increasing molecular weight; b) at critical gel point, network reaches percolation threshold; c) final gel network with defects.

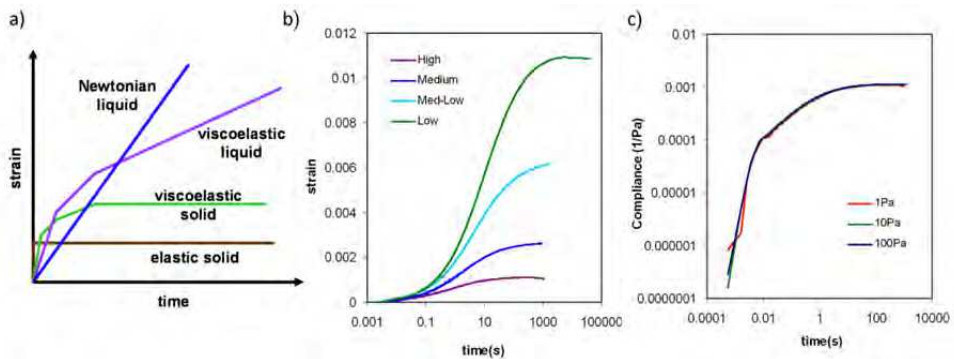


Fig. 4. Compliance curves for creep tests of dilute silicone gels showing the effect of gel stiffness on compliance. a) typical creep behavior for different classes of materials; b) time dependent strain of gels of varying stiffness under a constant stress of 1 Pa; c) creep compliance J of a polymer gel under varying stresses.

2.2 Swelling and sol extraction

Gels will also behave differently than liquids when exposed to solvents. Viscoelastic polymer liquids will dissolve in a good solvent as the physical entanglements unravel. A

chemically crosslinked gel will swell in the solvent, but the chemically crosslinked gel network will not completely dissolve. For the lightly crosslinked silicone polymers shown in Figure 5, 1 gram pieces of cured gel were placed in 100mL of methylethylketone (MEK) for 24 hours before being drained and weighed. Each of the gels swelled to more than ten times its original weight. The degree of swelling of the gel is related to the gel equilibrium modulus where stiffer gels will swell less than softer gels (Patel et al., 1992). The degree of swelling is presented as the volume fraction of gel in the swollen state (v_s). Assuming simple additivity of volumes, the volume fraction can be calculated as:

$$v_s = \frac{m_g / \rho_g}{m_g / \rho_g + m_{MEK} / \rho_{MEK}} \quad (1)$$

where m_g and m_{MEK} are the masses of the gel and MEK respectively and ρ_g & ρ_{MEK} are their densities.

The soluble fraction of a gel, or sol fraction, can be determined by using a Soxhlet extraction to remove all of the material which is not bound into the gel network (Gottlieb et al, 1981). A Soxhlet extractor continuously rinses the gel with freshly condensed solvent allowing any unreacted polymer to diffuse out of the gel. For an ideal end-linked polymer gel, the sol fraction can be less than 1% (Patel et al, 1992). As discussed previously in order to form a space filling gel network, the probability that a given polymer chain is attached to the backbone must be at least 1/3 for tetrafunctional crosslinkers ($f=4$) (Flory, 1941) indicating that the maximum sol fraction can be 2/3. Below that degree of crosslinking, the polymer will still be a liquid and completely dissolve. However, once reacted, a gel can swell to many times its original size as shown in Figure 5 reaching much higher sol fractions.

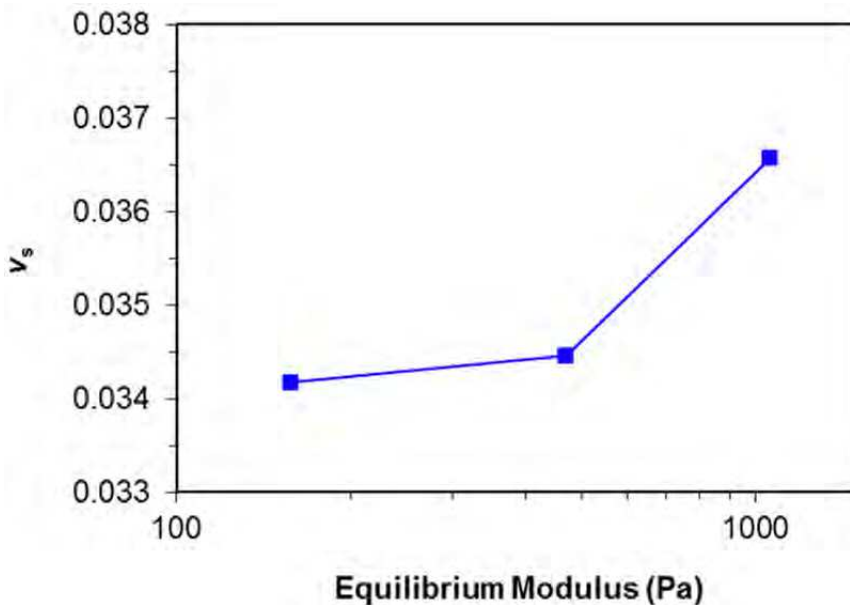


Fig. 5. Volume fraction of polymer in swollen gel as a function of elastic modulus.

2.3 Linear oscillatory rheology

While creep and extraction techniques can provide effective indications of when a material is a gel, oscillatory rheology provides the most sensitive measure of the critical gel point, the point when the material changes from a viscoelastic liquid to a viscoelastic solid. Linear oscillatory rheology subjects the material to a small oscillatory strain (or stress) of the form:

$$\gamma = A \sin(\omega t) \quad (2)$$

where γ is the strain, A is the amplitude of the oscillation and ω is the frequency of oscillation. The resulting response of the material is measured. For a purely elastic solid, the stress required to impose the deformation is proportional to the strain whereas for a viscous liquid, the stress is proportional to the strain rate

$$\dot{\gamma} = A \omega \cos(\omega t). \quad (3)$$

Viscoelastic solids such as gels will have a response that is somewhere between the two extremes. The complex shear modulus G^* can be separated into the fraction that is in-phase with the deformation and the part that is out-of-phase with the deformation. These are generally represented in terms of the elastic G' and viscous G'' shear moduli:

$$G' \propto \sin(\omega t), \quad G'' \propto \cos(\omega t), \quad G^* = (G'^2 + G''^2)^{1/2}, \quad \tan(\delta) = \frac{G''}{G'} \quad (4)$$

The phase angle δ shows the relative importance of the liquid-like viscous modulus G'' and the solid-like elastic modulus G' .

Oscillatory rheology is a powerful characterization tool because by varying the amplitude and frequency of the applied strain, a wide range of timescales and behaviors can be studied (Anseth et al., 1996). For this chapter, we will limit our discussion to small amplitude experiments within the linear viscoelastic regime which allows an investigation of the gel response without disruption of the gel structure. In the linear regime, the measured moduli are independent of the applied strain. Figure 6 shows an example of the shear moduli where the applied strain amplitude was varied at a fixed frequency of 1Hz. At very low strains ($\gamma < 0.01\%$), the signal is very weak and the data can be noisy. In Figure 6, the linear viscoelastic regime extends to strains of $\sim 40\%$. At higher strains, changes occur in the gel structure (ruptured bonds or entanglements) resulting in a decrease in the measured moduli.

2.3.1 Determination of the critical gel point

To determine the gel point during a crosslinking reaction, the complex moduli are measured as a function of time as shown in Figure 7. At early times, both of the moduli are low and the elastic portion G' is much smaller than the viscous portion G'' . This is characteristic of a polymer liquid at low frequencies. The presence of a small elastic contribution well before the critical gel point is due to the stretching of the polymers under deformation and potentially physical entanglements between the polymers. As the crosslinking reaction progresses, the molecular weight of the polymers increases, increasing both the viscosity and relative contribution of the elastic modulus G' . Longer polymers have longer relaxation times and more entanglements. At a time known as the cross-over point, the elastic modulus becomes

larger than the viscous modulus. As the reaction progresses to completion, the elastic and viscous moduli approach their equilibrium values. Stiffer gels will have a higher elastic modulus and a smaller phase angle δ . In the limit of a very stiff gel, the viscous contribution may be negligible.

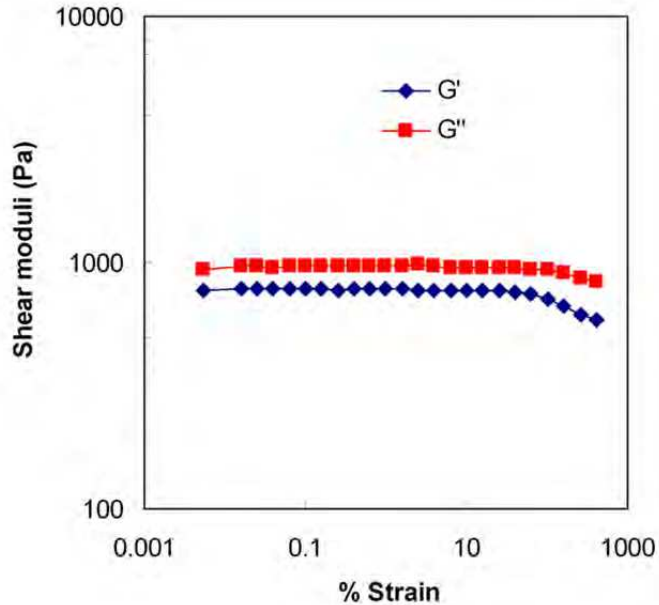


Fig. 6. In the linear viscoelastic regime, the measured shear moduli G' and G'' are independent of the applied strain or stress.

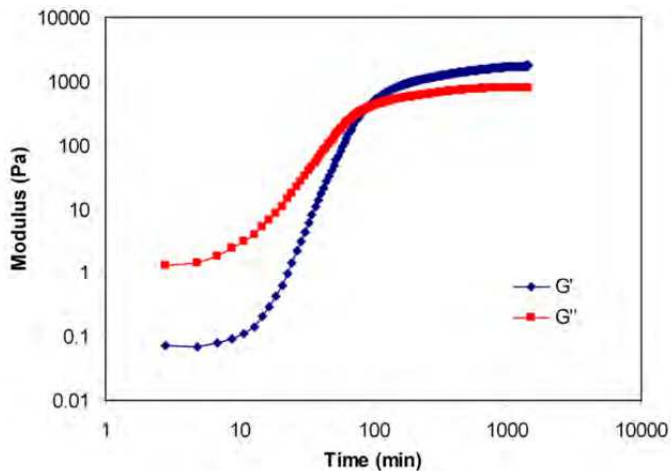


Fig. 7. Shear moduli as a function of time during crosslinking reaction of a silicone gel ($\omega=1\text{Hz}$, stress=5Pa).

For ideal end-linked polymer gels, the critical gel point can be defined as the cross-over point where the elastic and viscous moduli are equal ($G'=G''$). However for non-ideal gels where network defects or physical entanglements are present, the cross-over point depends on the applied frequency. The critical gel point represents a physical transition from a liquid to a solid and hence should not depend on the measurement parameters. Chambon and Winter (1987) proposed what is now the definitive criterion for determination of the critical gel point. The critical gel point is when the two moduli exhibit a power law dependence on the applied frequency over a wide range of frequencies. Alternately at the critical gel point, the ratio of the shear moduli, $\tan(\delta)$, is independent of frequency (Gupta, 2000)

$$G', G'' \propto \omega^n \quad \frac{G''}{G'} = \tan(\delta) = \tan\left(\frac{n\pi}{2}\right) \tag{5}$$

For ideal gels, the shear moduli at the critical gel point are equal and $n=0.5$. For gels which contain defects, the phase angle $\delta=n\pi/2$ will be independent of frequency with n in the range of 0.5 to 1, with gels containing more non-idealities having a larger value of n . An example is illustrated in Figure 8 for a lightly crosslinked silicone containing many defects. Winter & Mours (1997) summarize in detail other characteristics of a gel at the critical gel point.

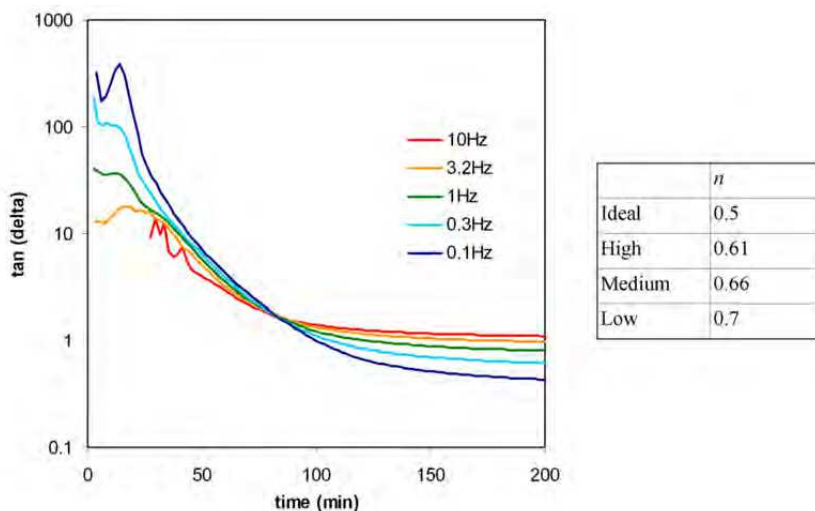


Fig. 8. Determination of critical gel point and network quality from oscillatory rheology. The critical gel point is the time when the curves of $\tan(\delta)$ at various frequencies coincide. The table shows the relaxation exponent n for gels of various equilibrium moduli.

2.3.2 Frequency dependence of gels

Ideal gels have an almost purely elastic response where the elastic modulus is much higher than the viscous modulus and is independent of frequency. In gel networks with imperfections, the response of the polymer gel will depend on frequency with both shear moduli increasing with frequency. Various time scales of a polymer gel can be investigated by adjusting the frequency of the applied oscillation to probe different relaxation times as

illustrated in Figure 2. At low frequencies, both gel and sol polymers are rearranging due to Brownian motion so the measured properties are dominated by the equilibrium elastic deformation of the gel network (c.f. Figure 2d). Physical entanglements are created and broken quickly compared to the rate of deformation so they do not contribute drag or store elastic energy. At high frequencies the polymer does not have time to rearrange (c.f. Figure 2b). Physical entanglements persist longer than the oscillation frequency so they physically constrain the polymers, store elastic energy and contribute to viscous dissipation (Patel et al., 1992).

This timescale dependence is demonstrated in Figure 9 for two silicone gels. At low frequencies, the stiffer gel (red curves) shows a higher elastic modulus and smaller phase angle relative to the softer gel (black curves). As the frequency approaches zero, the elastic modulus approaches a plateau value known as the equilibrium modulus of the gel network. The equilibrium modulus reflects only the chemical crosslinks in the gel because the lifetime of physical entanglements is much shorter than the oscillation period. At higher frequencies, the solvent and polymer entanglements begin to contribute to the material response increasing both the elastic and viscous moduli. At the highest frequencies, the shear moduli almost overlap because the response is dominated by local interactions between polymer chains and physical entanglements are indistinguishable from chemical crosslinks (Mrozek et al., 2011).

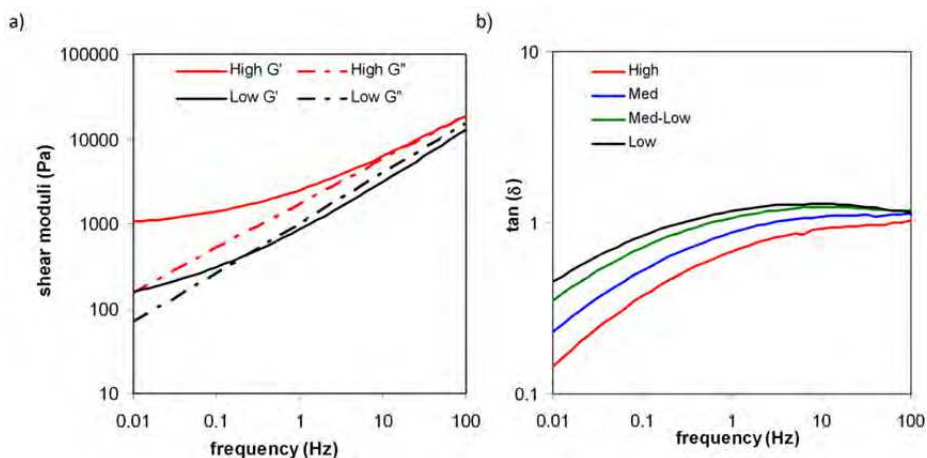


Fig. 9. Frequency dependence of (a) shear moduli and (b) phase angle $\tan(\delta)$. The high modulus gel is shown in red and the low modulus gel in black..

3. Adhesion properties of polymer gels

When an uncrosslinked or lightly crosslinked polymer is brought into contact with the surface of another material at a temperature above its glass transition temperature, an adhesive bond of measurable strength is formed in most cases (Zosel, 1985). The adhesion of the polymer to the substrate is highly influenced by the viscoelasticity of the polymer as well as the surface and interfacial tensions of the polymer and substrate (Zosel, 1989). To function properly, polymeric adhesives must combine liquid-like characteristics to form

good molecular contact under an applied pressure and solid-like characteristics to resist an applied stress once the bond has been formed. This combination of liquid-like and solid-like properties usually requires a high molecular weight polymer to form the backbone of the adhesive, and a low molecular weight fraction which favors flow and deformation (Roos et al., 2002). One common criterion for a material with good adhesive properties is an elastic modulus less than 10^5 Pa (Dahlquist criterion, Creton, 2003). Materials with elastic moduli exceeding the Dahlquist criterion have poor adhesion characteristics due to the inability to dissipate energy via viscous contributions or to deform to make good contact with a surface. Further, these materials have a high peak adhesive force, but fail quickly upon further strain (brittle failure with no fibril formation). However, not all polymer gels which meet the Dahlquist criterion are good adhesives. Many hydrogels have low equilibrium moduli, but have negligible viscous moduli. With no dissipative modes in the materials, even these soft materials undergo brittle failure and are poor adhesives. For the discussion in this section, only materials meeting the Dahlquist criterion ($G' < 10^5$ Pa) will be considered.

Adhesive bond formation also requires a sufficiently high segmental mobility in order to obtain contact at molecular dimensions between the adhesive and solid substrate during the possibly very short contact time. During the separation phase, the adhesive must be able to accommodate large deformations in order to store and dissipate a large amount of energy before fracture occurs (Zosel, 1991; Gay, 2002). When a surface comes in contact with the gel, initially there are only small contact zones where the polymer wets the surface. The number and size of the contacts increase with the contact time and contact force by wetting of the surface and deformation of the polymer to accommodate surface roughness. Contact formation is an important factor in determining the strength of an adhesive joint (Zosel, 1997).

Adhesion between soft polymeric materials and a substrate is typically measured in one of two ways: peel testing or probe (tack) testing. Peel testing is typically done by casting and/or curing a polymer film on a substrate. Once the polymer is cured, one edge of the film is gripped by a mechanical pulling device and subsequently peeled from the substrate at a constant velocity and at a constant peel angle (frequently 90°). During the peel test, the force required to peel the polymer from the substrate is recorded. A variety of analysis techniques can then be applied to the resulting data including recording the maximum force measured during the peel process. This maximum force can then be compared with maximum forces obtained for other polymer materials. The total peel energy may also be calculated by integrating the force versus displacement curve. To obtain meaningful data that can be compared to data for other materials or measurements made on different equipment, the data must be normalized by the width of the polymer film as the measured properties are highly dependent on film width. Peel testing results are difficult to interpret because the stress distribution near the advancing peel front greatly complicates the distribution of applied force. Further, the measured quantities will depend on the peel angle, peel velocity, and process of forming the interface (Crosby, 2003; Gent, 1969).

Probe tests to measure the tack adhesion are accomplished by bringing a probe into contact with the surface of the polymer material being tested under a given force for a specified period of time. The probe is then raised at a constant velocity while measuring the force required to do so. The resulting force versus distance curve provides valuable information on the adhesion properties of the material. The measured adhesion depends on the probe

speed, contact time and force as well as the probe shape and surface characteristics. Probe testing eliminates several of the complicating factors associated with peel testing and is the focus of this section.

3.1 Tack adhesion measurement

In a typical tack adhesion test for polymer gels, a rigid probe is brought into contact with a polymer gel film at a given rate (c.f. Figure 10a). Once contact between the probe and gel is established, a holding period is performed where a constant force is applied to the gel for a given period of time. The probe and gel film are then separated at a constant rate while measuring the force (normal force) required for separation (c.f. Figure 10b). The adhesion energy, or work of adhesion, is then determined from the integral of the resulting stress versus strain curve (c.f. Figure 10c). Other useful information obtained from the resulting curve includes the peak adhesive force and the strain to failure. Critical variables impacting the measured adhesion energy are the contact force, contact time, and separation speed (Gent, 1969; Zosel, 1985, 1997, 1998; Hui, 2000). Researchers have reported that the roughness of the probe surface also plays an important role in the tack adhesion measured, with rough surfaces resulting in poorer molecular contact between the polymer and the probe (Gay, 2002; Hui, 2000). The overall shape of the force versus distance curve is determined by the viscoelastic and molecular properties of the gel as well as the microscopic debonding mechanisms (Derks, 2003; Lakrout et al., 2001; O'Connor & Willenbacher, 2004).

For the measurements reported here, fluorosilicone films were prepared by casting uncured fluorosilicone gel onto aluminum plates (50 mm in diameter) and then curing at 82°C for 24 hours. The samples were then cooled to room temperature before use. The cured gel films were 0.9 ± 0.05 mm thick. Tack measurements were performed on a TA Instruments ARES G2 rheometer. The probe used was an 8 mm diameter, flat plate fixture.

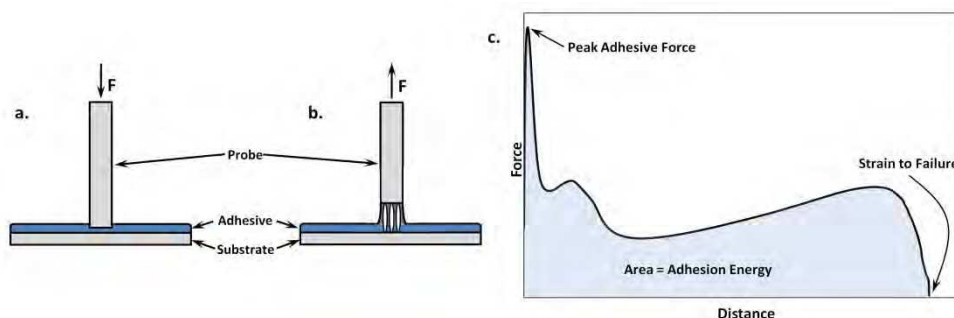


Fig. 10. Schematic representation of a typical tack adhesion measurement apparatus during (a) contact and (b) separation steps. (c) A typical force vs. distance curve obtained from a tack measurement.

3.2 Contact force and contact time

For soft materials such as polymer gels, adhesion is largely dictated by two factors. First, the ability of the material to achieve intimate contact with the substrate. If the material is cured on the substrate, then intimate contact is determined by the ability of the uncured material

to wet the substrate surface (Lenhart & Cole, 2006). If the gel is brought into contact with the substrate after curing, the contact between the gel and the substrate is influenced by the contact force, contact time, and rheology of the gel. Generally, increasing the contact force results in better contact and, thus, better adhesive strength (Zosel, 1997). Obtaining intimate molecular contact between the gel and the substrate greatly determines the strength of the adhesive joint (Zosel, 1997). Second, gel adhesion is largely dictated by the ability of the bulk material to dissipate energy effectively. The energy dissipating ability of the material is directly related to its viscoelastic properties.

For lightly crosslinked polymer gels, the adhesion energy is observed to increase with the contact force while holding contact time constant for low to moderate contact forces (Figure 11a). However, the adhesion energy reaches a plateau value as the contact force is further increased. The contact force has a pronounced effect on the shape of the force versus displacement curves as well (Figure 11b). As the contact force is increased, increases in both the peak adhesive force and the strain to failure are also observed. The increased adhesion energy, peak adhesive force, and strain to failure indicate that better molecular contact is achieved between the polymer gel and the probe when the contact force is increased.

The peak at small distances in the force versus distance curve is related to the onset of cavitation, or the formation of small air pockets between the polymer gel and the probe (c.f. Figure 11b). Once cavitation occurs, the measured force decreases significantly. The air pockets then grow as the polymer gel is stretched further and fibrils are formed. The force increases as the fibrils are stretched and strain harden. Finally, the fibrils detach cleanly from the probe and the measured force returns to a value of zero. The debonding mechanisms are discussed further in Section 4.

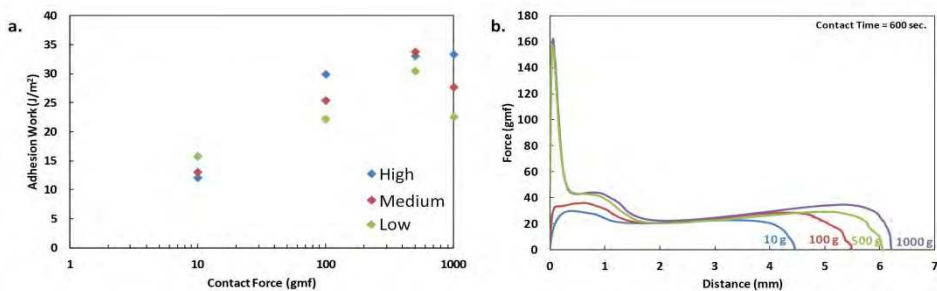


Fig. 11. (a) Work of adhesion as a function of contact force for three different polymer gels of varying equilibrium moduli (low, medium, high). (b) Force versus distance curves measured for a polymer gel (medium) for several different contact forces.

The contact between the gel and substrate is also influenced by the contact time. If the contact force is held constant, increasing the contact time can result in better adhesive strength as intimate molecular contact is enhanced. The correlation between contact time and adhesive strength is dependent on the rheology of the polymer gel. Gels with a lower modulus are better able to relax under the applied force and conform to the substrate which results in better contact. On the other hand, gels with a higher modulus take much longer to relax and may not be able to completely conform to the substrate because of network

limitations. The inability to conform to the substrate results in a poorer contact and, thus, lower adhesion energy.

For lightly crosslinked polymer gels, a slight dependence on contact time is observed for differing values of the contact force (c.f. Figure 12). For a contact force of 10 grams, the adhesion energy increases by 25% when the contact time is increased from 30 seconds to 1000 seconds. The increase in adhesion energy at long contact times indicates that under a force of 10 grams, contact between the probe and the polymer gel is enhanced with time. However, for a contact force of 1000 grams, there is very little change in adhesion energy over the same range of contact times for the same material indicating that contact between the polymer gel and the probe is independent of time over the range reported here. Further, the magnitude of the adhesion energy is higher (180%) for the higher contact force indicating that better molecular contact between the probe and the polymer gel was achieved. At high contact forces, the measured work of adhesion reaches a plateau where the best possible contact between the gel and the probe has been achieved.

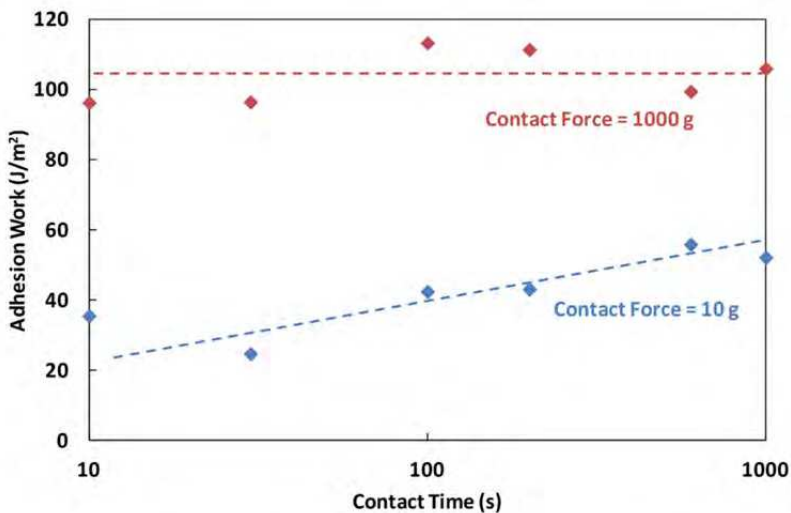


Fig. 12. Work of adhesion as a function of contact time for two different values of contact force for a polymer gel with an equilibrium modulus of 470 Pa.

3.3 Separation speed

The separation speed is important in the tack behavior of polymer gels because changing the separation speed changes the time scale of the deformation of the polymer. Based on the rheological behavior of the polymer gel, changes in the time scale of the deformation can result in significantly different viscoelastic behavior which, in turn, results in significantly different adhesion behavior. For lightly crosslinked polymer gels, the adhesion energy and the peak adhesive force are observed to increase with increasing separation velocity (c.f. Figure 13a). At separation velocities below 0.01 mm/s, a plateau is observed where the adhesion energy is independent of separation velocity. As the separation velocity increases, there is a power law relationship between adhesion energy and separation velocity. At high

separation velocities, the adhesion energy again plateaus and becomes independent of separation velocity.

The trends in adhesion energy observed for a lightly crosslinked polymer gel can be better understood by examining the rheological behavior of the gel over a wide range of deformation time scales or oscillatory frequencies. The ratio of the viscous modulus (G'') to the elastic modulus (G') provides insight into the behavior of the gel at various time scales. At low frequencies (long time scales), the value of $\tan(\delta)$ approaches zero as the elastic response dominates the viscous modulus (c.f. Figure 13b) indicating that, at very long time scales, the gel response is dominated by the equilibrium behavior of the gel network. Thus, most of the energy applied to the polymer gel is stored elastically in the equilibrium deformation of the network. The plateau in the adhesion energy curve at low separation velocities corresponds to the behavior of the polymer gel at long time scales. At very long deformation time scales, the polymer chains rapidly rearrange releasing physical entanglements and are able to maintain an equilibrium configuration while the gel network is being deformed. All of the applied force is stored elastically in the gel network since the viscous contributions (friction between polymer chains, chain disentanglement and rearrangement, etc.) are small.

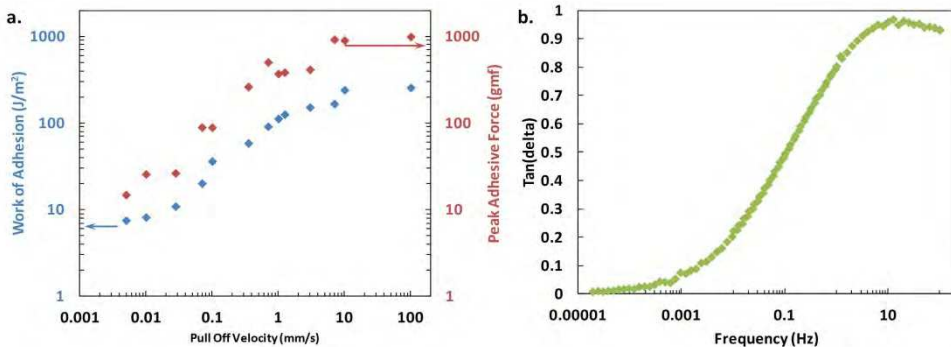


Fig. 13. Correlation in time scale dependence between adhesion and linear rheology. a) Adhesion energy (blue points) and peak adhesive force (red points) as a function of separation velocity for a polymer gel with an equilibrium modulus of 470 Pa; b) $\tan(\delta)$ as a function of oscillation frequency.

A plateau is also observed in the $\tan(\delta)$ function at high frequencies (short time scales, Figure 13b). Above an oscillation frequency of 10 Hz, $\tan(\delta)$ maintains a constant value that is independent of the applied frequency. Although the magnitude of the moduli change above 10 Hz, the ratio of the moduli remains constant. At short time scales, the polymer chains do not have sufficient time to rearrange or disentangle when a stress is applied. Thus, the physical entanglements between chains persist contributing both to the viscous dissipation and also increasing the effective number of crosslinks. The force applied is now distributed almost equally between the viscous and elastic modes, thus much more force is required to deform the gel. The work of adhesion for short time scales (high separation velocities) is about a factor of 100 higher than at long time scales.

Further insight into the polymer gel behavior during the tack test can be gained by examining the stress versus strain curves for several different separation velocities (c.f. Figure 14). At a separation velocity of 0.01 mm/s relatively low forces are required because only the gel backbone is being deformed (c.f. Figure 2d) while most of the polymers are able to relax. For separation velocities between 0.1 mm/s and 10.0 mm/s, much of the increase in adhesion energy can be attributed to the development and enhancement of the peak adhesive force observed at low strain values. The development of the peak adhesive force greatly increases the area beneath the stress versus strain curve (adhesion energy). For separation velocities above 10.0 mm/s, the stress versus strain curves become very similar in both shape and values. This similarity corresponds to the plateau in $\tan(\delta)$ at high oscillation frequencies (i.e., the polymer gel behaves similarly at 10.0 mm/s and 100.0 mm/s). At low oscillation frequencies and slow tack measurement speeds, the response is dominated by the equilibrium modulus due to deformations of the gel network. At high frequencies or fast probe speeds, the physical entanglements dissipate energy through internal friction requiring a larger peak force to deform the gel and a larger overall work of adhesion.

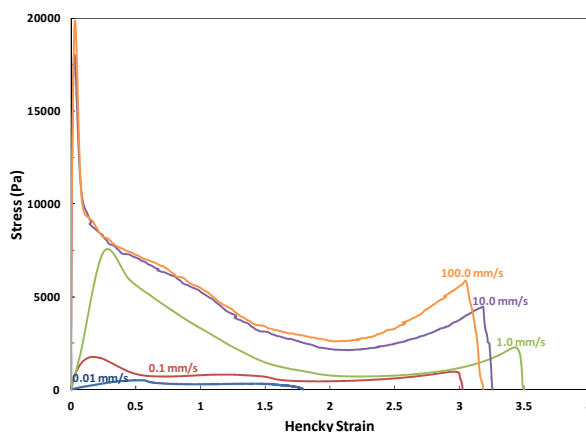


Fig. 14. Stress versus strain curves for a polymer gel with an equilibrium modulus of 470 Pa (medium) at several different pull off velocities (0.01 mm/s – 100 mm/s).

4. Failure modes

The mechanism of failure of an adhesive bond is complicated because not only interfacial interactions, but also bulk rheology, can play a significant role (Moon et al., 2004). There are two main failure mechanisms for adhesive applications; adhesive separation and cohesive failure. Adhesive separation for materials below the Dahlquist criterion is generally characterized by the formation, extension, and eventual failure of fibrillar structures within the polymer material. In cohesive failure, the failure is due to a fracture within the polymer film rather than separation at an interface. Typically, if a cohesive fracture occurs both of the resulting surfaces will be covered in the polymer material. For materials to have high tack and peel strength, the material must be able to dissipate a large amount of deformation energy during separation. Studies indicate that the large degree of energy dissipation is connected to formation of fibrillar structures during separation (Zosel, 1998).

4.1 Adhesive separation

Adhesive separation of soft polymer gels ($G' < 10^5$ Pa) is generally characterized by the formation of fibrillar structures during the separation process. The molecular conditions necessary for fibril formation have been discussed by Zosel, who argued that a high molecular weight between crosslinks (i.e., a low equilibrium modulus) is a necessary condition for the formation of the fibrillar structure (Zosel, 1989, 1991, 1998). A slight degree of branching and crosslinking is beneficial for the stability of the fibrils but excessive crosslinking can lead to a premature failure of the fibrils, therefore significantly reducing the adhesion energy (Lakrouf et al., 1999). For a fibril forming polymer gel, it can be clearly seen that the material is split into separate filaments or fibrils which are anchored on both the fixed bottom substrate and the moving probe surface. These fibrils are increasingly stretched as the probe is raised from the gel causing the storage and dissipation of energy (Zosel, 1989). The microscopic mechanisms of adhesive separation are commonly divided into 4 parts (c.f. Figure 15a).

1. Homogeneous deformation
2. Cavitation
3. Rapid lateral growth of cavities
4. Fibrillation

First, there is a homogeneous deformation of the polymer gel where the stress is distributed throughout the material. Upon further deformation, cavitation occurs and small air pockets form near the probe surface. Next, the air pockets grow and the fibrils are formed. At this point in the deformation, the stress is no longer supported by the entire volume of polymer material. The bulk of the stress is supported by the newly formed fibrils. As the fibrils are stretched, strain hardening may occur, which causes a slight upturn in the stress versus strain curve at high strain values (Figure 13b). Upon further deformation the fibrils either break cohesively or detach adhesively from the probe surface, causing complete debonding (Roos et al., 2002).

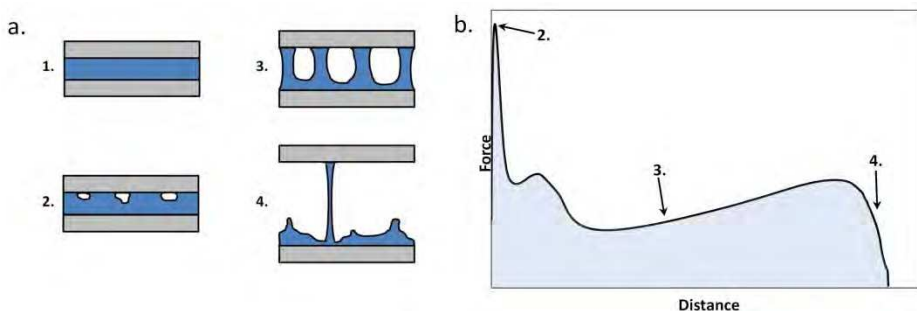


Fig. 15. (a) Schematic representation of the separation of a fibril forming adhesive and the substrate in a tack adhesion experiment. (b) Typical curve of force versus distance for a fibril forming polymeric material.

4.2 Cohesive failure

Cohesive failure is observed when a crack propagates in the bulk of the polymeric material which leads to failure (Figure 16a). In most cases, the surfaces of the adherents (substrate

and probe in the case of a tack experiment) will be covered with the polymeric material following separation. The crack may originate and propagate near the center of the polymer material or near an interface. For a material exhibiting cohesive failure, the measured force during separation quickly reaches a maximum then gradually decreases to zero (Figure 16b). The debonding process is generally governed by the viscous nature of the polymer (Zosel, 1989). Studies of debonding mechanisms show that yield stress fluids exhibit cohesive failure where air enters (crack propagation) the center of the fluid layer (Derks et al., 2003).

While cohesive failure is interesting and desired in many applications, materials that fail cohesively do not generally exhibit a high degree of tack adhesion. For the polymer gel materials discussed here, cohesive failure is not observed in any case.

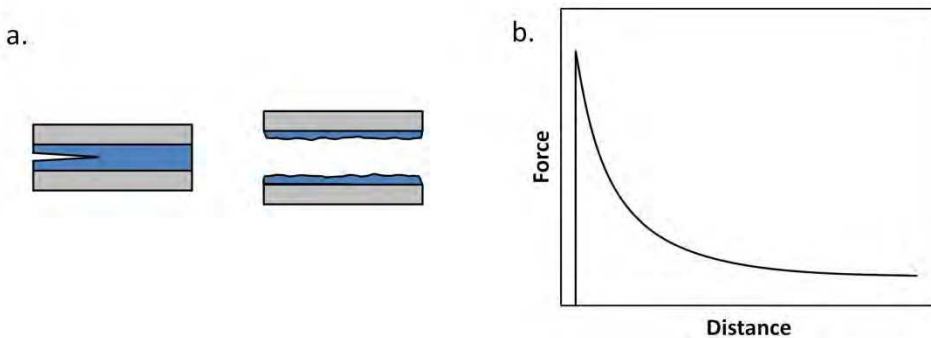


Fig. 16. (a) Schematic representation of a material exhibiting cohesive failure. (b) Typical curve of force versus distance for a cohesively failing material.

5. Hardness

Another useful parameter in characterizing the stiffness of a gel network is hardness. Hardness is measured by indenting a probe into the gel at a specified velocity while measuring the force required for the indentation. The force required to indent the gel to a certain depth is the hardness. While the measured hardness does depend strongly on the modulus of the gel, it also depends on many other measurement parameters such as the size and shape of the gel sample, probe size, speed, and indentation depth. Additionally, the applied strain field is very non-uniform. The strain and strain rate near the probe can be high, but because the gel is incompressible, the entire volume of the gel experiences deformation due to the displacement of gel by the probe. Thus hardness is at best a relative measure of gel material properties. However, since hardness is used by some common gel manufacturers to specify their materials, it is important to understand it in the context of other rheological characterization methods.

For the measurements here, a 1.27 cm diameter probe with a hemispherical cap was used to indent 50g of polymer gel cured in a 5cm diameter glass jar on a Texture Technologies TA.XT Plus Texture Analyzer. Figure 17 shows results for four lightly crosslinked polymer gels of varying equilibrium modulus. As with other characterization methods we have discussed, the measured hardness is strongly dependent on the measurement speed.

At very low speeds, the indentation probes primarily the response of the gel network and hence the measured hardness shows a strong dependence on the equilibrium modulus. Defects cause both the gel equilibrium modulus as well as the hardness to decrease. At fast measurement speeds, physical entanglements and viscous friction between polymer chains contribute substantially to the measured response. The measured hardness increases and becomes less dependent on the quality of the polymer network as quantified by the equilibrium modulus.

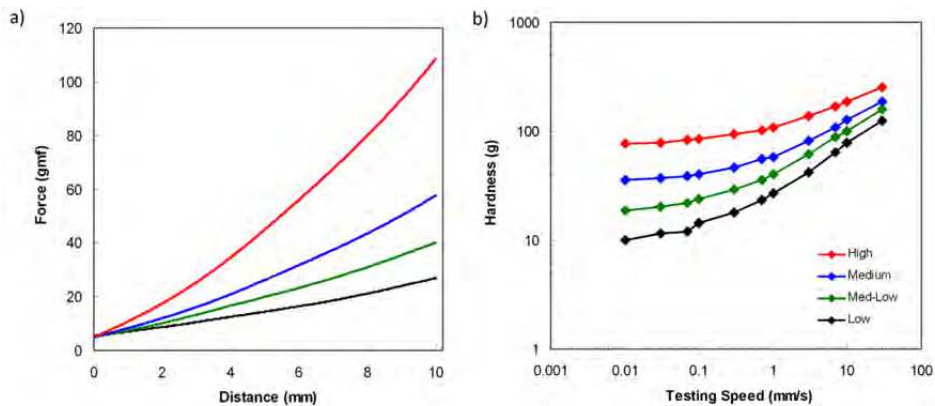


Fig. 17. Hardness test results: a) for four different polymer gels, b) as a function of speed.

Figure 18 shows a direct comparison between the measured hardness and other gel characteristics. As mentioned above, the hardness correlates well with the measured equilibrium modulus and the inverse of the creep compliance. The correlation with adhesion properties is more complex. There is a striking similarity between the dependence

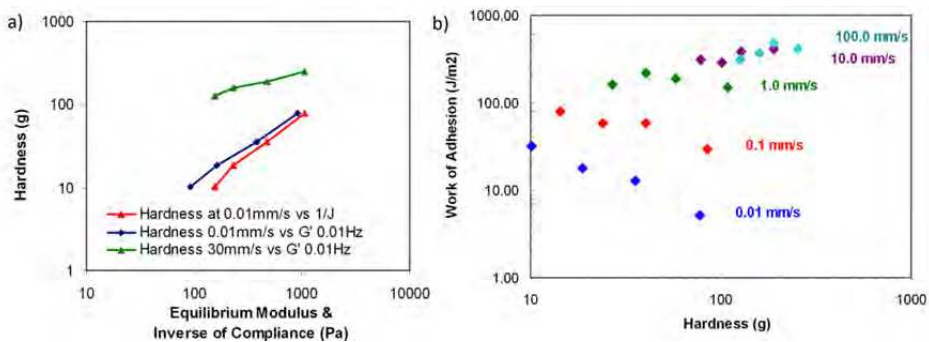


Fig. 18. Gel rheological properties as a function of hardness. a) Hardness at 2 speeds as a function of equilibrium modulus (G' at 0.01Hz) and the inverse of the compliance ($1/J$); b) Work of adhesion as a function of hardness.

of the hardness as a function of indentation speed (Figure 17b) and the work of adhesion as a function of pull off speed (Figure 13a). Figure 18b shows the relationship between the work of adhesion and the measured hardness for a variety of probe indentation and pull-off

speeds. For slow speeds where the hardness is primarily probing the response of the gel network, the measured work of adhesion depends strongly on the hardness. Higher hardness gels have a lower work of adhesion. At high speeds, the work of adhesion becomes almost independent of hardness of the gel suggesting that hardness testing retains more dependence on the equilibrium modulus of the gel at higher speeds than the tack testing. Whereas tack testing at high speed imposes a fairly uniform high strain rate on the gel, hardness testing imposes a non-uniform strain field such that a large fraction of the gel experiences only small strains and strain rates due to displacement of the gel by the probe.

6. Conclusions

Polymer gels are viscoelastic solids which exhibit a wide variety of dynamic rheological behavior demonstrated here using a series of lightly crosslinked fluorosilicone gels with a range of equilibrium moduli. At long time scales, the elastic response of the gel network dominates and the measured equilibrium parameters are highly dependent on the gel microstructure and the presence of defects. The equilibrium gel response is almost purely elastic and shows a plateau at low frequencies where the gel response becomes independent of frequency. That plateau is more apparent for stiffer polymer gels. In non-ideal gels which have entanglements, network defects and polymer solvent, viscoelastic effects become more important as the frequency is increased. At short time scales, physical entanglements and solvent effects become dominant and the measured gel response becomes almost independent of the gel network quality. The importance of time scales is readily apparent in all forms of characterization including linear oscillatory rheology, adhesion and hardness testing.

Linear oscillatory rheology provides a precise tool for determining the critical gel point and for understanding gel behavior by manipulating both the applied strain and frequency. The viscoelastic properties are critically important for good adhesive properties. The presence of dissipation mechanisms (as evidenced by the viscous modulus) are important for creating a large work of adhesion whereas the presence of an equilibrium modulus is required for keeping the adhesive in place. The frequency dependence of the work of adhesion closely mirrors the linear oscillatory rheology. At low frequencies, the work of adhesion is strongly dependent on the equilibrium modulus of the gel. At high frequencies, the adhesive response becomes independent of the gel network quality and instead is dominated by physical entanglements. Hardness testing can also provide useful qualitative information about gel dynamic response, though because of the non-uniform strain field applied, the frequency dependence is not as pronounced.

7. Acknowledgements

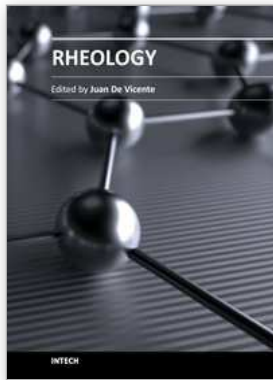
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